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Nonalternating inorganic heterocycles containing hydrazine as building block

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Contents

Abstract

Hydrazine as bifunctional molecule is found in a large variety of inorganic heterocycles that are called 'nonalternating', since they do not have a simple $(-A-B-)_n$ constitution. The synthesis and properties and structures of many title-molecules stemming from reactions of P, S, C(+IV), Si, B and other related element compounds with hydrazine and substituted hydrazines are described in this review. Unusual ring conformations such as twist- and boat-conformations are found in six-membered rings of this type. Effects that favour these unusual conformations against the 'normal' chair conformation of saturated six-membered rings are discussed. The description of some metal complexes of thiophosphoric acid hydrazine derivatives and their various X-ray structures completes this article.

Keywords: Nonalternating inorganic heterocycles; Hydrazine; Building block

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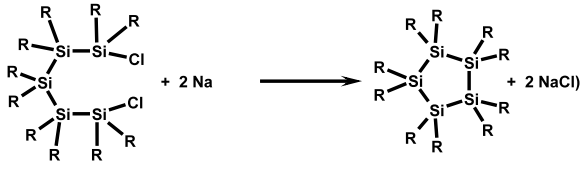
1. Introduction

Inorganic rings are defined according to Haiduc as molecular ring compounds that contain no carbon atoms in the ring system (carbon may be present in organic substituents though) [1,2]. A less strict definition might include ring systems containing one or more isolated carbon atoms in the formal oxidation state of + IV and no C–C bonds in the ring, thus being derivatives of carbonic acid or carbonates, that are generally considered to be inorganic compounds. Inorganic heterocycles are then systems having at least two different atom sorts in the ring. Since many very stable and well known inorganic heterocycles are built according to the scheme $(-A-B-)_n$ (silicates, siloxanes, phosphates, phosphazenes, borates, borazenes etc.) these may be termed 'alternating' heterocycles in contrast to non-alternating heterocycles that do not follow this scheme.

A systematic synthesis of a ring compound needs one or more bifunctional starting molecules that react in a foreseeable way to form new bonds constituting the ring molecule. Oligomers or polymers may be by-products besides other products resulting from leaving groups necessary to form the new bonds. Examples are given in Eqs. 1 and 2 [3–5]. Hydrazine is one of the most simple bifunctional inorganic compounds that should be able to introduce two vicinal N atoms into a ring system. When we started our research on hydrazine heterocycles in the late 60s, the underlying idea was that it might be possible to synthesise an 'inorganic quinone' starting with hydrazine and sulfuric acid derivatives according to Eq. 3. The so-called azodisulfonic acid (**4**) or imidodisulfonic acid



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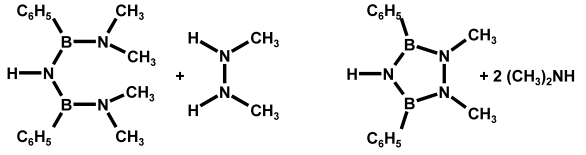
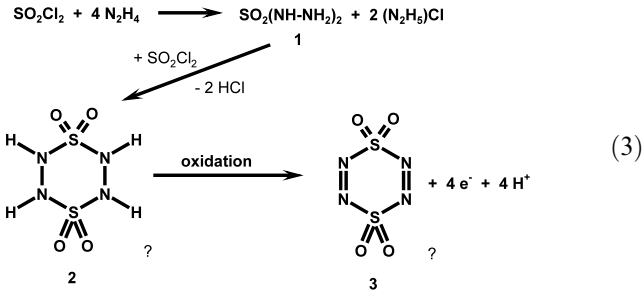


(2)

and salts of both, i.e. **5**, had been described in the literature together with their rather simple synthesis starting from the corresponding hydrazido-compound [6–8].

$$\underset{\mathbf{4}}{HO_3S{-}N{=}N{-}SO_3H} \qquad \underset{\mathbf{5}}{K_2^+[O_3S{-}N{=}N{-}SO_3]^{2-}}$$

The dihydrazide of sulfuric acid (**1**) was also claimed by early authors [9]. Yet our attempts to synthesise **1** were not successful as well as direct reactions of SO_2Cl_2 with hydrazine hydrate or absolute hydrazine in a 1:1

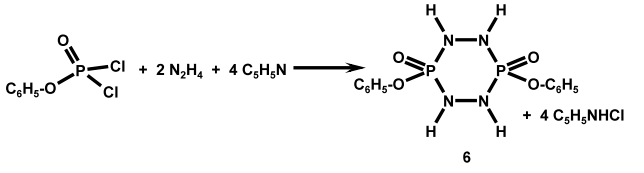


(3)

molar ratio [10]. Only products with excess hydrazine content—hydrazinium salts?—could be obtained. An explanation could be an acidic character of the intermediate hydrazide **1**. The diamide of hydrazidodisulfonic acid is reported to be also slightly acidic and to possess a strong reducing power in addition [11]. This was the reason, why we decided to focus our research on phosphorous acid derivatives.

2. Hydrazine derivatives of phosphoric and thiophosphoric acid

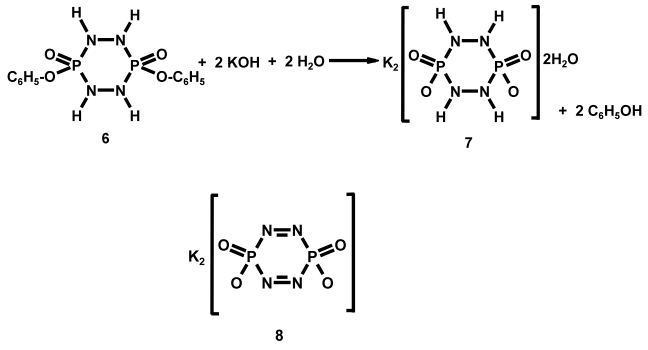
First we wanted to reproduce some older results, where a ring synthesis analogous to Eq. 3 was described starting from hydrazine hydrate and derivatives (esters and amides) of dichlorophosphoric acid [12,13]. Encountering some problems during the workup of the complex reaction mixtures we switched to anhydrous conditions using pyridine as base and tetrahydrofurane as solvent (Eq. 4).



(4)

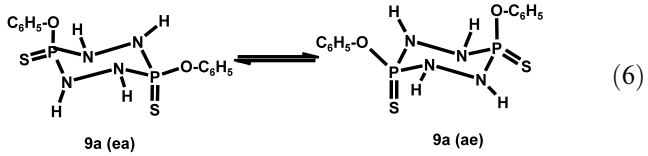
Compound **6** was obtained in about 13% yield after several recrystallisations from alcohol [14]. ^{31}P- and ^{1}H-NMR spectra as well as molecular weight determinations and analytical data were in accordance with the assumed structure, whereas the melting point 259–260 °C was much higher than that reported in the literature. Reaction of **6** with KOH in absolute ethanol under reflux gave the carbon-free dipotassium-salt **7** (Eq. 5). This salt could not be oxidised to the corresponding azo-compound **8** [11]. No colour change was observed as reported in the case of noncyclic hydrazidophosphonates [15,16]. Decomposition under evolution of nitrogen was always observed [11].

Resynthesizing the phenylester of the corresponding dithio-ring compound described by Tolkmith and Britton [17] gave similar results. The melting point reported

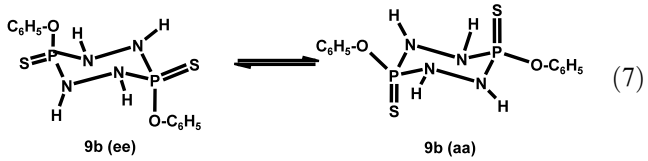


(5)

could not be reproduced. In this case we could isolate two isomers using preparative chromatography on silica gel [18]. Both isomers had very similar NMR-spectra again proving the ring structure, but different Rf-values, IR-spectra, crystal forms and melting points, that again were considerably higher than the reported value of 185 °C. Our conclusion then was that as result of a ring synthesis according to Eq. 4 a *cis*- and a *trans*-isomer (*Z* and *E* isomers) would be expected. Both isomers **9a** and **9b** were anticipated to possess a cyclohexane-like puckered ring conformation. Interconversion of chair forms would then lead to identical conformers in the case of **9a** (Eq. 6). In contrast, the *trans*-isomer **9b** could exist in two distinct conformations differing in ee- or aa-positions of the sulfur or phenoxy-substituents, respectively (Eq. 7).



(6)



(7)

It was assumed then that, due to the large S substituents, the ee conformation of **9b** would predominate in solution to a rather large extent, so that only this form should be present in the crystalline state [19]. X-ray structure determinations of both isomers **9a** and **9b** revealed surprising results. Whereas, the *trans*-isomer adopts the expected centrosymmetric chair conformation with S in the equatorial positions (Fig. 1), the *cis*-isomer exists in a twist-conformation that possesses a twofold axis of symmetry. Both S and phenoxy-groups are in the so-called isoclinal positions (Fig. 2) [20–22]. Our conclusion was that **9a** adopts this unusual conformation to avoid the unfavourable axial positions of one of the two S substituents in a hypothetical chair conformation (Eq. 6). In the case of the corresponding methoxy-substituted ring also, two isomers could be isolated. They differ slightly in their ^{1}H-NMR spectra ($^{2}J_{PNH} = 34$ and 36 Hz, respectively). IR- and Raman-spectra differ, too, but no attribution to a distinct isomer could be made so far on spectroscopic arguments [23]. This could be done later by an X-ray structure determination of one of the isomers, that turned out to be the *trans*-(*E*) compound and that adopts a 'normal' chair conformation in the crystal [24]. The corresponding ethoxy-disubstituted ring could also be obtained as *cis*- and *trans*-isomers by fractional crystallisation. The X-ray structure analysis of the *cis*-isomer revealed the expected twist-conformation of the six-membered ring. The molecule possesses a twofold axis of symmetry. Sulfur and ethoxy-groups at P are again in isoclinal positions (Fig. 3) [25]. A later result was very surprising to us at first. We prepared the corresponding dioxo-compound **9c** to compare the conformations with those of the dithio-compounds **9a** and **9b**. Two isomers could be isolated again by crystallisation from tetrahydrofurane. They differ only very slightly in their spectroscopic data but have different crystal forms. Only one of them gave suitable crystals for an X-ray structure determination. It turned out to be the *trans*-(*Z*)isomer, but the ring adopts a typical twist-conformation in the crystal (Fig. 4). Since according to our argumentation above intramolecular effects should not be sufficient in this molecule to destabilise a chair conformation, only intermolecular forces could be responsible for the unusual conformation we found.

In fact inspection of the structure shows relatively strong hydrogen bridges in the crystal, that force the molecules into the twist-conformation. Each molecule is connected via eight hydrogen bonds to four neighbouring molecules (Fig. 5) [26]. In the case of a trichloromethylphosphonic acid derivative **9d**, the existence of two isomers was shown also by thin-layer chromatography. But only one isomer could be isolated. It probably is the *cis*-(*Z*)isomer. Since the crystals decompose in the X-ray beam, no detailed structure informations are available. The NMR data prove the constitution ($\delta(^{31}P) = 17.2$ ppm triplet, $^{2}J_{PNH} = 37$ Hz, $\delta(^{1}H, NH) = 8.2$ ppm doublet) [27].

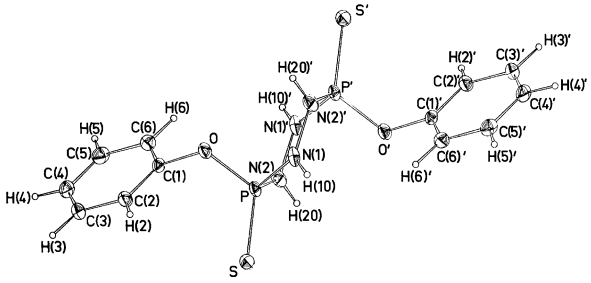


Fig. 1. Molecular structure of the *trans*-isomer **9b**, monoclinic, $P2_1/c$, $Z = 2$.

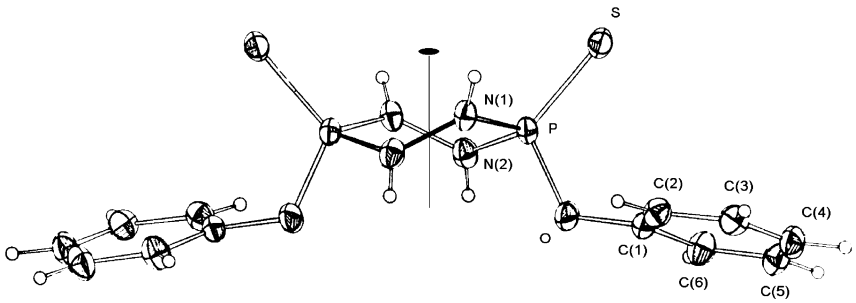


Fig. 2. X-ray structure of the *cis*-isomer **9a** in its twist conformation of C_2 symmetry, monoclinic, $C2/c$, $Z = 4$.

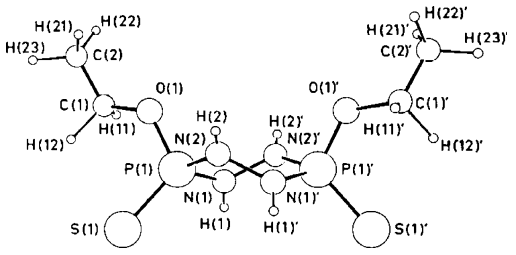


Fig. 3. Molecular structure of the *cis*-(*Z*)isomer of 3,6-diethoxy-1,2,4,5-tetraaza-3λ^5,6λ^5-diphosphacyclohexane-3,6-disulfide (primed atoms are related to the atoms in the asymmetric unit by a twofold axis of symmetry; tetragonal, $P4_2/n$, $Z = 4$).

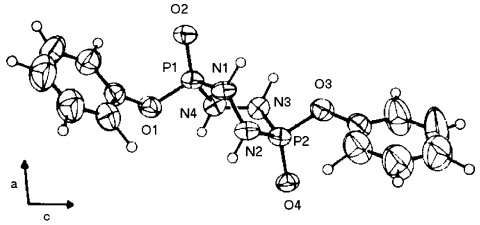
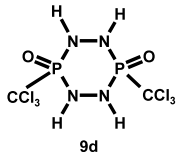


Fig. 4. Molecular structure of the *trans*-(*E*)isomer **9c**, monoclinic, $P2_1/c$, $Z = 4$.



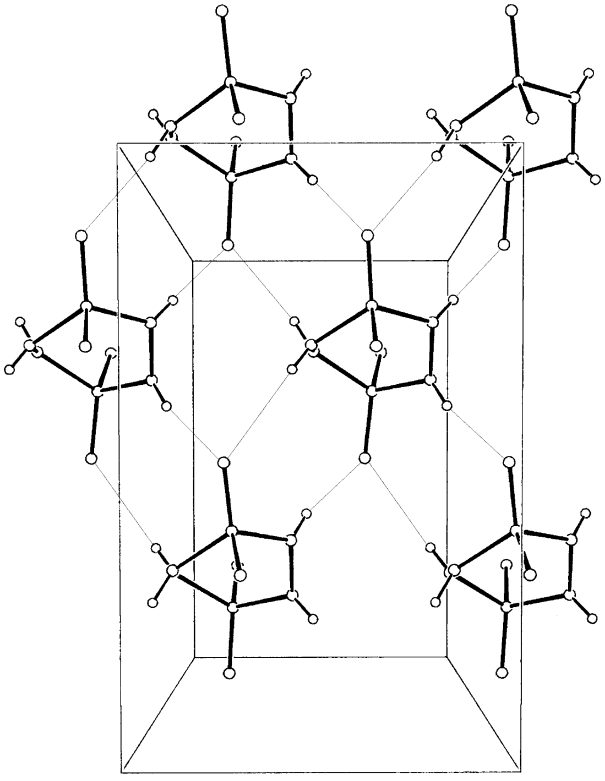


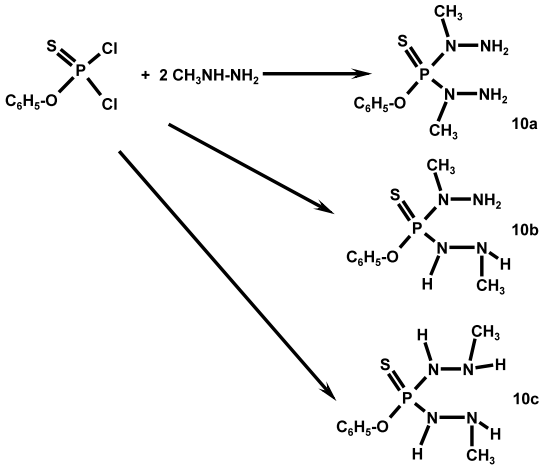
Fig. 5. Hydrogen bonds (thin lines) in the unit cell of **9c** (phenyl-groups omitted for a better survey).

3. Monomethylhydrazine derivatives of phosphorus(III) and (V) compounds

Because of fast proton exchange processes of the NH-protons in our molecules there was no possibility of monitoring conformational changes in solution by NMR-spectroscopy. The results of our X-ray structural determinations could be singular and maybe due to crystal packing effects, too. In *N*-methyl-substituted compounds it could be expected that NMR-spectra would reveal conformational informations also in solution. Reacting monomethylhydrazine with phenoxythiophosphoryldichloride in the presence of excess base gives a mixture of three isomeric dihydrazides **10a**, **10b** and **10c**, that can be isolated by chromatographic methods (Eq. 8) [28–30]. The molar ratio is about **10a**–**10b**–**10c** = 10:2:1 at 0 °C as well as at 40 °C reaction temperature [28]. At lower temperatures **10a** is formed almost exclusively [29]. The identity of the isomers is easily proved by NMR-spectroscopy. For instance the ^{31}P-NMR of **10a** is a septet with $^3J_{PNCH}$ = 11.5 Hz centered at 81.3 ppm due to the coupling of six α-methyl-protons with the phosphorus. In contrast, the coupling in **10c** between phosphorus and α-NH-protons is $^2J_{PNH} = 30$ Hz [28].

A terminally tetramethyl-substituted phenoxythiophosphoryldihydrazide **10d** was also synthesised later starting with 1,1′-dimethylhydrazine in a similar reac-

tion as well as the corresponding oxo-compound **10e** [31].



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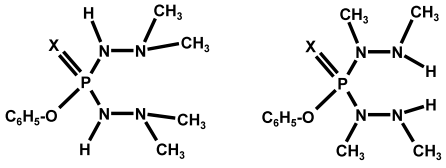
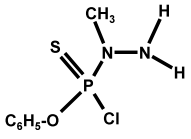


10d X = S **10f** X = S
10e X = O **10g** X = O

The oxo-compounds analogous to **10a**, **10b** and **10c**: **10h**, **10i** and **10j** were also prepared and characterised by thin-layer chromatography in our laboratory. Compound **10j** is only formed in very small amounts and was not isolated in substance [28,29,31,32]. Melting points and some NMR data of these hydrazine derivatives of phosphoric and thiophosphoric acid phenylesters are summarised in Table 1. Some corresponding phosphonic and phosphinic acid derivatives published by other authors are included for comparison [33–36].

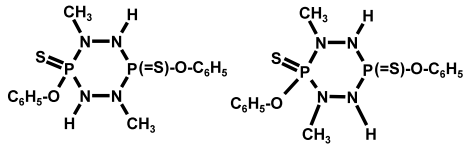
A monochloro–monohydrazido derivative **10k** can be obtained also at low temperatures [29].



10k

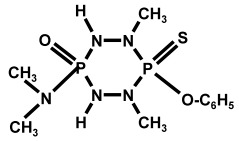
IR-spectroscopic data for a large number of α-*N*-methylated dihydrazides in the solid state as well as in solution have been published [30].

Dimerisation of **10k** [29] or reaction of **10a** and/or **10b** in the presence of excess base [28] leads to two different ring constitutions. The symmetrical compound **11** apparently exists in two isomers as expected, the *cis*- and *trans*-configurations. The same is true with the asymmetrical ring compound **12** [28,29,37].



11 **12**

The isomers of **12** can be separated by column chromatography and have sharp melting points of 161 (*trans*-Rf = 0.32) and 135 °C (*cis*-Rf = 0.24) in contrast to the mixture that has a melting range between 115 and 157 °C. The vibrational spectra of the two isomers differ distinctly especially in the ν(NH) and $\nu(CH_3)$ region. In the ^{1}H-NMR, a doublet of doublets is observed in the CH_3 region for both isomers. Fig. 6 shows that the δ-values differ, so that even in the mixture all signals can be dissolved. As an example, the ^{31}P-NMR of *cis*-**12** is shown in Fig. 7. It consists of a septet for the P adjacent to the methyl-N atoms (coupling with six methyl-protons) and a triplet for the P adjacent to the H–N atoms (coupling with two H atoms at N). No splitting due to $P_{NN}P$ coupling is observed in the *cis*-isomer. In contrast, the proton-decoupled spectrum of *trans*-**12** consists of two slightly split doublets: $^3J_{PNNP} = 4.4$ Hz. Since a PNNP torsion angle of about 63° can be expected for a twist-conformation in *cis*-**12**, a $P_{NN}P$ coupling should be very weak. A chair-conformation of the *trans*-isomer with an anticipated PNNP torsion angle of about 48° is in consistence with the observed $P_{NN}P$ coupling of 4.4 Hz [37]. Low temperature ^{1}H-NMR spectra confirm these assumptions [38]. From these spectra, it can be concluded that in solution *trans*-**12** exists predominantly in a chair conformation (about 95%). In the case of *cis*-**12** the twist-conformation prevails (about 93%). In both isomers ring inversion is slow compared with the NMR time scale at room temperature. Below a coalescence temperature of 191 (*trans*) or 230 K (*cis*), a characteristic splitting of the peaks of the methyl and NH protons is observed. In the case of *trans*-**12**, this splitting is probably due to a hindrance of the nitrogen inversion, that renders the equatorial and axial substituents at N magnetically nonequivalent at low temperatures ($\Delta G^{\#} =$ 39.7 kJ mol^{-1}). In the case of *cis*-**12** the experimental results (Fig. 8) can be best interpreted assuming a hindered pseudorotation cycle of twist-conformations below room temperature ($\Delta G^{\#} = 49.8$ kJ mol^{-1}; details see original publication [38]). Interestingly, the molecule **13**, a mixed P=O/P=S compound with an



13

dimethylamino-substituent at one P atom, also adopts a

Table 1
Melting points and NMR data of dihydrazido-phosphoric and thiophosphoric acid phenylesters (if not otherwise indicated, solvent for ^{1}H-NMR is $CDCl_3$, standard TMS; signals for phenyl–H's are found in the usual range 7.0–7.5 ppm)

Compound	R	M.p. (°C)	δ(^{1}H) ppm				$^3J_{PNCH}$ (Hz)	δ(^{31}P) ppm in toluene
			α-NH	β-NH	α-NCH	β-NCH		
$PhOP(S)(NH-NH_2)_2$ [b]	32	96	4.5 D	3.4 S	–	–	–	75.2 (in DMSO)
10a	31	62	–	3.7 S	2.96 D	–	11.5	81.3 septet
10b	31	51	4.7 D	3.6 S	2.94 D	2.62 S	11.5	78.3
10c	31	100	4.7 D	3.6 S	–	2.64 S	–	68.4 triplet
10d	31	76	4.1 D	–	–	2.60 S	–	61.3 triplet
10f	31	55	–	3.3 S	2.94 D	2.60 [a]	10.5	76.5 septet
$Ph-P(S)(NH-(Me)_2)_2$	33	–	3.67 D	–	–	2.94 S	[a]	61.1
$Ph_2P(S)-NH-N(Me)_2$	33	–	4.79 D	–	–	2.39 S	[a]	57.3
$PhOP(O)(NH-NH_2)_2$	32	111	4.5 D	3.6 [a]	–	–	–	12.9 in $CDCl_3/C_6D_6$
10e	31	118	4.1 D	–	–	2.59 S	–	5.4 triplet
10g	31	38	–	3.2	2.96 D	2.61 S	8.5	9.9 septet
10h	31	Oil	–	3.8	2.96 D	–	8.5	13.8 septet
10i	31	Oil	4.6 D	3.4 [a]	3.01 D	2.66 S	8	10.6
$O=P(NH-N(Me)_2)_3$	33		3.95 D	–	–	2.57 S	–	12.5
$O=P(N(Me)-NH_2)_3$	29							26
$Ph-P(O)(N(Me)-NH_2)_2$	34							31
$Ph_2P(O)-NH-N(Me)_2$	33		3.95 D	–	–	2.58	–	22.0
$Me_2N-(O)P(N(Me)-NH_2)_2$	29							26
$(Cl-CH_2CH_2)_2N-(O)P(N(Me)-NHMe)_2$	35	76	–	?	2.72	2.64	8 [c]	?
$(Cl-CH_2CH_2)_2N-(S)P(N(Me)-NHMe)_2$	35	Oil	–	?	3.04	2.88	15 [d]	?

[a] Coupling is obscured, not dissolved or not observed.
[b] X-ray structure, see Ref. [36].
[c] $^4J_{PNNCH}$ observed: 0.7 Hz.
[d] $^4J_{PNNCH}$ observed: 2 Hz.

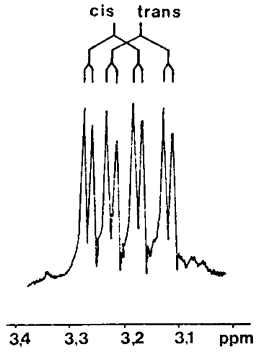


Fig. 6. ^{1}H-NMR spectrum of a mixture of *cis*- and *trans*-**12** in the region of the methyl-protons.

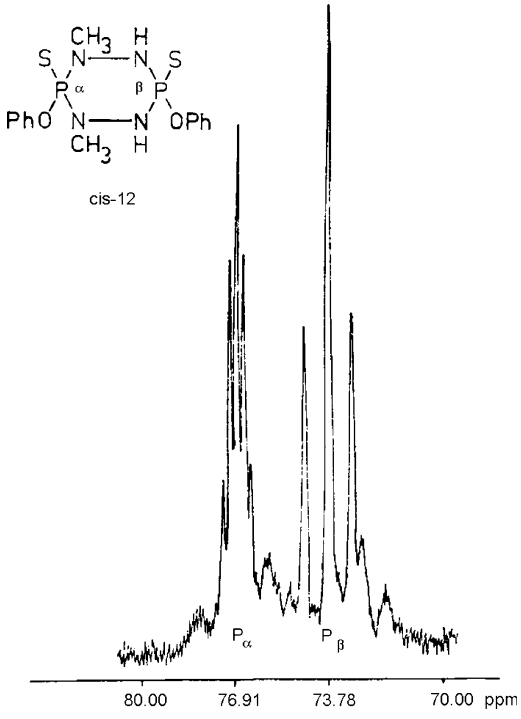


Fig. 7. ^{31}P-NMR of *cis*-**12**.

slightly distorted twist-conformation in the crystal. The molecule isolated is the *Z*-isomer (othorhombic, $P2_12_12_1$, $Z=4$; Fig. 9) [39]. α,α′-Dimethyldihydrazides of phenoxythiophosphoric acid (**10a**) and analogous thiophosphonic acid derivatives react also with organic aldehydes to form a great number of organic six-membered rings containing at least one C atom in the ring. NMR data and a few X-ray structures have been published. In some cases, ring conformations are discussed. The literature is cited here for interested readers but no details are given [34,40–44]. In almost all cases the organic rings have 'normal' chair-conformations with only a few exemptions [38,45–47].

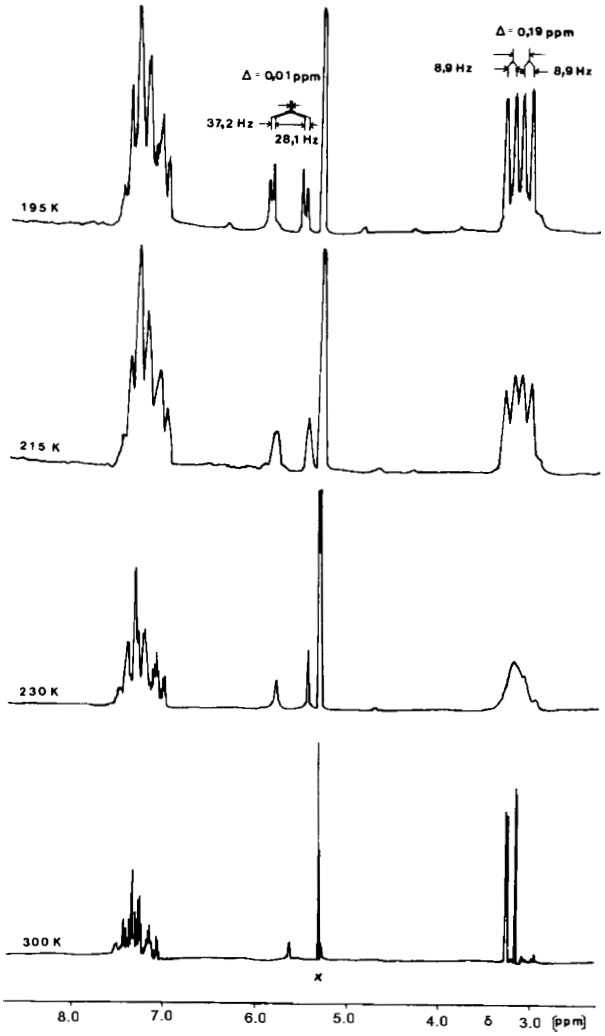


Fig. 8. Temperature-dependent ^{1}H-NMR spectra of *cis*-**12**, from right to left: methyl-protons, x = solvent $CDCl_3$, NH-protons, phenyl-protons.

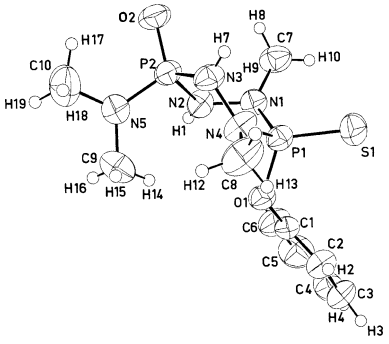
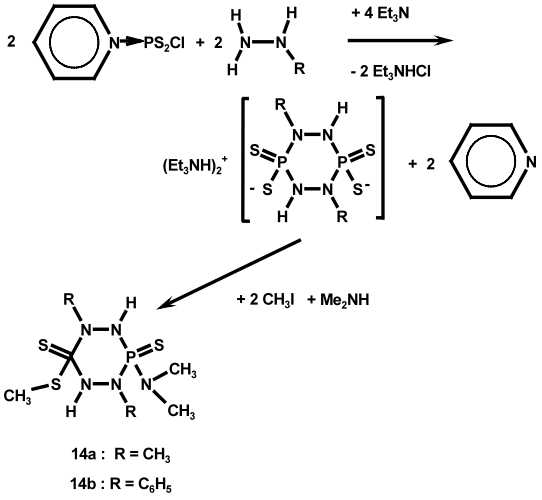


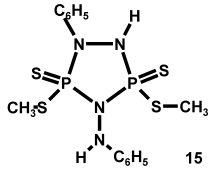
Fig. 9. X-ray structure of **13** (1,5-dimethyl-3-dimethylamino-3-oxo-6-phenoxy-1,2,4,5-tetraaza-$^3\lambda^5$,6λ^5-diphosphacyclohexane-6-sulfide).

Symmetrical *N*,*N*′-dimethyl-substituted molecules of type **11** with two S atoms at each P atom (dithiophosphoric acid derivatives) have been synthesised later from a completely different starting point. The so-called donor stabilised dithiomonometaphosphorylchloride reacts according to equation 9 with N-monosubstituted hydrazines to yield six-, five- and four-membered rings depending on the bulkiness of the hydrazine substituent (Eq. 9) [48]. Compound **14a** is obtained in 87% yield, whereas **14b** is formed in 4% yield besides a five-membered ring **15** as main product. The reaction with *t*-butyl-hydrazine leads to a four-membered ring with



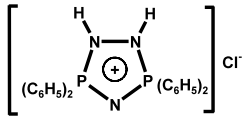
(9)

two exocyclic NH–*t*-butyl-groups. Compounds **14a** and **14b** are obtained as *cis*/*trans* isomer mixtures, that can be separated by column chromatography [48].



15

The X-ray structure of *cis*-**14b** (monoclinic, $C2/c$, $Z = 4$) shows a distorted twist-conformation of the molecule, that has C_2 symmetry [49]. A salt of a cyclic diphosphinic acid derivative **16** is also described in the literature. It is formed in the reaction of trichlorodiphenylphosphorane with hydraziniumchloride besides an open-chained product [50].



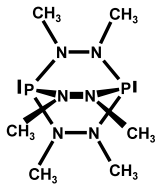
16

4. Rings with two phosphorus atoms and *N*,*N*′-dimethylhydrazine and other *N*,*N*′-disubstituted hydrazines

4.1. Monocyclic systems and bicyclic cage compounds

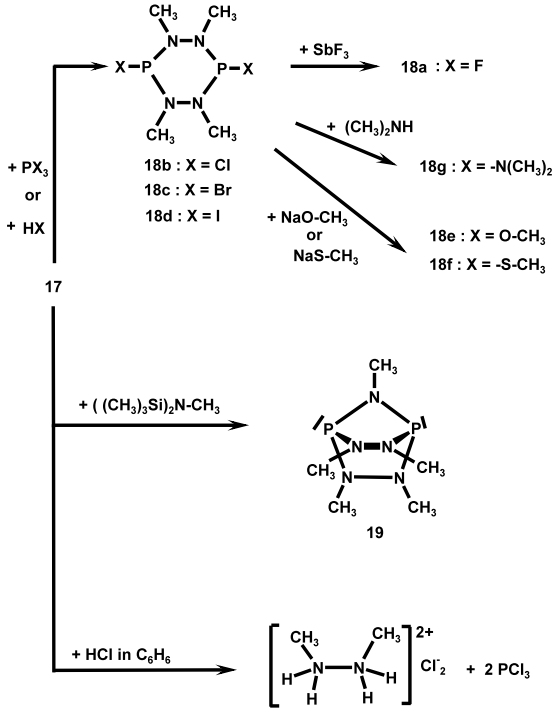
1,2-Dimethylhydrazine is a symmetrical bifunctional molecule that should lead to rings with a rather simple

symmetrical structure. Amazingly the first reported synthesis was that of a bicyclic cage [51]. A transamination of tris(dimethylamino)phosphane, $P[(NCH_3)_2]_3$, with 1,2-dimethylhydrazine is the best method with a yield of 96%! [52,53]. Phosphorus trichloride with the hydrazine or $P[(NCH_3)_2]_3$ with the hydrazine bishydrochloride also give this spectacular molecule **17**. The product is rather stable and can be purified by sublimation at 70 °C/10^{-5} Pa.



17

The ^{1}H-NMR spectrum of **17** does not have the features that would be expected. Not a simple doublet is observed but a pseudo-triplet [47–49]. This type of spectrum had been described and theoretically calculated by Harris in detail for a number of $X_6AA'X'_6$ molecules like $(CH_3)_2P–P(CH_3)_2$ and others and includes not only the coupling between A and X ($^3J_{PNCH}$ in **17**) but also between A and X′ and vice versa ($^4J_{PNNCH}$ in **17**) [54,55]. A later X-ray structure determination (monoclinic, $P2_1/c$, $Z=2$) confirmed the constitution of the molecule, which has nearly C_3 symmetry (the structure is disordered and of only limited accuracy) [56]. The photoelectron spectrum of **17** is also reported and a comparison is made with similar organic cage compounds [57]. Compound **17** reacts with a number of substances under a partly ring opening to form six-membered rings and finally open-chained products (Eq. 10) [51–53,58].



(10)

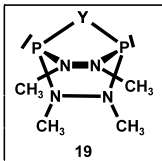
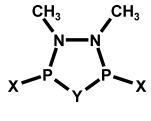
Some NMR data are summarised in Table 2 together with those of a phenylphosphonous acid derivative **18i** that has been synthesised from dichlorophenylphosphane and 1,2-dimethylhydrazine in the presence of excess triethylamine [59] or of **18b** with methyllithium and some corresponding phosphorous acid derivatives [60].An X-ray structure determination of **18b** (monoclinic, $P2_1/c$, $Z=2$) reveals a 'normal' somewhat flattened chair conformation of the six-membered ring in the crystal [61]. The degradation product **18c** (Eq. 10) reacts with 1,2-dimethylhydrazine under rebuilding the cage **17**. Methylamine itself gives only undefined reaction products, whereas hexamethyldisilazane yields the expected bycycloheptane derivative **19** (Eq. 10). Similar compounds with oxygen **19a** or sulfur **19b** in the ring instead of the $N–CH_3$-group can be synthesised from **18c** by controlled hydrolysis or by reaction with hexamethylsilthiane (bis(trimethylsilyl)sulfide) [59]. The compounds $Cl_2P–(CH_3)N–N(CH_3)–PCl_2$ and $Cl(CH_3)P–(CH_3)N–N(CH_3)–P(CH_3)Cl$, that can also be obtained by degradation of the cage molecule **17** (Eq. 10), or alternatively by the direct reaction of 1,2-dimethylhydrazine with PCl_3 or $CH_3–PCl_2$, respectively, undergo ring closure reactions under suitable conditions to form the corresponding five-membered rings **20** (Eq. 11) [59]. Table 3 summarises some NMR data of three-coordinate phosphorus hydrazine derivatives of the bicycloheptane **19** and cyclopentane **20** [59]. The X-ray structure of **20d** (monoclinic, $C2/c$, $Z=4$) shows the

Table 2
NMR data of some six-membered ring compounds with 1,2-dimethylhydrazine as ring component (C_6D_6 as solvent if not otherwise quoted)

Compound	δ(^{31}P) (ppm)	δ(^{1}H) (ppm)	$^3J_{PNCH}$ (Hz)	Reference
17 cage	109.0	2.74	14.9 'T' [a]	[53]
18a: X = F		2.85	15.0 D [b]	[57]
18b: X = Cl	120.1	2.65	16.8 D	[59]
		2.98	16.5 D [b]	
18c: X = Br	125.3	2.51	17.8 D	[60]
18d: X = I	132.8	2.20	18.8 D	[59]
18: X = –O–CH_3	127.7	2.92	14.7D	[59]
		X: 1.87	X: 13.8	
18f: X = –S–CH_3	117.5	2.94	14.3 D	[59]
		X: 1.87	X: 12.6 D	
18g: X = –$N(CH_3)_2$	130.0	2.77	9.6 D	[59]
		X: 2.80	X: 12.6 D	
18h: X = CN	50.4	2.55	14.8 D	[59]
18i: X = CH_3	91.1	2.84	13.0 D	[59]
		X: 1.45	X: 1.45 D	
18j: X = C_6H_5	29.9	3.04 [c]	14.5 D	[58]

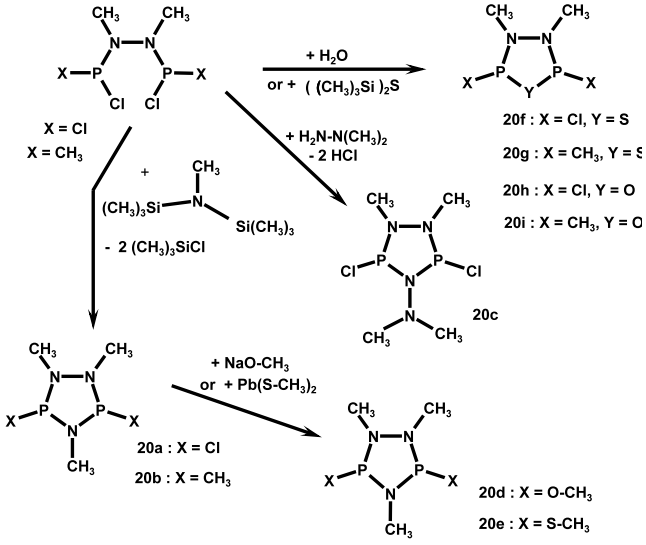
[a] Pseudo-triplet, $J' = {}^3J_{PNCH} + {}^4J_{PNNCH}$.
[b] Solvent $CDCl_3$.
[c] Multiplet of phenyl-protons at 7.56 ppm.

Table 3
NMR data of some compounds with tricoordinate phosphorus, bicycloheptanes **19** and cyclopentanes **20** (solvent C_6D_6 if not otherwise quoted) [60] [a]

		δ^{31}P ppm	δ^{1}H hydraz-CH_3 ppm	$^{3}J_{PNCH}$ Hz	δ^{1}H Y-NCH_3 ppm	$^{3}J_{PNCH}$ (Y) Hz	δ^{1}H X(ElCH_3) ppm	$^{3}J_{PelCH}$ Hz
 19	**19**, Y = N-CH_3	101.8	2.57 D	15.4	2.79 T	12.8		
	19a, Y = O	114.0	2.51 D	14.8				
	19b, Y = S	113.0	2.54 D	17.8				
 20	**20a**, X = Cl, Y = N-CH_3	144.8	2.21 D	17.3	2.34 T	12.3		
	20b, X = CH_3 Y = N-CH_3	117.8	2.92 D	14.3	2.64 T	11.1	0.95 T	6.5
	20c, X = Cl Y = N-N(CH_3)$_2$	129.6	2.66 D	17.8	2.72			
	20d, X = O-CH_3 Y = N-CH_3	122.0						
	20e, X = S-CH_3 Y = N-CH_3	149.8	2.90 D	15.4	2.91 T	11.9	2.07 D	9.0
	20f, X = Cl Y = S	145.5	2.59 D	18.0				
	20g, X = CH_3 Y = S	125.9	2.82 D	13.4			1.48 D	11.2
	20h, X = Cl Y = O	150.8	2.42 D	13.2				
	20i, X = CH_3 Y = O	129.3	3.05 D	12.8			1.21 D	7.3 [b]

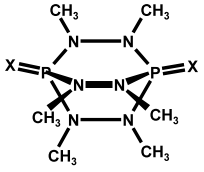
[a] Some ^{14}N-NMR data are also given in Ref. [60].
[b] Solvent THF.

molecule to be of C_2 symmetry. The NN distance of 145.5(7) Å is remarkably long [62].



(11)

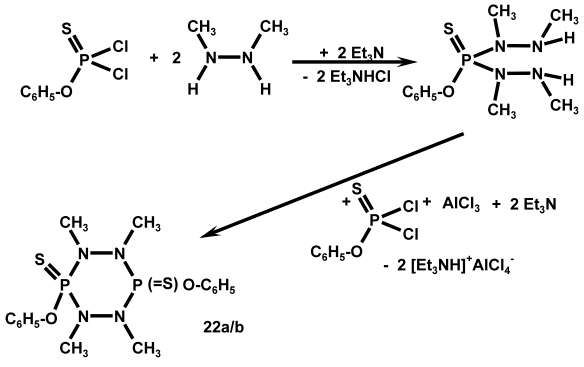
The phosphorus(+III) in **17** can be oxidised without ring cleavage. Hydrogen peroxide gives the dioxide **21a**, S_8 or Se_8 the corresponding dichalcogenides **21b** and **21c** [51,52]. Phenylazide yields the bis(C_6H_5–N=) substituted product **21d**. Tellurium does not react under the tested conditions [63].



Diborane also reacts with **17** to form the bis(BH_3)adduct. Coordination occurs exclusively at the phosphorus atoms. The analogous BF_3-complexes are instable [51,52,57]. Complex-forming reactions of **17** with $Mo(CO)_6$, Ni(+II) salts and $Al_2(CH_3)_6$ are also reported [51,57]. As expected the ^{31}P-NMR shifts are strongly influenced by oxygenation or complex formation: compound (δ_{31}P): **21a** (8.6), **21b** (66.5), **21c** (not measured, pure solubility), bis(BH_3)adduct (101.5 ppm) [52]. Detailed investigations of ^{31}P–^{31}P spin–spin couplings in molecules of type **21c** and of mixed selenides/oxides/imides are reported in the literature in comparison with corresponding organic rings and cages [64,65]. X-ray structures of the two molecules **21a** and **21d** have been investigated. The molecule of **21a** (monoclinic, $C2/c$, $Z=4$) has nearly **32** ($D3_d$) symmetry. The structure is disordered like that of the parent compound **17**, that is: both enantiomers (second half of the molecule canted-clock wise or counter-clockwise against the first half) are present and superimposed in the structure [66]. Similar results have been obtained later with the bis(phenylimido) derivative **21d** (monoclinic, $P2_1/c$, $Z=2$) [67].

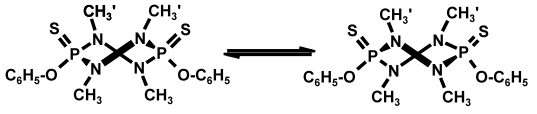
All these cage compounds adopt twisted boat forms of the individual six-membered phosphorus hydrazine rings, since chair forms are impossible because of sterical factors (bridging!!). But what are the influences of four *N*-methyl-substituents on the conformation of unbridged P-hydrazine rings?

Dichlorothiophosphoric acid phenylester reacts with 1,2-dimethylhydrazine only in marginal yields to the corresponding six-membered ring under normal conditions (triethylamine as base) [68]. Pre-isolation of the open-chained dihydrazide and the addition of aluminumtrichloride as catalyst to the reaction mixtures achieved much better yields up to 25% of a mixture of *cis*- and *trans*-isomers **22a/b** (Eq. 12) [69]. The isomers could be separated by fractional



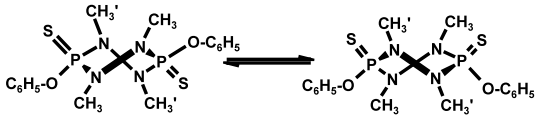
(12)

crystallisation or by sorting of the different crystal forms (needles and flat plates) under a microscope and succeeding recrystallisation. Chromatographic separation experiments were unsuccessful. The melting points of the pure substances differ only slightly: **22a** 148 °C, **22b** 152 °C. The NMR spectra differ also, δ^{31}P (ppm): **22a** 76.5/75.5; **22b** 74.3/72.1, solvent d_6-$(CH_3)_2SO$/toluene. Fig. 10 shows the methyl-signals in the ^{1}H-NMR of **22a** at different temperatures. At low temperatures, two doublets are observed for two inequivalent types of methyl-groups ($\delta = 3.27$ and 3.06 ppm, $^3J_{PNCH} = 10$ and 9 Hz (solvent $CDCl_3/CS_2$). On warming of the probe coalescence occurs to one broad signal at 309 K (+35 °C). At higher temperatures, splitting is again seen and finally a multiplet of the 'Harris'-type [54,55] emerges. This $AX_6X'_6A'$ spectrum means that all four methyl-groups are magnetically and thus sterically equivalent now in the NMR time scale. This can be interpreted as a fast equilibrium of enantiomeric twist forms. The free energy of activation can be estimated as $\Delta G^{\#} = 63 \pm 1$ kJ mol^{-1} (Eq. 13) [70].



(13)

The methyl-protons of **22b** show a 'Harris'-type spectrum already at room temperature in the ^{1}H-NMR. Apparently, all four methyl-groups are magnetically equivalent in the NMR time scale. Coalescence is observed at 228 K (−45 °C). At 190 K (−83 °C) two sharp doublets appear: $\delta = 3.26$ and 3.14 ppm, $^3J_{PNCH} = 8.0$ and 6.8 Hz. So here the equilibrium is frozen (slow in the NMR time scale), so that two different types of methyl-protons appear. $\Delta G^{\#} = 47 \pm 1$ kJ can be estimated [69]. This value is much lower than that for **22a**. The best interpretation is the assumption of a twist-conformation for the *trans*-isomer **22b** also, where the equilibrium between the two enantiomeric twist-conformations is accomplished over half-chair intermediates (Eq. 14) [69].



(14)

The X-ray structures of both isomers support the interpretations given above and reveal interesting details for the argumentation, why also the *trans*-isomer adopts the 'unusual' twist-conformation and not the at first expected 'normal' chair conformation [71,72].

In the structure of **22b** (orthorhombic, $P2_12_12_1$, $Z = 4$) one molecule of no special symmetry constitutes the asymmetric unit (Fig. 11). The rather high PNNP torsion angles of 68.1(5) and 74.8(4)° are striking. They are considerably larger than the corresponding angles in the twist-conformations of the not N-methylated compounds **9a** (twist-*cis*-enantiomer) with 63° (mean value) and more over the corresponding *trans*-chair isomer **9b** with maximal values of 50° [20,21]. Similar large PNNP torsion angles are found in the X-ray structure of the twist-*cis*-isomer **22a** (orthorhombic, *Pbca*, $Z = 8$): 70.6(5) and 74.8(4)°. For comparison, the corresponding CCCC torsion angles in the chair conformation of cyclohexane are given as less than 60° (ideal value) [73] and calculated for a hypothetical twist-conformation of cyclohexane as 62.8° [74]. The large PNNP torsion angles in **22b** can be at least partly attributed to the sterical interaction of the vicinal methyl-groups. Their nonbonding CC distances are with 323.7(6) and 314.3(6) Å relevantly smaller than the calculated van der Waals distance of two carbon atoms of 340 Å [75].

In a hypothetical chair conformation of **22b** with essentially the same bond distances and angles, PNNP torsion angles can be calculated to be much smaller such as 46–48° [22,24,72]. Since this would lead to an even stronger sterical interaction of the vicinal methyl-groups, this interaction can be conceived as the main reason for **22b** to prefer a less strained twist-conformation in the solid state as well as in solution.

In addition, large PNNP torsion angles, as found in the twist-conformations, lead to larger nonbonded P···P

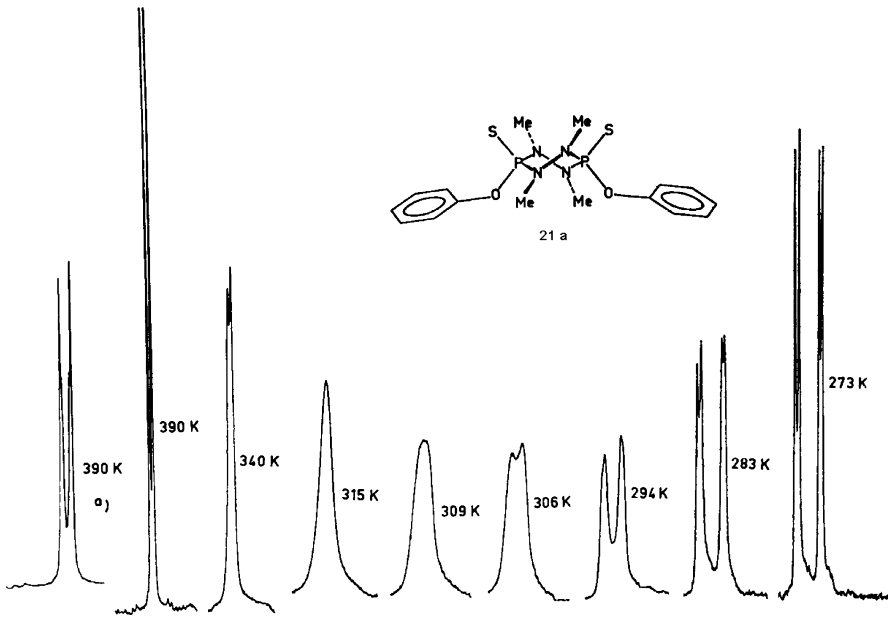


Fig. 10. Two hundred and seventy megahertz ^{1}H-NMR of the methyl-protons of **22a** at different temperatures. (a) Same as to the right but at another scale.

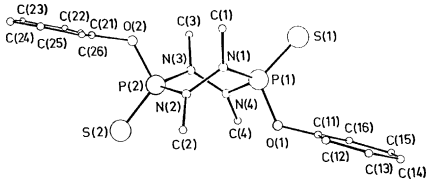


Fig. 11. Molecular structure of **22b**, H atoms omitted for clarity [72].

contact distances across the ring. These are also remarkably short: 320(2) Å in chair forms and 332(2) Å in twist-conformations [72], compared to a van der Waals P···P distance of 390 Å [75]. This fact also favours twist-conformations, although it apparently is not sufficient to destabilise chair forms enough in not N-methylated *trans*-substituted rings.

To support our argumentation, we synthesised an organic ring compound with a carbon atom in the ring across to the phosphorus. Of course, a C atom is much smaller than a P atom. As expected, the molecule **23** has a normal chair conformation (Fig. 12) [46].

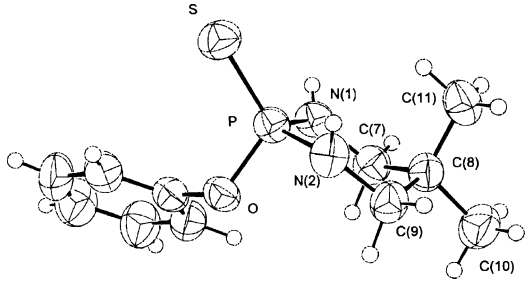
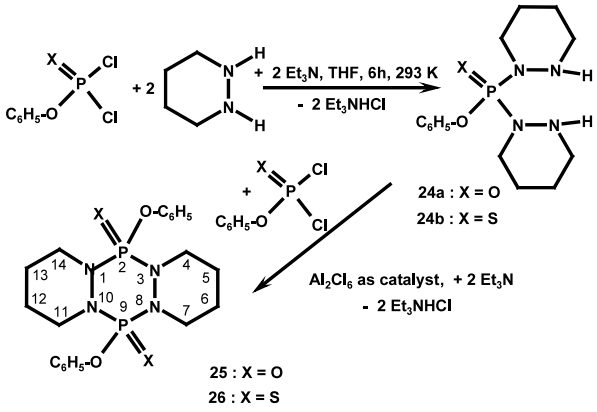


Fig. 12. X-ray structure of the organic ring molecule **23** (5,5-dimethyl-2-phenoxy-1,3-diaza-2λ^5-phosphacyclohexane-2-sulfide; monoclinic, $P2_1/c$, $Z=4$).

4.2. Polycyclic systems

How can PNNP torsion angles be influenced in a given molecule? Why not annealing other rings, six- or even five-membered organic rings for instance that could restrict the torsion angles around the NN bonds?

The synthesis of ring compounds using hexahydropyridazine, instead of hydrazine or methylated hydrazines, could be successfully accomplished in our laboratory to yield the expected fused systems (Eq. 15) [76].

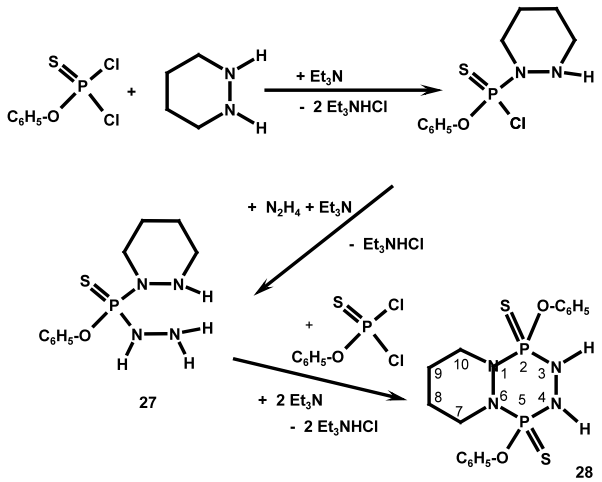


(15)

(systematic names **25**: 2,9-dioxo-2,9-diphenoxy-1,3,8,10-tetraaza-2λ^5,9λ^5-diphosphatricyclo[8.4.0.0^{3,8}]tetradecane; **26**: 2,9-diphenoxy-1,3,8,10-tetraaza-2λ^5,9λ^5-diphosphatricyclo[8.4.0.0^{3,8}]tetradecane-2,9-disulfide).

Besides the symmetric dihydrazides **24a** and **24b**, an asymmetric compound **27** has been also made by first reacting 1 mol of hexahydropyridazine and then 1 mol

of hydrazine with phenoxythiophosphoryldichloride (Eq. 16). Compound **27** reacts with the dichloride in the usual way to give the bicyclic compound **28** (2,5-diphenoxy-1,3,4,6-tetraaza-2λ^5,5λ^5-diphosphabicyclo[4,4]decane-2,5-disulfide).



(16)

Compounds **25**, **26** and **28** exist in the expected *cis*- and *trans*-configurations. Separation has been achieved by thin-layer chromatography or by sorting of crystals and recrystallisation. Only the *trans*-isomer **25b** [76] could be isolated in substance and both isomers of **26**—*cis*-isomer **26a** and *trans*-isomer **26b**. Good crystals could be obtained of all three molecules, and X-ray structure determinations have been made [77,78]. Both *trans*-configured molecules **25b** and **26b** adopt all-chair conformations of the central inorganic and of the outer organic hydrazine rings (Figs. 13 and 14). For **25b**, the PNNP torsion angles are 55.3(3)° with rP···P = 319.7 Å. In the structure of **26b** there are two symmetry independent molecules in the asymmetric unit with PNNP torsion angles of 57.1° (mean value) and rP···P = 322.1 Å.

Almost not surprising, the *cis*-isomer **26a** has a twist-conformation of the central inorganic ring but normal

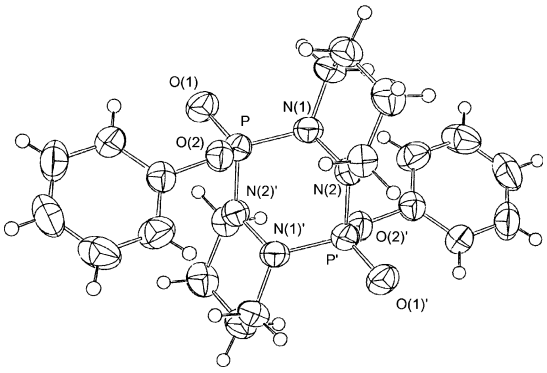


Fig. 13. Structure of the centrosymmetric molecule **25b** (orthorhombic, *Pbca*, $Z = 4$, [77]).

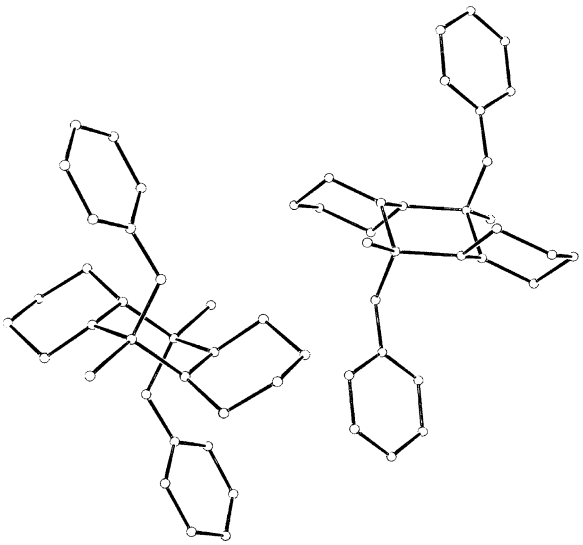


Fig. 14. Molecular structures of the two independent centrosymmetric molecules of **26b** (monoclinic, $P2_1/c$, $Z = 4$ [78]).

chair conformations of the outer organic rings (Fig. 15). Here the PNNP torsion angles are ±74.4(5)° resulting in a P···P contact distance across the ring of 333.4(2) Å [78]. ^{13}C-NMR spectra in solution show that an interconversion of the two possible enantiomeric twist-forms of **26a** is already slow at ambient temperature (line broadening!). At 193 K, four distinct signals for not symmetry-equivalent C atoms are detected. The free energy of activation is estimated as 68 ± 5 kJ mol^{-1}, a remarkable high value for a twist-conformation [76].

The bicyclic compound **28** could also be separated into the isomers **28a** and **28b** by preparative thin-layer chromatography. The identity of the isomers has been derived from Rf values and ^{31}P-NMR shifts and additional ^{13}C-NMR data. Only one signal for α- and β-C atoms are observed in **28b**. This *trans*-isomer apparently exists in only one conformation of C_2 symmetry (chair or twist?). Only one doublet is found for the NH protons at 5.06 ppm in the ^{1}H-NMR ($^2J_{PNH} = 32$ Hz). Though no suitable crystals for an X-ray structure analysis could be obtained, a chair conformation is assumed. Since the two P atoms in the molecule are centers of asymmetry (*N*, *N*′, *S* and *O* as substituents), a pair of enantiomeric configurations is expected for **28b**: *S*,*S* and *R*,*R* configurations for P,P′.

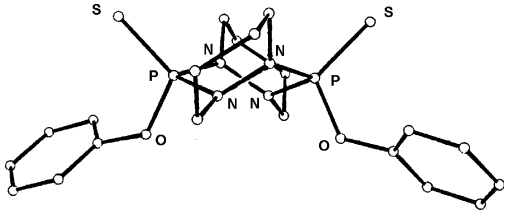
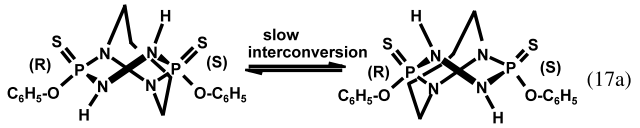
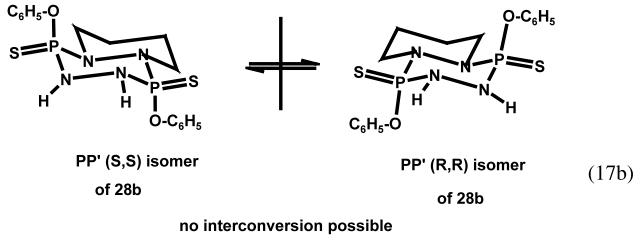


Fig. 15. Structure of *cis*-**26a** (orthorhombic, *Pccn*, $Z = 4$, [78]). The molecule possesses a twofold axis of symmetry.

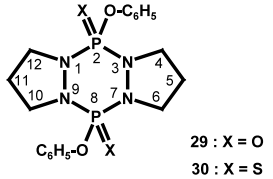
Since these configurations are enantiomers, they have identical NMR spectra or course [76].

In contrast to these findings the *cis*-isomer **28a** has no symmetry-equivalent pairs of either P or C atoms. Peaks in the proton-decoupled ^{13}C-NMR are broad at ambient temperature. Coupling to P is unresolved. ^{31}P-NMR spectra show two groups of signals at 293 K: a doublet at 72.9 ppm and a doublet of doublets at 68.5 ppm. The lines collapse to two singlets on decoupling of protons. The rather broad lines at ambient temperature grow sharp at lower temperatures (233 K). These features of the spectra obviously indicate a beginning strongly hindered interconversion of (probably) twist-conformations. Only a fast interconversion, that does not occur, would be able to render both enantiomers to a time-averaged 'meso-form' with symmetry-equivalent and thus magnetically equivalent pairs PP′ (*R*,*S*) and PP′ (*S*,*R*) and α- and β-C atoms. Coalescence of signals is approached but not complete at 323 K (experimental limit). A sketch of the most probable conformations of **28a** and **28b** is given in Eqs. 17a and 17b [76].





The five-membered ring molecule pyrazolidine instead of hexahydropyridazine also reacts with phenoxyphosphoryl- and phenoxythiophosphoryldichloride to form first the corresponding dihydrazides and then the polycyclic compounds **29** and **30** analogous to Eq. 15.



(systematic names: **29**: 2,8-dioxo-2,8-diphenoxy-1,3,7,9-tetraaza-2λ^5,8λ^5-diphosphatricyclo[7.3.0.0^{3,7}]dodecane; **30**: 2,8-diphenoxy-1,3,7,9-tetraaza-2λ^5,8λ^5-diphosphatricyclo[7.3.0.0^{3,7}]dodecane-2,8-disulfide). Only the *trans*-isomers **29b** and **30b** could be isolated in substance. The X-ray structure of **29b** (monoclinic, $P2_1/c$, $Z=2$) clearly shows the expected centrosymmetrical chair conformation of the phosphorus-hydrazine ring

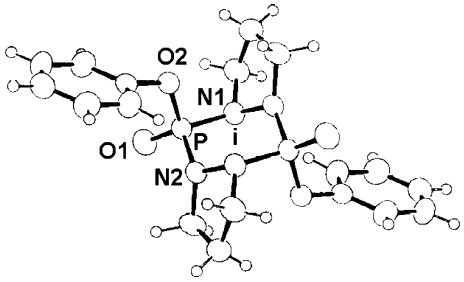
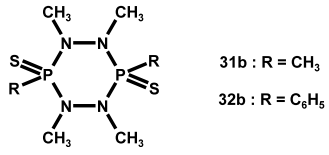


Fig. 16. Molecular structure of the chair conformation of the *trans*-oxo-compound **29b**.

(Fig. 16). The annellated five-membered organic rings have almost planar envelop conformations as in the parent compound pyrazolidine and other five-membered organic rings. The torsion angles are: PNNP 55.3(2)° (CNNC 34.8(1)°); r P···P 322.1(1) Å, values very similar or almost identical to those of **25b** [79]. Very similar results have been obtained with **30b** (orthorhombic, *Pbca*, $Z=4$) [80]. Fig. 17 shows the again centrosymmetrical chair conformation of the inorganic ring; torsion angles: PNNP 57.8(2)° (CNNC 31.2(3)°) (negative values in the presented ORTEP-sketch); r P···P 325.9(1) Å.This value is slightly larger than in **29b** due to the 2.5° larger PNNP torsion angle.

4.3. Phosphonic acid derivatives

Interestingly two cyclic thiophosphonic acid derivatives incorporating 1,2-dimethylhydrazine apparently follow the same trends according to their ring conformations [81]. Both published molecules possess a *trans*-configuration. The less sterically hindered methylphosphonic acid derivative **31b** adopts a chair conformation, whereas the phenyl phosphonic derivative **32b** has a typical twist-conformation in the crystal with S atoms and phenyl-groups in isoclinal positions.



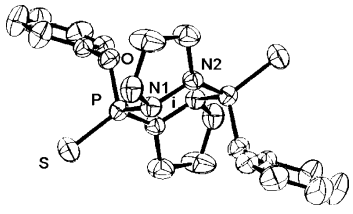
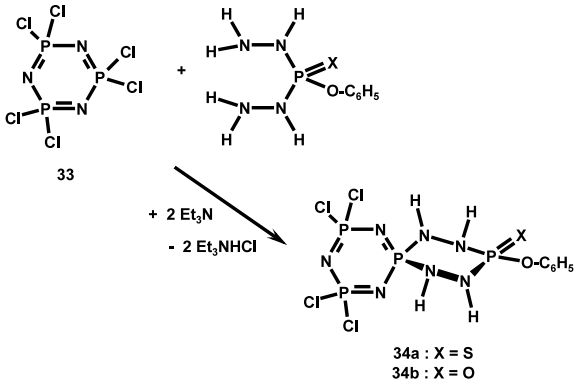


Fig. 17. Centrosymmetric chair conformation of the disulfide **30b**.

5. Spirocycles containing two or more phosphorus atoms—combination of hydrazine rings and cyclophosphazenes

Hexachlorocyclotri(phosphazene) (**33**) is a long known and easily accessible molecule that reacts with organic amines preferably to form vicinal disubstituted products. Bifunctional compounds such as alkane-diols, -diamines, or aminoalcohols for instance yield spiro-compounds [82]. Dihydrazidothiophosphoric acid phenylester reacts accordingly (Eq. 18). At room temperature in THF as solvent **34a** (4,4,6,6-tetrachloro-6′-phenoxy-cyclotri(phosphazene)-2-spiro-3′-cyclodi(phosphadiazane)-6′-sulfide) can be synthesised in about 70% yield. The constitution was proved by the usual spectroscopic methods (MS, IR, NMR).The ^{31}P-NMR is of the type $A_2BX_2X'_2C$ as expected (Fig. 18) [83].



(18)

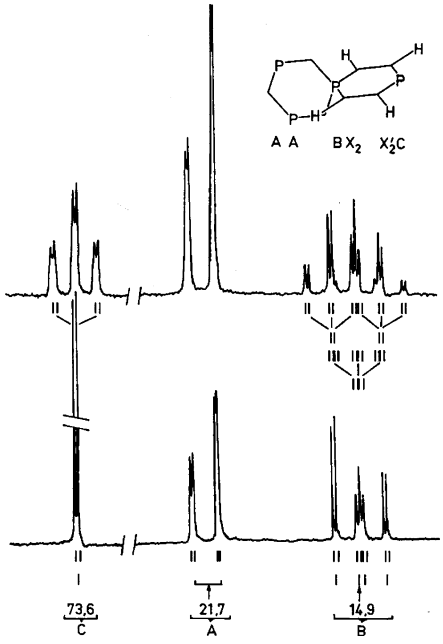
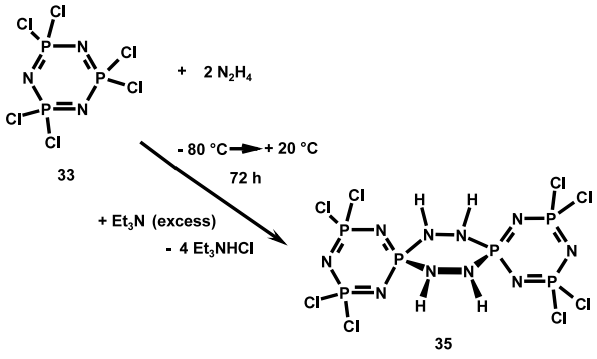


Fig. 18. ^{31}P- (top) and $\{^1H\}^{31}$P-NMR (bottom) of the spiro-compound **34**; $^2J_{AB} = 41.3$, $^3J_{BC} = 5.8$, $^5J_{AC}$ = smaller than 0.6 Hz, $^2J_{BX} = 37$, $^2J_{CX'} = 36$ Hz.

In the corresponding oxo-compound **34b** the proton-decoupled ^{31}P-NMR spectrum shows the two P atoms in the cyclotri(phosphazene) part to be inequivalent. The spectrum thus is of the ABCD type, $\delta_A = 22.44$, $\delta_B = 22.19$, $\delta_C = 15.65$, $\delta_D = 16.07$ ppm; $^2J_{AC} = 33.9$, $^2J_{BC} = 44.3$, $^2J_{AB} = -0.74$, $^3J_{CD} = -3.0$ Hz; in the ^{1}H-NMR: $\delta_{H(X)} = 7.4$, $\delta_{H(X')} = 7.1$ ppm; $^2J_{H(X)NP(C)} = 39$, $^2J_{H(X')NP(D)} = 30$ Hz (values partly from calculated spectrum with 56 peaks [84,85]).

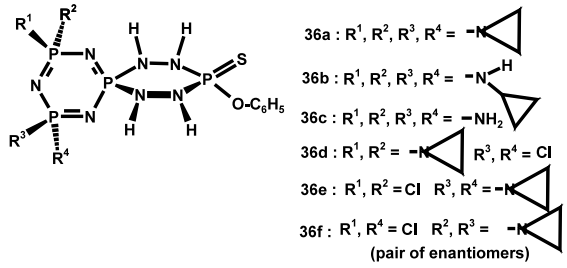
Hexachlorocyclotri(phosphazene) also reacts directly with absolute hydrazine to yield the dispiro-system **35** (Eq. 19).



(19)

The proton decoupled ^{31}P-NMR spectrum is of the expected $A_2BB'A'_2$ type (pseudo A_2B type) with a doublet in the A part and a triplet in the B part: $\delta_A = 21.58$, $\delta_B = 15.72$ ppm; $J_{AB} = 41.1$ Hz [85].

A further substitution of Cl atoms in the phosphazene part of the molecules for instance in **34a** leads to a variety of derivatives such as **36a**–**36f**. All of them have been well characterised by their ^{31}P-NMR spectra [86,87].



A reaction of hexachlorocyclotri(phosphazene) with 1,2-dimethylhydrazido-thiophosphoric acid *O*-phenylester leads to the corresponding *N*-tetramethylated spiro-derivative **37**. The X-ray structure of this molecule reveals a twist-conformation of the hydrazine ring and a planar cyclotri(phosphazene) ring (Fig. 19) [88]. Very similar results have been found for the *N*,*N*′-dimethyl-spiro-compound **38** (monoclinic, $P2_1/c$, $Z = 8$) [89,90] and the tricyclic compound **39** (Fig. 20) [90].

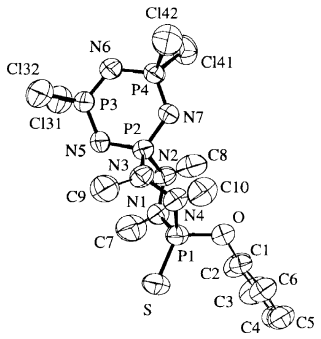


Fig. 19. X-ray structure of the spiro-compound **37** (triclinic, $P\bar{1}$, $Z = 2$, H atoms omitted for clarity).

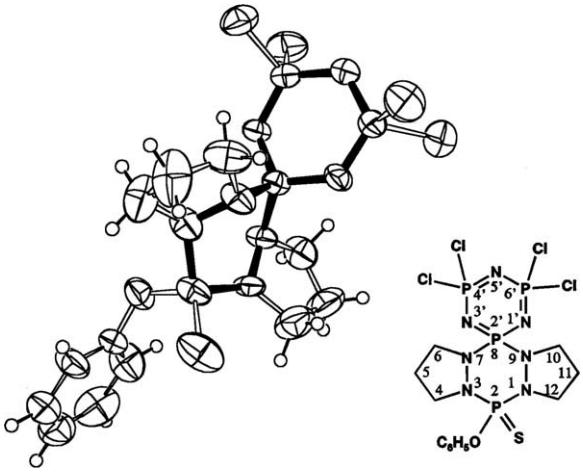
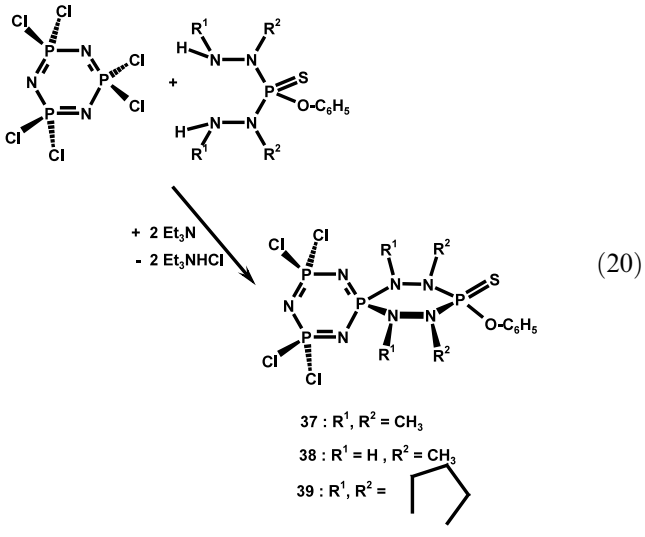
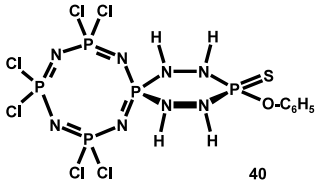


Fig. 20. X-ray structure of the spiro-system **39** (monoclinic, $P2_1/n$, $Z = 4$) (4′,4′,6′,6′-tetrachloro-2-phenoxy-1,3,7,9-tetraaza-2λ^5,8λ^5-diphosphatricyclo[7.3.0.0^{3,7}]dodecane-spiro[8,2′]cyclotri(phosphazene)-2-sulfide).



(20)

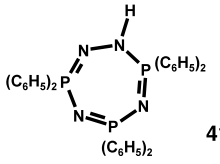
The eight-membered octachlorocyclotetra(phosphazene) reacts in the same way to yield the spiro-compound **40**. The rather complicated ^{31}P-NMR spectrum of this molecule of the type ABCDX2X′$_2$E has been successfully simulated. For details, see original publication [90].



40

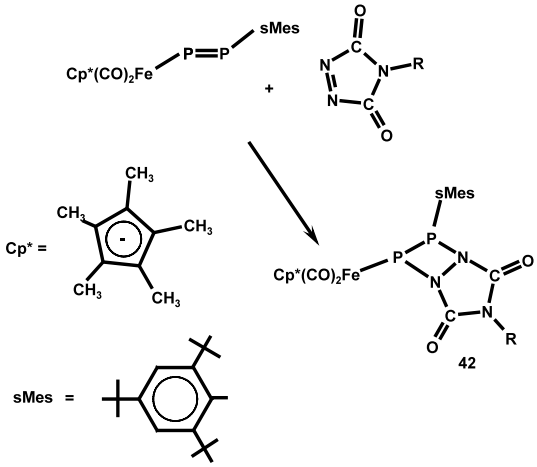
6. Different ring sizes with N–N bonds

A seven-membered ring **41** that almost resembles a cyclophosphazene but contains a N–N single-bond in the ring is described in the literature with its X-ray structure. The ring is strongly puckered [91].



41

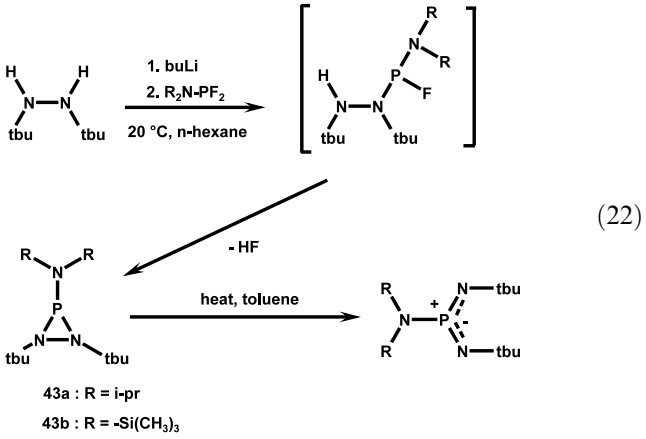
A four-membered hydrazine-ring is formed in a (2+2) cycloaddition reaction of a special 'phosphene' with a N-substituted azodicarbonimide. The resulting bicyclic molecule **42** may be considered a diphosphane hydrazine derivative (Eq. 21) [92].



42

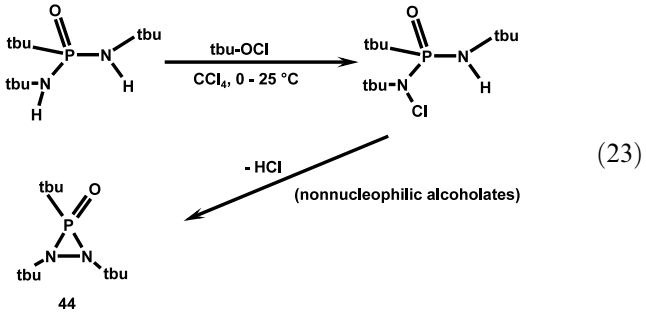
(21)

With bulky substituents at the hydrazine even three-membered rings can be synthesised. The diazaphosphiridines **43** are surprisingly stable at ambient temperature but isomerise at higher temperatures to form the valence-isomeric diiminophosphoranes (Eq. 22). Compound **43a** was characterised also by an X-ray structure analysis (monoclinic, $P2_1/c$, $Z = 4$ [93]).



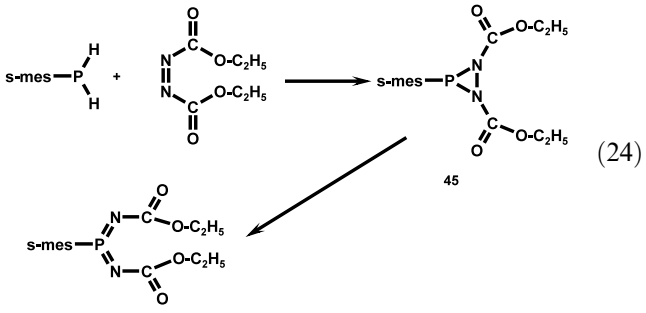
(22)

Corresponding phosphonic acid derivatives, diazaphosphiridine-3-oxides **44** are also known. They have been obtained from the N-chlorinated diamides by HCl elimination (Eq. 23) [94–96].



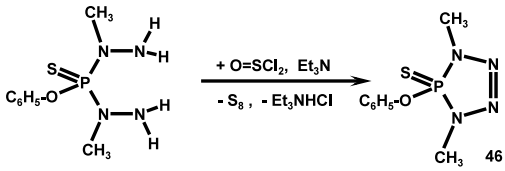
(23)

Monosubstituted phosphanes such as supermesitylphosphane react with azodicarbonic acid diethylester to yield the diazaphosphoridine **45** as an intermediate, that spontaneously isomerises to the corresponding diiminophosphorane (Eq. 24) [97].



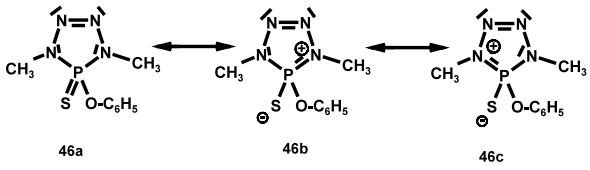
(24)

Eq. 23 describes the formation of a three-membered ring by oxidation of a phosphonic acid diamide. This means that a new N–N bond is formed during the ring closure. The hydrazine is not yet present in one of the starting materials but is formed during the ring synthesis. Such an oxidative ring closure also leads to a five-membered heterocycle, when the starting component is not a diamide but a *N*,*N*′-dimethyldihydrazide of thiophosphoric acid phenylester (Eq. 25) [98].The five-membered ring is planar and the atoms N(1) and N(4)



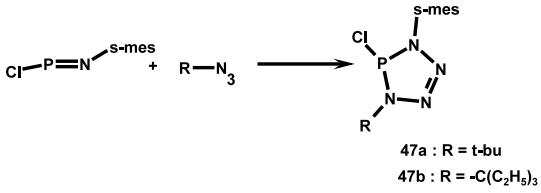
(25)

are also sp^2-hybridised (sum of bond angles 360° within experimental errors). Bond distances in the ring may be interpreted to fit an almost aromatic λ^5-phosphatetrazole: N(1)–N(2) 137.2(9), N(2)–N(3) 127.5(1), N(3)–N(4) 138.5(1), N(1)–P 166.5(6), N(4)–P 168.0(6) Å (Fig. 21) [99], although a mesomeric formula **46a** (1,4-dimethyl-5-phenoxy-tetraaza-5λ^5-phosphacyclopentene-5-sulfide) apparently has a strong weight (Eq. 26).



(26)

Similar compounds containing phosphorus(+III) in the ring have been synthesised from iminophosphanes and organic azides with bulky substituents (Eq. 27).



(27)

The chlorine in **47** can be exchanged with other substituents using Li–NH–*s*-mes, Li–O–*s*-mes, Li–S–*t*-bu or Li–*t*-bu/*t*-bu–NH_2 below ambient temperature. The X-ray structure of **47c** has been determined (monoclinic, $P2_1/n$, $Z=4$). Again the five-membered ring is almost planar. Strong sterical interaction of the bulky substituents at the three N atoms bound to phosphorus can be seen from angle distortion [100,101].

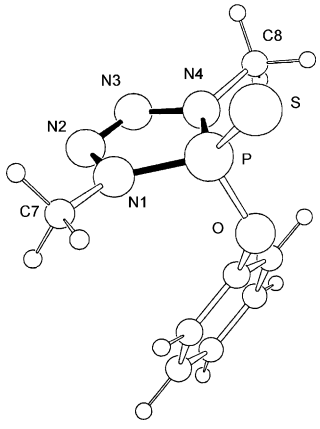
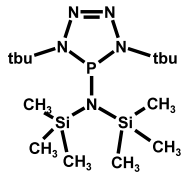


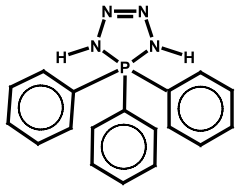
Fig. 21. X-ray structure of **46** (monoclinic, $P2_1/c$, $Z=4$).



47c

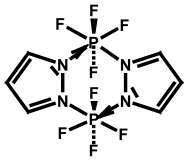
On warming to room temperature or above, these compounds lose nitrogen and are transformed into the corresponding bis(imino)phosphoranes (see Eq. 24) [100,102–105].

It should be mentioned here that as early as 1921, a reaction of triphenylphosphane with hydrogen azide led to a compound, that was described as a salt—$[(C_6H_5)_3P{=}NH_2]^+N_3^-$ [106]—later turned out to be a [2+3] cycloaddition product **48** of triphenylphosphane-imine and hydrogen azide [107].



48

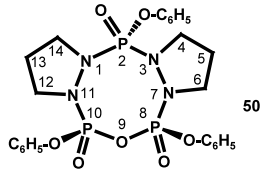
A cyclic dimer of a reaction product of *N*-trimethylsilylpyrazole with phosphoruspentafluoride **49** has a tricyclic structure. The inner inorganic ring adopts a flat boat conformation (low temperature X-ray structure analysis, monoclinic, $P2_1/c$, $Z=4$). The P atoms are octahedrally coordinated [108].



49

A by-product **50** formed by hydrolysis during the synthesis of phosphoric acid, pyrazolidine compounds in our laboratory proved to be an eight-membered ring molecule containing a P–O–P unit in the ring. The X-ray structure shows the central ring to have a boat–chair conformation (Fig. 22) [109].

Not really hydrazine derivatives but five-membered isocycles with N–N bonds and only nitrogen in the ring are the *para*-phenyl-substituted pentazoles **51**,



50

that decompose to N_2 and the corresponding phenylazides at ambient temperature. They are usually made from the diazoniumchlorides and lithium-azide in methanol and can be isolated in crystalline form below −30 °C. ^{15}N-NMR data and a low-temperature X-ray

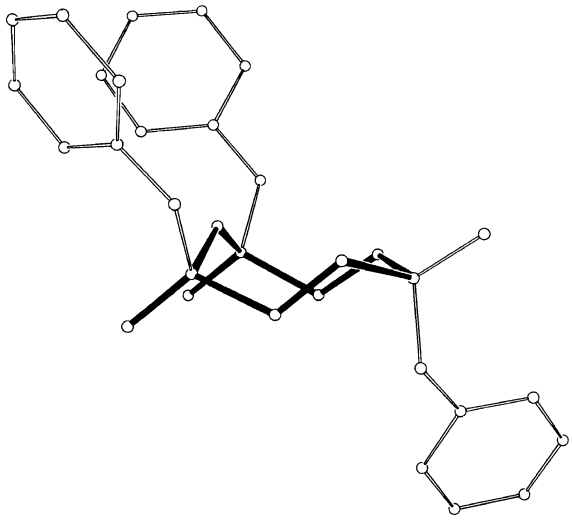
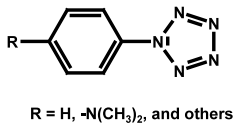
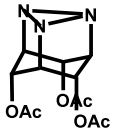


Fig. 22. Boat-chair conformation of the eight-membered central inorganic ring of compound **50** (monoclinic, *Cc*, $Z=4$; the annellated outer pyrazolidine rings and H atoms are omitted for clarity).

structure analysis prove the constitution of these interesting ring systems [110–112].



51

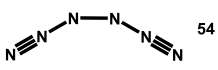


52

A substituted triaziridine **52** is also known with its X-ray structure at 105 K (monoclinic, $P2_1/n$, $Z=4$) [113].

The structure of a cyclic (?) N_6 compound described in the literature seems uncertain. Is it a ring, a hexaazabenzene (**53**), or an open-chained diazide 54? [114,115].

53



54

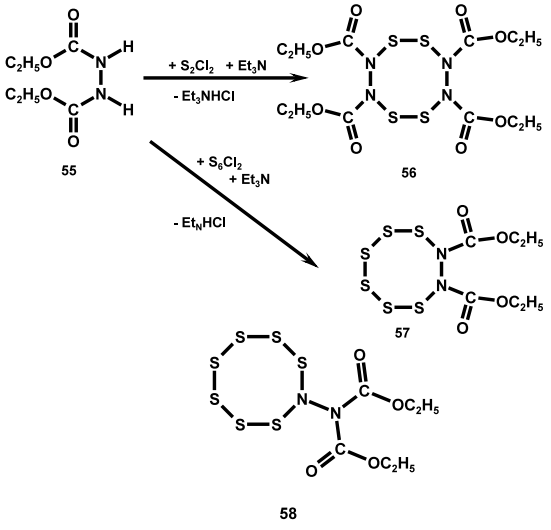
Last but not least, it should be mentioned that quite a lot of interesting chemistry on the borderline between inorganic and organic chemistry has been published related to cyclic hydrazine derivatives, for instance Schiff-base derivatives of thiophosphoric acid dihydrazides and dendrimers and other polymers containing these and similar building blocks. Since the compounds are no 'inorganic' ring systems in a rigid sense, no details are given here, but a few main publications are cited [116–127].

7. Hydrazineheterocycles containing sulfur in the ring

7.1. Two and more sulfur atoms in the ring

When we started our research on sulfur containing hydrazine heterocycles, quite a number of compounds with only hydrazine and sulfur in the ring were known.

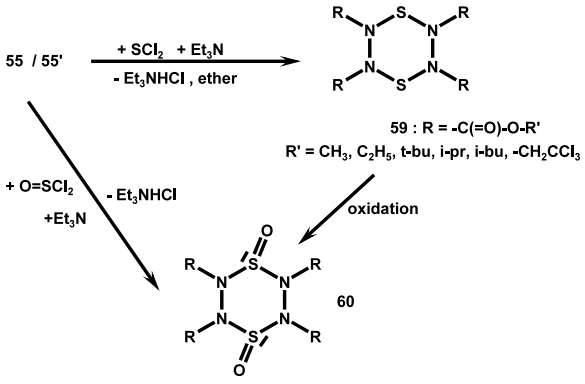
To avoid redox-reactions only hydrazines with electron-withdrawing substituents at the hydrazine N atoms can be used to get rings. Eight-membered rings were first described. They are formed in the reaction of 1,2-bis(ethoxycarbonyl)hydrazine (**55**) with S_2Cl_2 or S_6Cl_2 in the presence of triethylamine in diluted solutions (Eq. 28) [128]. X-ray structure determinations of both eight-membered rings **56** (monoclinic, $C2$) and **57** (monoclinic, $P2_1/c$) are known. The N atoms are sp^2 hybridised and the NN distances are rather short in both molecules: 137(4) and 139(1) Å, respectively. Both rings have crown conformations with large CNNC torsion angles: 97.3 and 102.0° [129]. An eight-membered ring compound **58** with an exocyclic hydrazine group is formed from 1,1-bis(ethoxycarbonyl)hydrazine and a mixture of S_2Cl_2 and S_6Cl_2 in low yields [130]. The X-ray structure again reveals a crown shaped heterocycle. An interesting feature of this molecule is that the N atom in the ring differs in the two independent molecules of the asymmetric unit: in one molecule it is sp^2 hybridised, rNN = 133 Å; in the other molecule this N atom is trigonal pyramidal coordinated with rNN = 142 Å. In both molecules the exocyclic N atom has a sum of bond angles near 360(1)° [131]. This shows that apparently packing effects in the crystal may influence the geometry (hybridisation) around N atoms and thus determine also NN bond distances.



(28)

Similar organic rings have been synthesised from Cl–S–CH_2–CH_2–S–Cl and Cl–S–S–CH_2–CH_2–S–S–Cl and **55** to give the corresponding six- and eight-membered heterocycles with two carbons in the ring [132–135]. Sulfurdichloride and thionylchloride react with **55** and similar substituted hydrazines in a 1:1 molar ratio to yield the six-membered rings **59** and **60**, respectively (Eq. 29) [136,137]. The 1,4-dithia-2,3,5,6-tetraazacyclohexane-1,4-dioxide system **60** can also be obtained by oxidation of **59** by means of *m*-chloroperbenzoic acid in trichloromethane as solvent [134].

Three-, five-, and six-membered sulfur hydrazine heterocycles with perfluoralkyl- or chlordifluormethyl-substituents in 1,2-positions of the hydrazine can be synthesised in low yields of **5** to 11% by photolysis of the corresponding substituted azoalkanes in the presence of disulfurdichloride in different stochiometric ratios (Eq. 30) [138,139].



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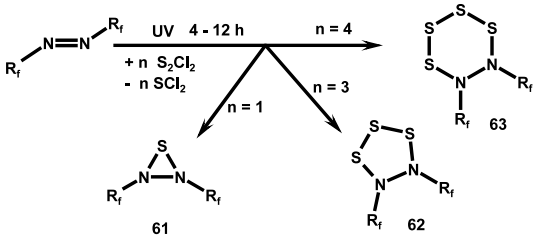
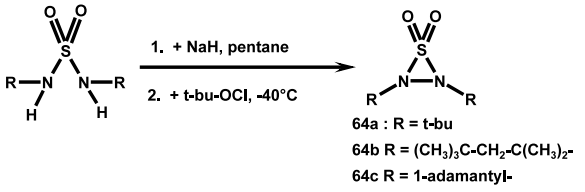


(30)

The compounds are high-boiling yellow liquids (vapour pressures 5–9 mbar/25 °C) They decompose at room temperature to form nitrogen and R_f–S_X–R_f ($X = 1, 3, 4$; $R_f = C_2F_5$, CF_2Cl) [128].

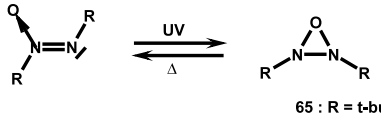
A few examples of three-membered rings containing S(+VI) are also known. The hydrazine unit is formed during the ring synthesis by oxidative ring closure (Eq. 31) [140–143]. An X-ray structure determination of **64b** (orthorhombic, $Pca2_1$) shows a NN bond distance 167 Å, which is the longest NN single bond observed so far [138]. The compounds are moderately stable. They decompose slowly at room temperature to yield SO_2 and the corresponding



(31)

azoalkanes. Moisture decomposes to the substituted hydrazinium-hydrogensulfate [139,140]. An excess of *t*-bu–OCl or Cl_2 gives the azoalkane [137].

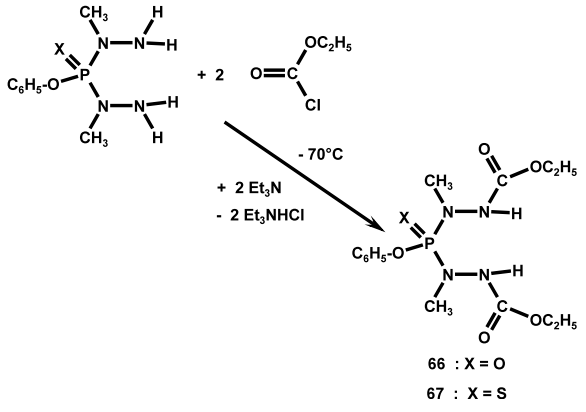
The photolytic isomerisation of certain azoalkane N oxides also yields three-membered hydrazine heterocycles **65** that contain oxygen in the ring (Eq. 32) [144–146].



(32)

7.2. Phosphorus and sulfur in the ring

Since we also found in our laboratory that N-unsubstituted dihydrazido-derivatives of phosphoric acid react with thionylchloride, sulfurylchloride or sulfurdichloride under redox-decomposition and not under formation of six-membered rings, we first tried to synthesise dihydrazides with carboethoxy-groups as electron withdrawing substituent at both N atoms. This was not successful apparently because of sterical hindrance. Only bis(β-carboxyethyl)-substituted dihydrazides have been obtained, that reacted with excess chloro-formic acid ethylester to yield rings that contained a –C(=O)-unit (see Section 8) [147]. Finally we succeeded in synthesizing the corresponding bis(α-methyl-β-carboxyethyl)-substituted dihydrazides of phosphoric and thiophosphoric acid phenylester **66** and **67** (Eq. 33) [147,148]. While sulfurylchloride did not react



(33)

with **66** and **67** in the expected way, thionylchloride and sulfurdichloride gave the corresponding six-membered heterocycles (Eq. 34) [148]. NMR data in solution as well as an X-ray structure analysis showed **69a** to have a somewhat distorted twist-conformation of the ring (Fig. 23) [149]. The energy of activation for the interconversion of the two enantiomeric twist forms is rather high: 74 ± 2 kJ mol^{-1}; the same is true for **69b**: 75 ± 2 kJ mol^{-1}, due to the rather bulky substituents at the N atoms (temperature dependent NMR data) [149].The structure of **69b** is seen in Fig. 24 [150]. In both molecules **69a** and **69b**, the NN bond distances are

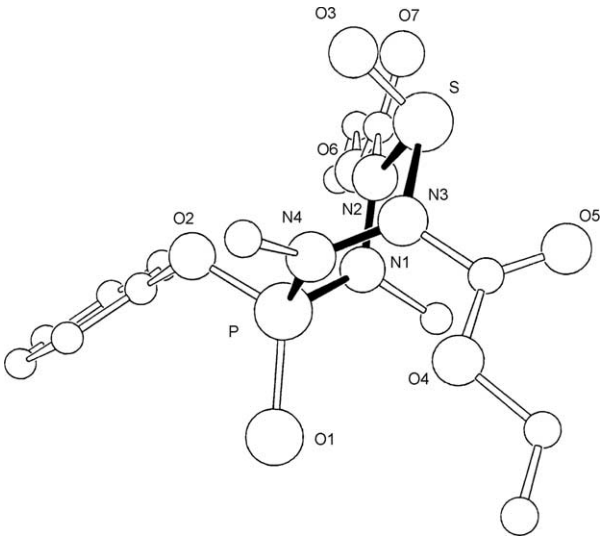
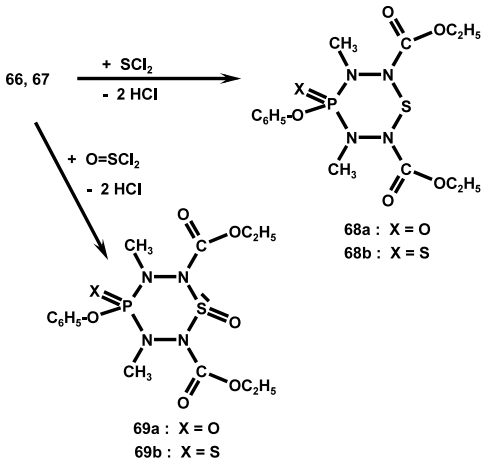


Fig. 23. Twist-boat conformation of **69a** (3,5-dimethyl-4-oxo-4-phenoxy-1λ^4-thia-2,3,5,6-tetraaza-4λ^5-phosphacyclohexane-2,6-dicarbonic acid diethylester; orthorhombic *Pbca*, $Z=8$). The centrosymmetric crystal contains both enantiomeric twist-conformations.

short due to the almost ideal sp^2 hybridisation of all N atoms: 138.9(7) and 137.7(6) Å (for more interesting details see original literature) [149,150].



(34)

8. Some carbon(+IV)-containing phosphorus hydrazine rings

During our attempts to synthesise *N*-carboethoxy-substituted dihydrazides of phosphoric and thiophosphoric acids, we also ended up with heterocycles containing carbon under certain reaction conditions. Since these may be termed 'inorganic' heterocycles, too—they are carbonic acid derivatives—they are mentioned here. Colourless needles (m.p. 171 °C) of compound **70** were obtained by reacting the bis(α-*N*-methyl)dihydrazide with carbonic acid bis(trichloro-

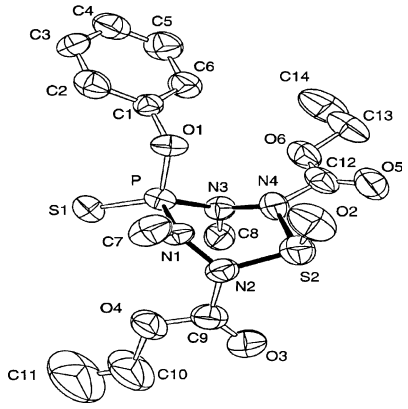


Fig. 24. X-ray structure of **69b** (triclinic, $P\bar{1}$, $Z = 2$). R-form is shown, the crystal also contains the enantiomeric S-configuration (ring twisted the other way).

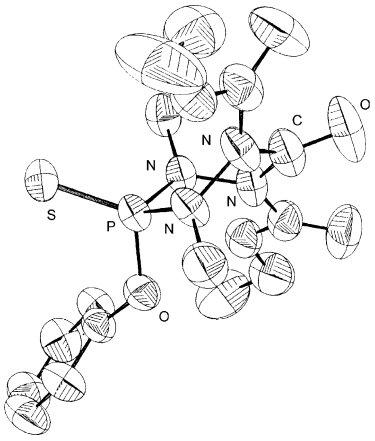
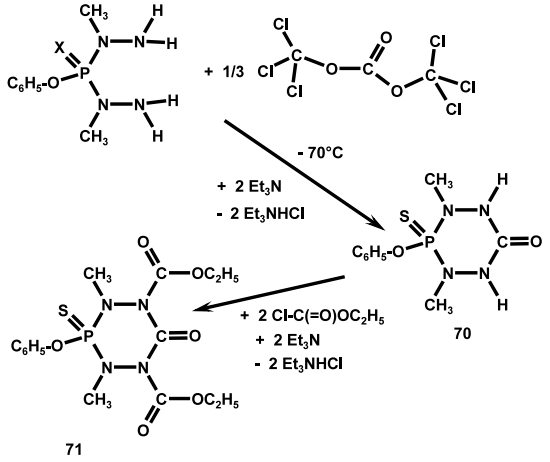


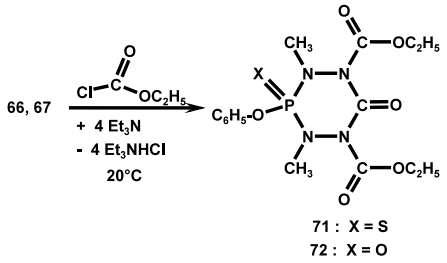
Fig. 25. X-ray structure of **71** (2,2-dimethyl-6-oxo-3-phenoxy-3-thioxo-1,2,4,5-tetraaza-3λ^5-phosphacyclohexane-1,5-diethylcarboxylate; triclinic, $P\bar{1}$, $Z = 2$). H atoms omitted for clarity.

methylester) ('triphosgene') in the presence of triethylamine (Eq. 35) [147]. Further reaction of **70** with two molecules of chloro-formic acid ethylester gave the N-tetrasubstituted product **71** in good yields (Eq. 35). Compound **71** could also be synthesised from the carboethoxy-substituted dihydrazide **67** and 'triphosgene' in the presence of excess triethylamine. But the reaction was sterically hindered and only almost complete after 1 week stirring in THF at room temperature [147].



(35)

The N-tetrasubstituted dihydrazides **66** and **67** also react with excess chloro-formic acid ethylester at 20 °C to form the ring compounds **71** and **72** (Eq. 36) [149].



(36)

The results of the reactions are strongly dependent on the reaction temperature. At 70 °C the dihydrazides are formed according to Eq. 33, at 0 °C the main product is the ring **70** (Eq. 35) or the corresponding P=O compound **70a**, and at +20 °C the main products are the N-tetrasubstituted rings **71** and **72** (Eq. 36) [149].

The X-ray structure of **71** reveals the expected twist-conformation of the ring (Fig. 25). The carbonyl and all four N atoms are sp^2 hybridised. The NN bond distances are again short: 139.7(3) and 140.7(3) Å [151]. Almost the same results were obtained in X-ray structure of **72** (Fig. 26). Here the NN bond distances are even slightly shorter: 138.5(3) and 139.6(3) Å [152].

Bis(1,2-dimethylhydrazido)-thiophosphoric acid *O*-phenylester also reacts with 'triphosgene' to give the analogous six-membered ring molecule **73** [153]. Suitable crystals for an X-ray structure analysis could only be obtained of a dimer, that is a 12-membered ring molecule **74** with high torsion angles around almost all ring bonds (Fig. 27) [154].

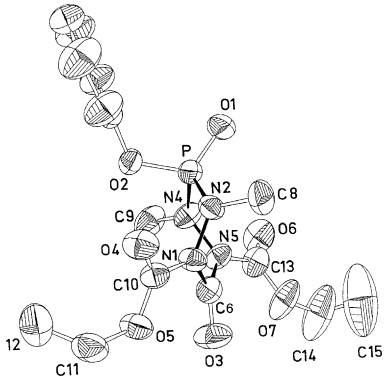


Fig. 26. The twist-conformation of the oxo-compound **72** (triclinic, $P\bar{1}$, $Z = 2$) H atoms not shown.

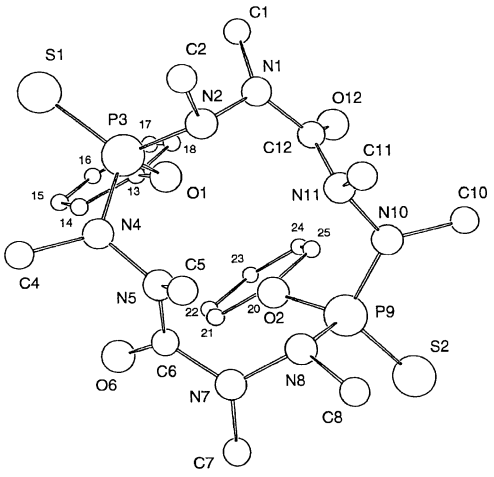


Fig. 27. Structure of the 12-membered ring of **73** (1,2,4,5,7,8,10,11-octamethyl-6,12-dioxo-3,9-diphenoxy-1,2,4,5,7,8,10,11-octaaza-3λ^5,9λ^5-diphosphacyclododecane-3,9-disulfide; orthorhombic, $Pna2_1$, $Z=4$).

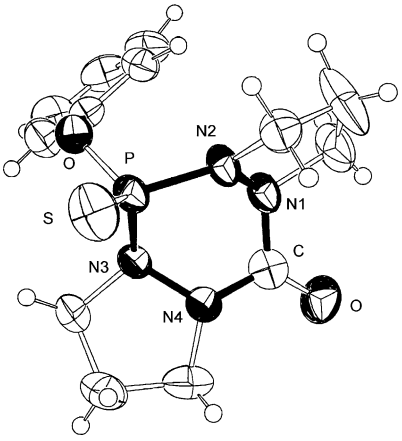
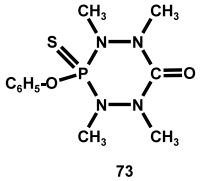


Fig. 28. The molecule **75** (8-oxo-2-phenoxy-1,2,7,9-tetraaza-2λ^5-phosphatricyclo[7.3.0.0^{3,7}] dodecane-2-sulfide, orthorhombic, $P2_1/n$, $Z=4$) [153].



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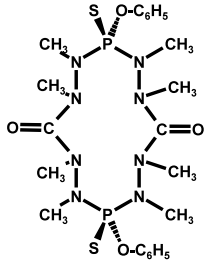


74

The two tricyclic molecules **75** and **76** have been synthesised in our laboratory starting from bis(pyrazolidinyl)- or bis(hexahydropyridazinyl)-thiophosphoric acid *O*-phenylester and 'triphosgene'. The X-ray structures shown in Figs. 28 and 29 again reveal a twist-

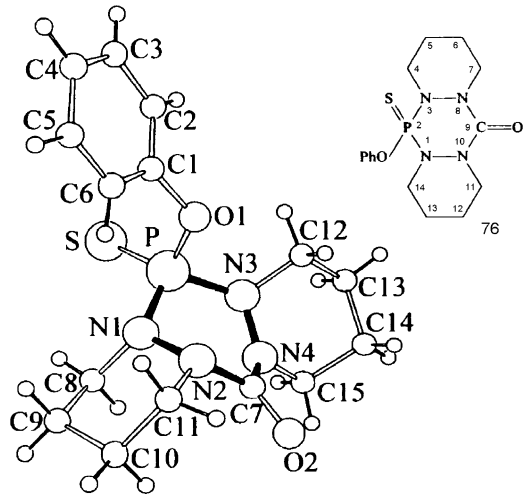
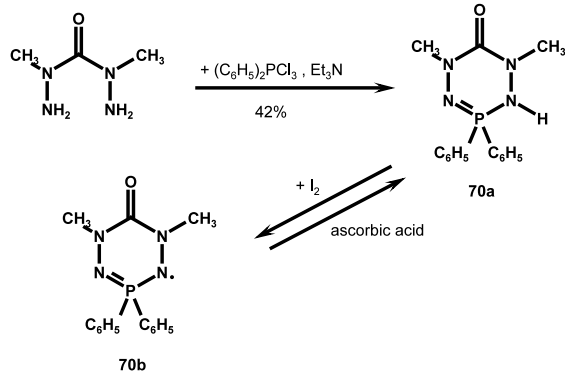


Fig. 29. Formula with numbering scheme and X-ray structure of **76** (9-oxo-2-phenoxy-1,3,8,10-tetraaza-2λ^5-phosphatricyclo[8.4.0.0^{3,8}]tetradecane-2-sulfide, monoclinic, $P2_1/n$, $Z=4$) [155].

conformations of the central inorganic rings. The outer organic rings have 'normal' envelope and chair conformations, respectively [153,155].Carbonic acid di(1-methylhydrazide) reacts with trichlorodiphenyl phosphorane in the presence of triethylamine to form the six-membered ring **70a**, which is a phosphinic acid derivative. The molecule can be oxidised by iodine to a moderately stable red–orange radical **70b**, which is reduced to the original leuko-form by succinic acid (Eq. 36a). Compound **70b** is a so-called 6-oxo-3-phospha-verdazyl. Its EPR-spectrum is discussed extensively in the original publication [155b].

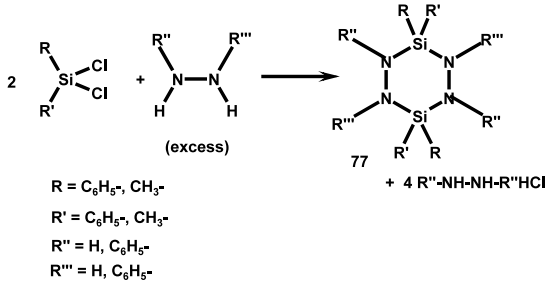


Other related molecules known, for example the original stable verdazyls, first synthesised by Kuhn and co-workers, some other phospha-verdazyls and cyclic carbonic and thiocarbonic acid hydrazides are not included here, since they are no 'inorganic' heterocycles according to the given definition in Section 1. The interested reader may refer to the literature cited here [155c–155k].

9. Silicon hydrazine heterocycles

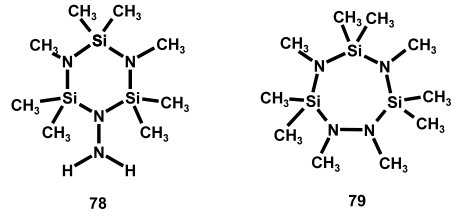
9.1. Only silicon and nitrogen in the ring

Title compounds especially six-membered rings have been first synthesised by Wannagat and by Gilman and co-workers [156–159]. Wannagat published an early survey in 1964 [160]. Starting materials were dichlorodiorganosilanes and hydrazine or substituted hydrazines (Eq. 37).

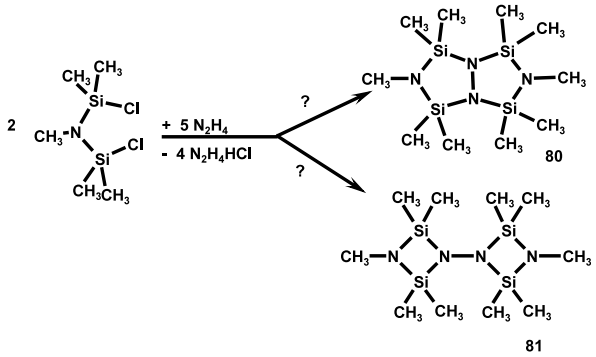


(37)

1,5-Dichloro-octamethyltrisilazane reacts with hydrazine or lithiated 1,2-dimethylhydrazine to yield the six- or seven-membered rings **78** and **79** [161,162].



The corresponding 1,3-dichloropentamethyldisilazane reacts with hydrazine itself to form a bicyclic system. It was not clear, which of the two isomers **80** or **81** was actually present or if it was a mixture of both (Eq. 38) [163–165].

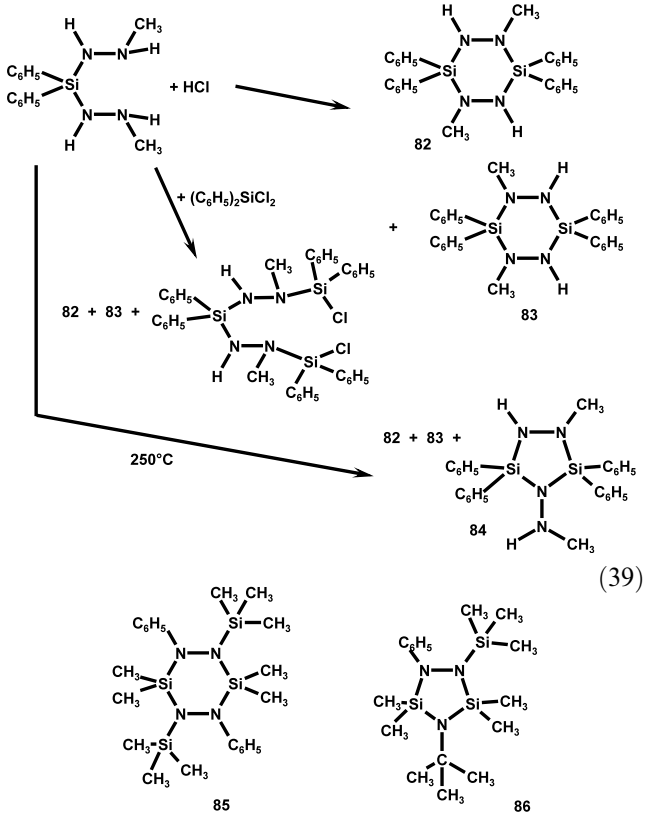


(38)

A later X-ray structure analysis of an analogue with mesityl-substituents at the N atoms (monoclinic, $C2/c$, $Z=4$) revealed the five-membered annellated constitution similar to isomer **80**. The molecule has a twofold axis of symmetry bisecting the NN bond that is rather long: 151.9(6) Å. The five-membered rings are not planar but twisted along the symmetry axis [166]. Later experiments with di(methylhydrazido)diphenylsilanes gave mixtures of isomers, that show equilibria to be present in the reaction mixtures, the composition being dependent on reaction conditions such as temperature and reaction time (Eq. 39) [167]. Similar equilibria have been observed with organic silicon hydrazine heterocycles obtained from 1,2-bis(chlorodimethylsilyl)ethane and hydrazine [168] or from dilithiated 1,2-bis(trimethylsilyl)hydrazine and trichloromethane [169].

Klingebiel et al. have synthesised silicon hydrazine heterocycles from SiF functionalised hydrazines. Since survey articles have been published by this author recently [170–172], only a short summary is given below.

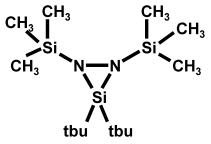
The lithiation of 1-fluorodimethylsily-2-trimethylsilyl-1-phenylhydrazine or the corresponding 2-($Si(CH_3)_2$–NH–*t*-bu)-substituted hydrazine yields the compounds **85** and **86**, respectively or an open chained product dependent on the solvent and on the reaction conditions [173]. A number of differently substituted



(39)

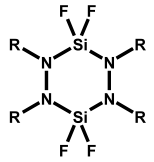
five-membered rings have been obtained in a similar way (substituents: F, CH_3, *t*-bu, mesityl, $-SiF_2C_6H_5$). An X-ray structure determination proved the five-membered ring constitution analogous to formula **86** (no details given) [174]. A three-membered ring **87** could be synthesised from 1,2-bis(trimethylsilyl)hydrazine and di(*t*-bu)difluorosilane via lithiation of the hydrazine. The ring is stable at room temperature but decomposes

above +80 °C. The Si in the ring has a remarkable high-field resonance signal in the ^{29}Si-NMR spectrum: −30.73 ppm [175].



87

The X-ray structure of a Si-fluoro-substituted six-membered ring molecule **88a** (tetragonal, $P4_22_12$, $Z=2$) reveals a twist-conformation probably caused by the bulky substituents at the four N atoms, which also leads to a rather large NN distance: 149.1(8) Å [176].



systematic name of 88a:

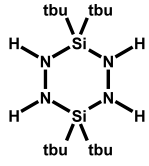
3,3,6,6-tetrafluoro-1,2,4,5-tetra(t-butyl-dimethyl-silyl)-

-1,2,4,5-tetraaza-3,6-disila- cyclohexane

88a : R = -Si(CH$_3$)$_2$-t-bu

88b : R = -Si(CH$_3$)$_3$

Di(*t*-butyl)difluorosilane reacts with hydrazine at −30 °C after lithiation to give mainly the monosubstituted di(*t*-butyl)fluorosilylhydrazine besides the ring compound **89** as a by-product. If the obtained substituted hydrazine is first lithiated and then reacted with further *t*-butyldifluorosilane, the ring **89** is the main product [177]. The ring size obtained is often dependent on the substituents at the silicon and at the hydrazine and more over on the reaction conditions, as can be seen from the formula **89**, **90** and **91**. Six-membered rings such as **92** are obtained under more drastic reaction conditions, or by heating **91** in hexane under reflux. Another possibility is LiF elimination from the corresponding lithiated fluoro-functionalised mono- or bis(silyl)hydrazines.



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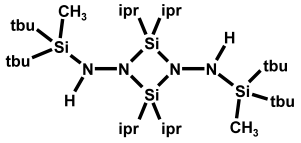

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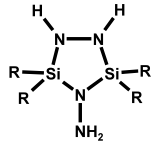
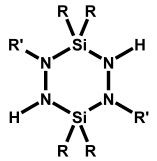


91 : R = -N(ipr)$_2$

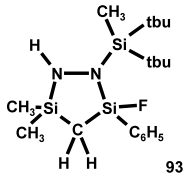


92 : R = ipr, -N(ipr)$_2$, t-bu

R' = H, -Si(CH$_3$)$_2$-t-bu, -Si(CH$_3$)$_3$

-Si(n-bu)$_3$

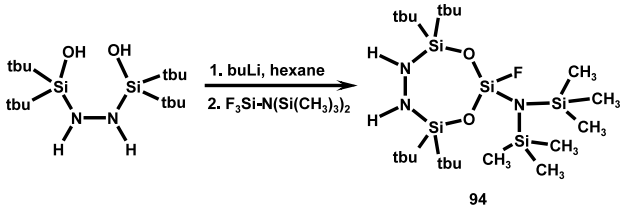
Low temperature X-ray structures of **90** (rNN = 144.4(1) Å) and of **92** (R = *t*-bu, R′ = –Si(CH$_3$)$_2$–*t*-bu) are known. The six-membered ring has a chair conformation (rNN = 1.48.0(2) Å). Both molecules are centrosymmetric (triclinic, $P\bar{1}$, $Z=1$) [178]. Under certain conditions methyl-groups at silicon may be lithiated by *n*-butyllithium resulting in organic five-membered rings of type **93**. The ring is not planar (triclinic, $P\bar{1}$, $Z=2$, rNN = 150.3(5) Å) [179].



93

9.2. Silicon, nitrogen and oxygen in the ring

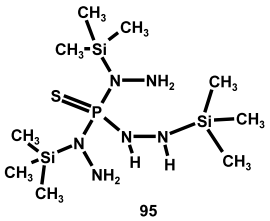
A five-membered hydrazine ring containing a trisiloxane unit **94** was synthesised according to Eq. 40 by Klingebiel and co-workers [180].



94

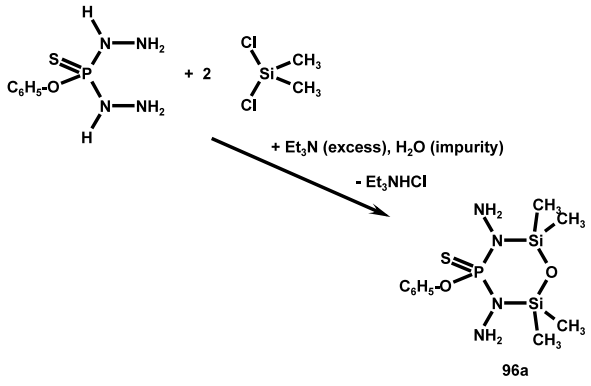
(40)

In our research group, we early tried to use *N*-silyl-substituted hydrazido-derivatives of phosphoric and thiophosphoric acid as starting materials for ring synthesis [181]. The reason was that for instance a trimethylsilyl-entity promised to be a good leaving-group in a reaction with an element-chloro-compound. The resulting chlorotrimethylsilane is highly volatile and could be removed with the solvent by evaporation. Thus an often-encountered separation problem of the target ring from the by-product triethylamine–hydrochloride could be eliminated. Yet the observed silatropy mentioned above was a great obstacle against a general application of this method especially in reactions with N-unsubstituted dihydrazides, where the trimethylsilyl-groups migrate preferably into the Nα-position of the dihydrazido-derivative. In solution, the equilibria can be studied using ^{1}H- and ^{31}P-NMR spectra [182]. An X-ray structure analysis of tris(trimethylsilyl)thiophosphoryl-trihydrazide (**95**), synthesised from thiophosphoryl-trichloride and 1,2-bis(trimethylsilyl)hydrazine, confirmed this migration. The molecule contains two α-trimethylsilyl-groups and one β-substituent. Obviously only sterical reasons are responsible for the fact that the third trimethylsilyl-group cannot achieve a α-position [183].



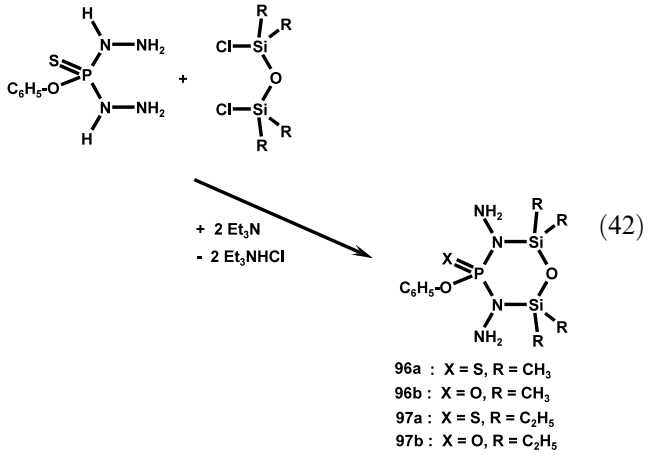
95

Besides this silatropy another difficulty stems from the high sensitivity of the Si–N bond to hydrolysis in the presence of even traces of water in the solvent used. So our first result in this area was a product of hydrolysis with exocyclic NH_2-groups **96** (Eq. 41) [184]. Later we synthesised this molecule and the



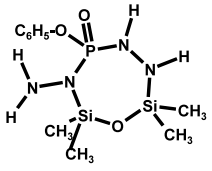
96a (41)

corresponding P=O compounds—also with ethyl-substituents at silicon—in a reaction purposely starting with the 1,3-dichlorotetraalkyldisiloxane (Eq. 42).



96a : X = S, R = CH_3
96b : X = O, R = CH_3
97a : X = S, R = C_2H_5
97b : X = O, R = C_2H_5 (42)

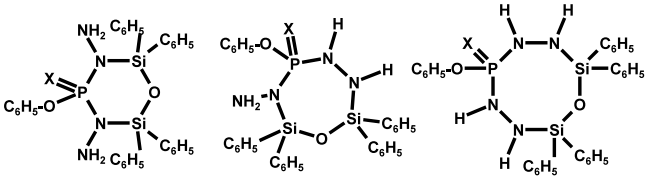
In the synthesis of **96b** also a seven-membered ring isomer **96c** could be detected in the reaction mixture by ^{1}H-NMR spectroscopy [185].



96c

The X-ray structure of **96a** is shown in Fig. 30. The six-membered ring has an almost planar slightly twisted conformation. The exocyclic NN bonds are rather long: 145.8(5) Å (mean), considering that only the ring N atoms are sp^2, the N atoms of the exocyclic NH_2-groups sp^3 hybridised [186].

The analogous reaction with dichlorotetraphenyldisiloxane is very slow and needs over 1 week for completeness at ambient temperature. Mixtures of the isomers **98a**, **98b**, **98c** and **99a**, **99b**, **99c**, respectively can be detected in the raw reaction solutions by NMR. The oily products obtained after removal of the solvent crystallise from toluene during several weeks. Compound **98a** is thus obtained as a first fraction in pure substance. Further fractional crystallisation yields **98c**, whereas **98b** could not be obtained in pure form. The transformation equilibria between six-, seven- and eight-membered rings are very slow in well dried solvents. In



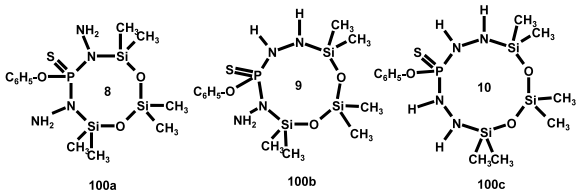
98a : X = S
99a : X = O

98b : X = S
99b : X = O

98c : X = S
99c : X = O

solution in toluene no ring transformation is observed of **98c** at ambient temperature. At 343 K, an equilibrium between the three species is achieved only after 25 days in a sealed NMR-tube. The concentration ratio is then about **98a**–**98b**–**98c** = 2.5:1.2:1. The same result is obtained starting with pure **98a**. Surprisingly, in the reaction mixture of the oxo-compounds **99a**/**99b**/**99c** the seven-membered ring **99b** crystallises at first. Compound **99c** could not be isolated in pure form.

The reaction of the P=S dihydrazide according to Eq. 42 (X = S) with dichlorohexamethyltrisiloxane yielded a mixture of eight-membered **100a**, nine-membered **100b** and ten-membered **100c** ring molecules as detected by NMR. Fractional crystallisation from *n*-pentane gave only **100b** in pure substance. Compound **100a** was always obtained in a mixture with **100b**. Compound **100c** could not be crystallised at all [187,188].



100a 100b 100c

9.3. Spirocyclic systems–substituted hydrazines

The results with organic cyclic dichlorosilanes as reactants are similar to those described with the

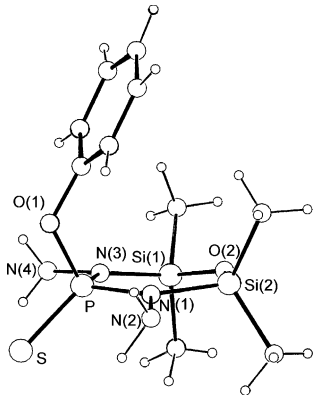
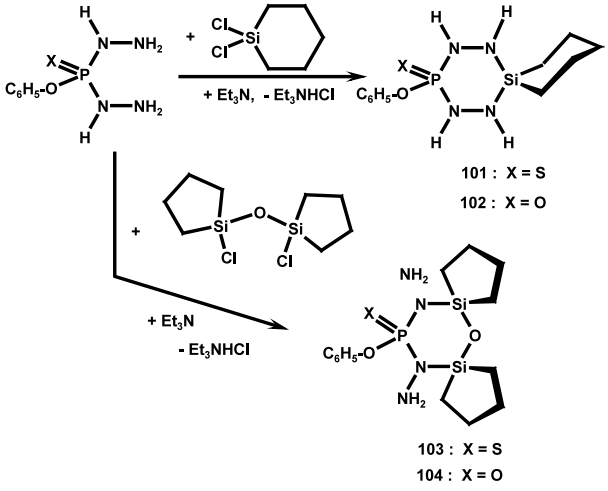


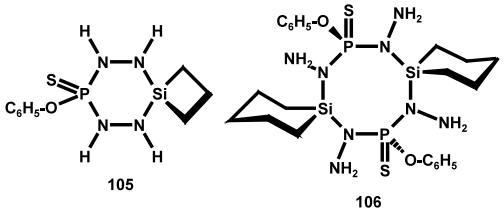
Fig. 30. X-ray structure of **96a** (3,5-diamino-2,2,6,6-tetramethyl-4-phenoxy-1-oxa-3,5-diaza-4λ^5-phospha-2,6-disilacyclohexane-4-sulfide; monoclinic, $P2_1/c$, $Z=4$).

siloxanes in Section 9.2, but spiro-compounds with silicon as spiro-center such as **101**, **102**, **103** and **104** result from these reactions (Eq. 43) [189,190]. A spiro-cycle corresponding to the first line of

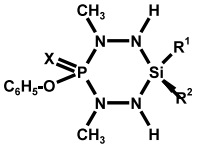


(43)

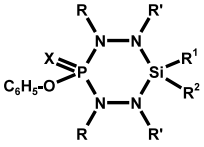
Eq. 43 but with a four-membered organic ring at the Si atom **105** has also been synthesised [189,191]. Besides the compound **101**, the reaction mixture also contained a dimer. This dispiro-compound **106** gave good crystals for an X-ray structure analysis (triclinic, $P\bar{1}$, $Z=1$) (Fig. 31). The molecule possesses a center of symmetry. The sila-cyclohexane rings have normal chair conformations [190].



If the dihydrazides are Nα-substituted or Nα,Nβ-disubstituted only one ring constitution is possible and no isomers can be formed. Many examples have been synthesised. Most of the compounds have been characterised by the usual spectroscopic methods (mainly NMR and MS) [188,191,192]. Some interesting examples are shown in the following formulas: **107**–**109**, **113a**, **113b**, **114** (monocycles), **118** (tricyclic system), **110**–**112** (spiro-cycles), **119** and **120** (polycyclic spiro-systems).

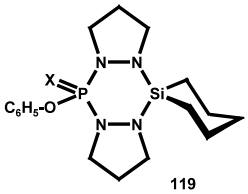


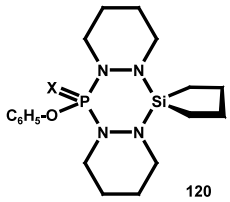
107 : $R^1 = R^2 = CH_3$; X = S
108 : $R^1 = R^2 = C_2H_5$; X = S
109a : $R^1 = R^2 = C_6H_5$; X = S
109b : $R^1 = R^2 = C_6H_5$; X = O



110 : $R^1/R^2 = -(CH_2)_3-$
111 : $R^1/R^2 = -(CH_2)_4-$
112 : $R^1/R^2 = -(CH_2)_5-$

113a : R = R' = CH_3 ; $R^1 = R^2 = C_6H_5$; X = S
113b : same as 113a ; X = O
114 : R = R' = CH_3 ; $R^1 = R^2$ = Cl ; X = S
115 : R = R' = CH_3 ; $R^1/R^2 = -(CH_2)_3-$; X = S
116 : R = R' = CH_3 ; $R^1/R^2 = -(CH_2)_4-$; X = S
117 : R = R' = CH_3 ; $R^1/R^2 = -(CH_2)_5-$; X = S
118 : R/R' = $-(CH_2)_4-$; $R^1 = R^2$ = Cl ; X = S





The *N*-tetramethylated compound **113a** with two phenylsubstituents at silicon showed an interesting temperature-dependent ^{1}H-NMR spectrum, that proves the existence of two slowly interconverting enantiomeric twist-conformations of the six-membered ring in solution (Eq. 44) [192]. This can be derived from the signals of the methyl-protons. At 230 K, where the hindered twist-to-twist interconversion is slow, the spectrum consists of four signals due to each of the

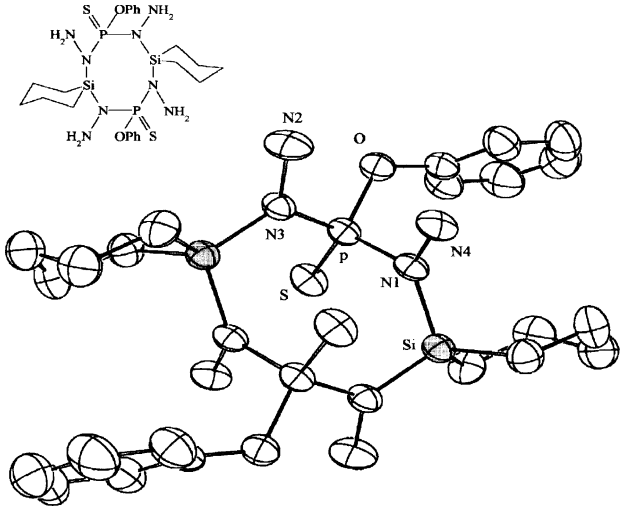
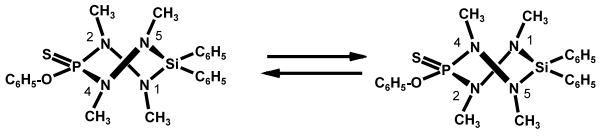


Fig. 31. Molecular structure of **106**.



(44)

four nonequivalent methyl-groups of both enantiomeric forms, which of course give identical spectra. Splitting by the phosphorus is clearly resolved for the methyl-protons in 2- and 4-position: $^{3}J_{PNCH} = 8.7$ and 9.7 Hz, respectively, whereas the coupling to the phosphorus is almost obscured for the methyl-protons in 1- and 5-positions because of the very small coupling constants: $^{4}J_{PNNCH}$ about 1 Hz. From the collapsing of the signals at higher temperatures (about 270 K), the free energy of activation for the interconversion process can be estimated to be 53 ± 2 kJ mol^{-1}. At 290 K, the ^{1}H-NMR spectrum consists of a doublet for the 2,4-*N*-methyl-protons ($\delta = 3.15$ ppm; $^{3}J_{PNCH} = 8.8$ Hz) and a broadened singlet of the 1,5-methyl-protons ($\delta = 2.79$ ppm; $^{4}J_{PNNCH}$ about 1.6 Hz).

The crystal of the solid compound **113a** (monoclinic, $P2_1/c$, $Z = 4$) contains both enantiomeric twist-forms in the centrosymmetric unit cell. One molecule constitutes the asymmetric unit (Fig. 32). The four methyl-groups are symmetrically independent as in solution. The substituents at the P and the Si atoms are in isoclinal positions (compare also with Eq. 44). The sums of bond angles around the N atoms vary from 350(2) to 358(2)°. Interestingly, the nonbonded contact distance between P and Si across the ring is with 322.8(5) Å again considerably shorter than the sum of the van der Waals radii (about 370 Å [75]) [192]. This is, as mentioned before, one of several other reasons why the twist-conformation is more stable than a chair conformation in this case, too. In a hypothetical chair conformation, the lesser torsion angles around the NN bonds would lead to an even shorter PSi contact and thus to more sterical stress in the molecule.

Our attempts to synthesise systems with silicon as spiro-center and with two inorganic hydrazine heterocycles according to Eq. 45 were so far unsuccessful. N-Unsubstituted or α*N*,α*N*-dimethylated dihydrazido-derivatives of thiophosphoric acid did not react in a clear

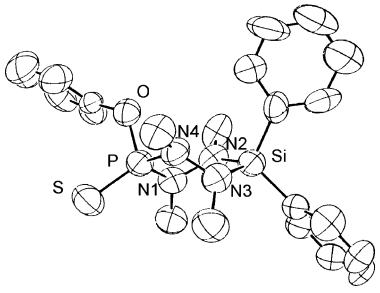
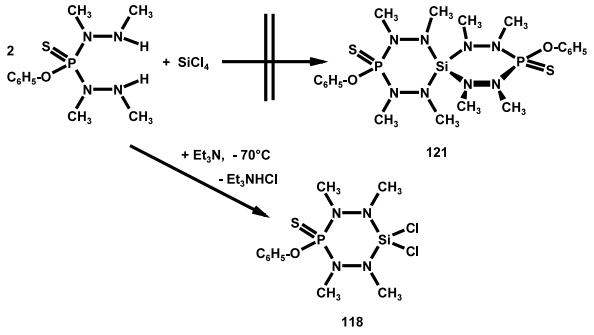


Fig. 32. One of the two enantiomeric twist-conformations of **113a**.

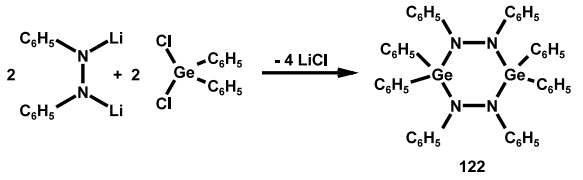
well defined way. Mainly decomposition was observed. The reaction of the corresponding *N*α,*N*β-methylated dihydrazide with silicontetrachloride stopped at the six-membered ring with two Cl atoms left at the silicon. Obviously, the *N*-methyl-groups stabilise the cyclic species, but also inhibit the complete substitution of the chlorine atoms at the silicon [191,193].



(45)

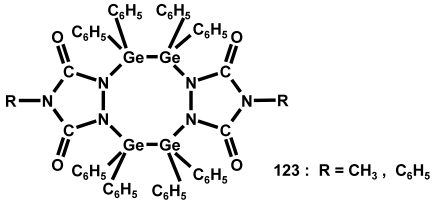
10. Hydrazine heterocycles with heavier main group elements in the ring: Ge, Sn, As

Reactions of lithiated 1,2-diphenylhydrazine (hydrazobenzene) and dichloro-organosilanes are described in Section 9. Gilman and co-workers also mention the formation of a tetraaza-4,6-digermacyclohexane (**122**) according to Eq. 46 [158].



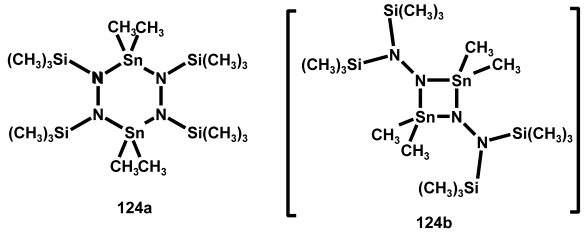
(46)

Urazoles (1,2,4-triazole-3,5-diones) react with 1,2-dichloro-tetramethyldigermane in the presence of triethylamine to the eight-membered ring compounds **123** [194].

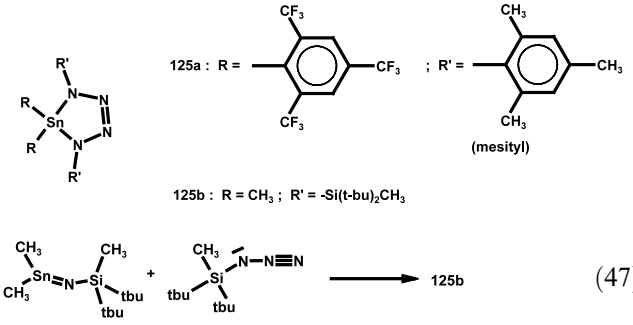


Reactions similar to Eq. 46 but with dichlorodiphenyltin and dichlorodiphenyllead did not yield the expected ring compounds. Redox-reactions gave polymeric diphenyltin and elemental lead instead [158]. Another group has reported a tin compound **124a** starting with dilithiated bis(trimethylsilyl)hydrazine

and dichloro-dimethylstannane. Mainly mass-spectroscopic data support the six-membered ring constitution and not an isomeric four-membered ring structure **124b** [169].



Five-membered rings containing Sn, namely tetraazastannacyclopentenes of the type **125** have also been synthesised. Compound **125b** is a product of a (2+3)-cycloaddition of di(*t*-butyl)methylsilylazide and a substituted stannane-imine (Eq. 47) [195]. Compound **125a** is formed in a similar reaction using compounds with different substituents [196].



(47)

A rather unique molecule **126** is the result of an addition of arsenic trichloride to a monophosphazene and a following intra- and intermolecular elimination of chlorotrimethylsilane. The X-ray structure analysis reveals a puckered, crown-shaped eight-membered ring bridged by two N–CH_3-groups (Fig. 33) (monoclinic, $P2_1/c$, $Z=2$; the molecules are centrosymmetric and may be described alternatively as two five-membered rings dimerised over two PN bonds [197,198].

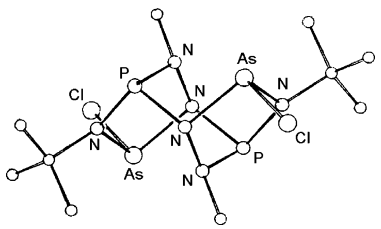
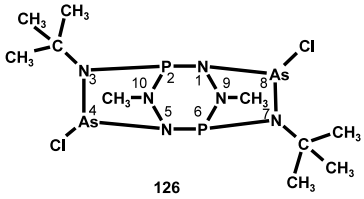


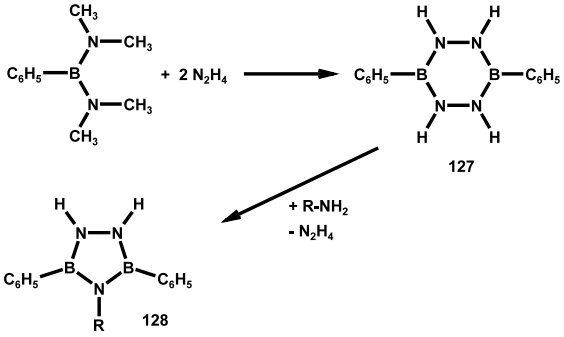
Fig. 33. X-ray structure of the As-containing tricyclic system **126** (3,7-di(*t*-butyl)-4,8-dichloro-9,10-dimethyl-1,3,5,7,9,10-hexaaza-2,6-diphospha-4,8-diarsatricyclo[4.2.1.1^{2,5}]decane).



11. Boron hydrazine heterocycles

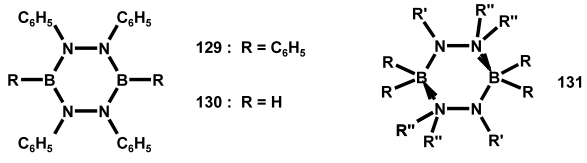
11.1. Only boron and nitrogen in the ring

The first title compounds have been made in the early 60s according to Eq. 48 by transamination of aminoboranes with hydrazine [199–201]. Further reactions of **127** with primary amines lead to the five-membered rings **128** [200].



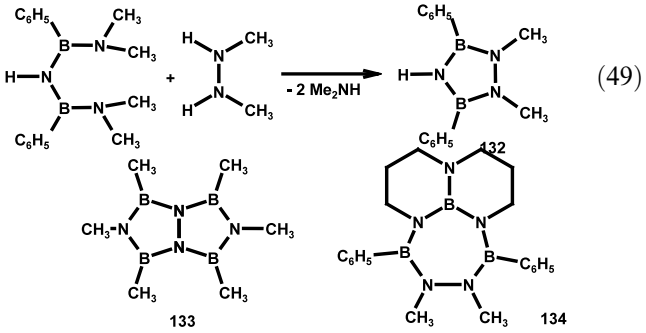
(48)

The elimination of LiCl from dilithiumdiphenylhydrazine and dichlorophenylborane was used to synthesise the hexaphenyl-substituted ring **129**. The reduction of azobenzene with diborane(6) yields the corresponding molecule **130**. Six-membered coordination heterocycles **131**, cyclic dimers of hydrazinodiorganoboranes, have been obtained in reactions starting with dimethylaminoorganoboranes [201].



Dialkylmercaptoboranes can also be used to synthesise compounds analogous to **127** by exchange of the sulfur group through hydrazine [202,203]. A five-membered ring similar to **128** has been also obtained by this method using ammonia, primary amines or 1,2-dimethylhydrazine in a second reaction or in a reaction according to Eq. 49. Compound **132** is converted to a compound with oxygen in the ring by partial hydrolysis [204,205]. Unsubstituted absolute hydrazine yields a bicyclic system **133** [204]. Hydrazinolysis of the corresponding bicyclic bis(dimethylamino)-system yields the

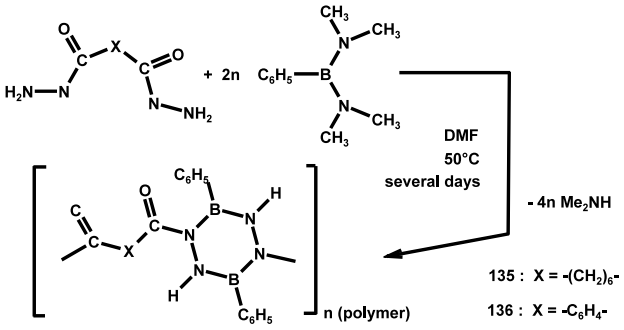
tricyclic molecule **134**, that contains



(49)

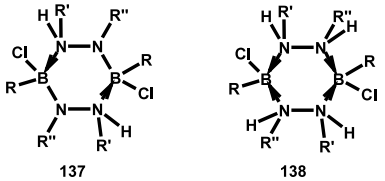
a seven-membered boron hydrazine ring (3,4-dimethyl-2,5-diphenyl-1,3,4,6,8-pentaaza-2,5,7-triboratricyclo[5.4.0.$3^{6,8}$]quatrodecane) [206]. The ring **127** has also been incorporated into polymers **135** and **136**. The reaction started with bifunctional dicarbonic acid hydrazides, that were treated with bis(dimethylamino)phenylborane (Eq. 50) [207,208].

The first structural data on six- and five-membered rings mentioned above are to be found in the literature since 1968. The proposed dimeric



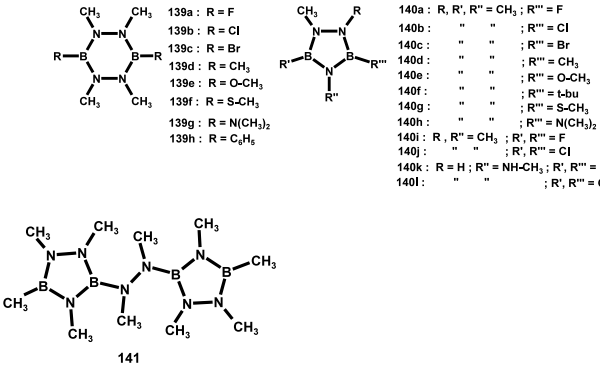
(50)

cage structure of a bis(*t*-butyl)-analogue of **127** [209] could be confirmed by an X-ray structure analysis (tetragonal, $P\bar{4}2_1c$) (Fig. 34) [210]. Adducts of this cage molecule with HCl, BCl_3, BF_3 and others have been reported. They are formulated and discussed as coordination dimers such as **137** and **138** [211].



Depending on the substituents at boron and nitrogen also monomers like **127** or polymers (for R = H) arise from reactions similar to Eq. 48 [212,213].

A first review has been published in 1969 including other boron nitrogen rings also with BB bonds [211]. Especially many compounds derived from 1,2-dimethylhydrazine and monosubstituted hydrazines have been described later including six- and five-membered rings of the types **139** and **140** [214–217]. Starting from the functional five-membered rings **140b**, **140c**, and **140g** the reaction with 1,2-dimethylhydrazine yields the molecule **141** [214].



First structural informations on five-membered rings came from photoelectron spectra. The rings are planar or almost planar [218]. Similar investigations together with theoretical calculations on some of the six-membered ring compounds suggested twist-conformations of these rings [219]. This was later confirmed by X-ray structure determinations of the molecules **139g** (monoclinic, $A2/a$, $Z = 4$; the molecule possesses an almost planar twist-conformation with a twofold axis of symmetry; the NN distance is rather long for nearly sp^2 hybridised N atoms: 143.1(2) Å [220]) and **139h** (monoclinic, $P\bar{1}$, $Z = 4$; the unit cell contains two symmetry-independent molecules, that also have flat twist-conformations and long NN bond distances: 144.5(3) and 144.0(3) and 143.7(2) Å; the highest torsion angles in the ring are the BNNB angles with values from 19 to 20° [221]). Molecule **139d** is reported to form radical cations in a one-electron oxidation with $AlCl_3$ in CH_2Cl_2 as solvent. Structural changes during this oxidation have been investigated by ESR spectroscopy [222].

Equilibria in solution between monomers and dimers of molecules of the types **139** and **140** have been investigated by NMR. Although compound **140j** is monomeric in the gas phase as well as in solution, the X-ray structure reveals a dimer to be present in the

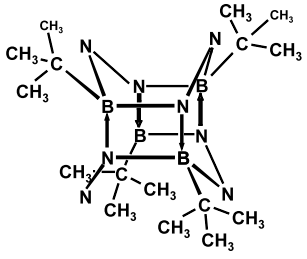
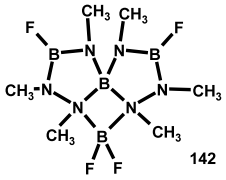


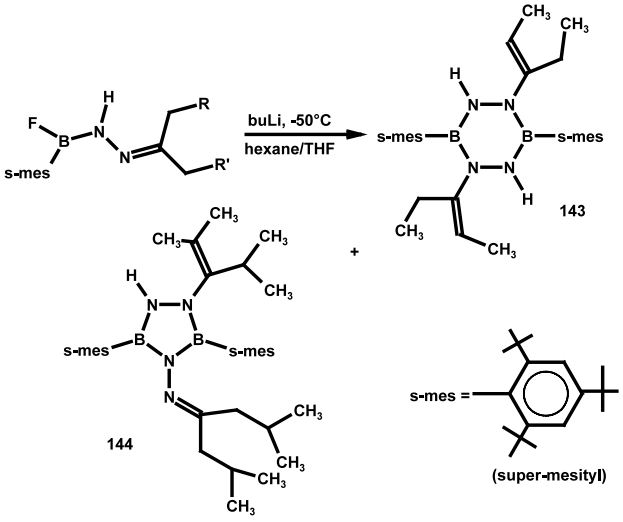
Fig. 34. Three-dimensional sketch of the molecular structure of the cage dimer of **127** (*t*-butyl instead of phenyl at boron, H atoms at N omitted).

crystal (monoclinic, $P2_1/n$, $Z=4$). The five-membered rings are planar as expected (Fig. 35) [223].

An anomalous dimerisation under F-exchange in molecule **140j** leads to a tricyclic system with a boron spiro-center **142** (orthorhombic, *Pcca*, $Z=4$; NN bond distance 144 (3) Å; Fig. 36) [224].

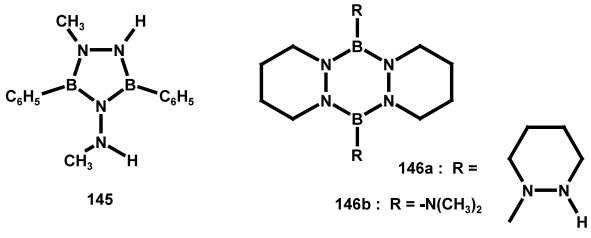


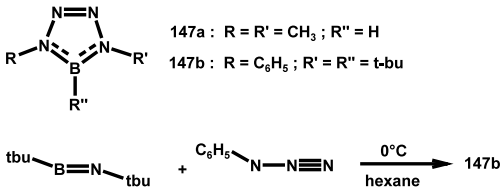
Dimerisation is not observed, if very bulky substituents at boron and/or nitrogen are present. Six- and five-membered inorganic rings as **143** and **144** are described, synthesised from the corresponding fluoroborylhydrazones (Eq. 51) [225]. The molecules **145** (X-ray structure, orthorhombic, *Pbca*, $Z=8$ [226]) and **146a** and **146b** are also reported to be monomeric [227]. Microwave spectra of an interesting unsaturated compound **147a** suggested a delocalised π-electron system in this planar five-membered ring with short N=N (129.1 Å), N–N (137.5 Å) and BN (141.3 Å) bond distances [228]. The differently substituted molecule **147b**



(51)

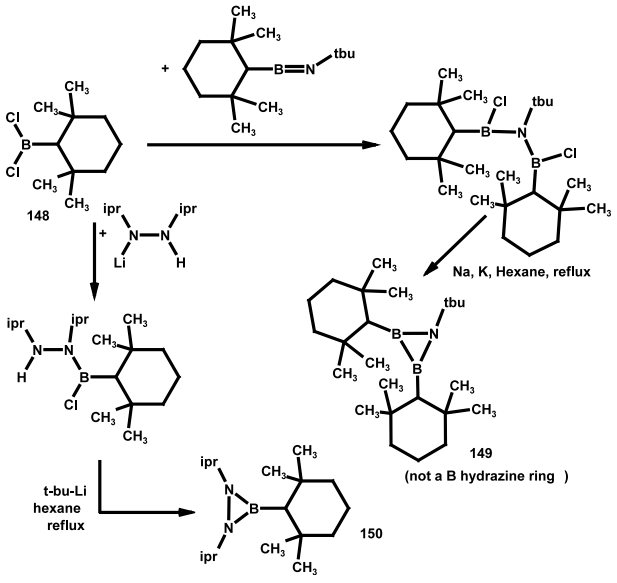
was later obtained by a (2+3)-cycloaddition of di(*t*-butyl)borazene and phenylazide (Eq. 52) [229].



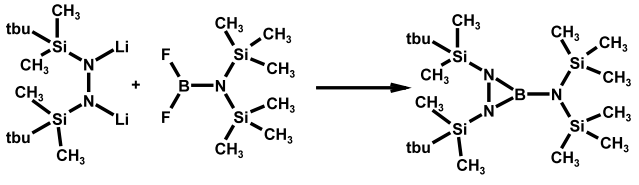


(52)

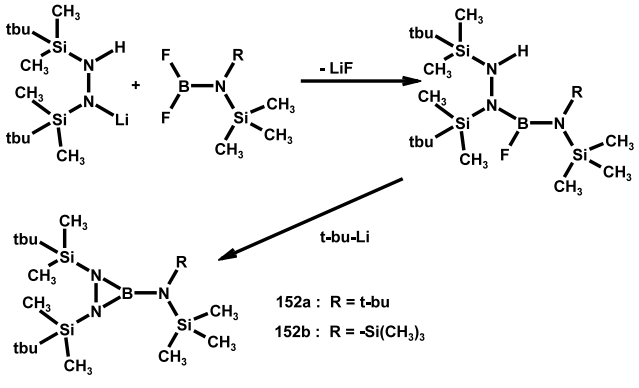
Boron compounds with extremely sterically hindering substituents have been used to prepare three-membered boron hydrazine rings (diazaboracyclopropanes) according to Eqs. 53 [230] or 54 and 55 [231,232].



(53)



(54)



(55)

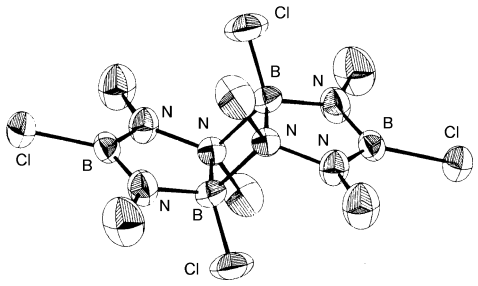


Fig. 35. The centrosymmetric structure of the dimer of molecule **140j**.

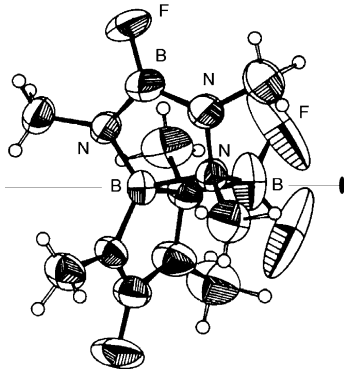
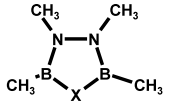


Fig. 36. Molecular structure of **142** with its twofold axis of symmetry (3,6,6,9-tetrafluoro-2,4,5,7,8,10-hexamethyl-2,4,5,7,8,10-hexaaza-1,3,6,9-tetraboratricyclo[5.3.0.0^{1,5}]decane).

The X-ray structure of **152b** shows a planar NBN_2 unit. The ring atoms are sp^3 hybridised and carry the bulky substituents in *trans*-positions (Fig. 37, trigonal, $P3_221$, $Z=3$). The NN bond distance in the ring is very long: 167.3(2) Å [232], even about 8 Å longer than found in a theoretical ab-initio calculation, that revealed an antiaromatic character of the diazaboracyclopropane basis-system [233].

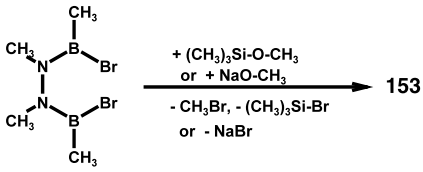
11.2. Additional other elements in the ring

Quite a number of the title molecules are known. Either a boron or a nitrogen is formally replaced by O, S, P, As, Si or C(+IV) (or derivatives thereof). The compound **153** has been described as a partial hydrolysis product of the corresponding NH ring **132** (see Section 11.1) [204] or of differently substituted rings [200]. Compound **154** was prepared in a similar reaction with hydrogen sulfide [205]. An X-ray structure analysis of **154** (monoclinic, $P2_1/n$, $Z=4$) shows an almost planar ring with sp^2-hybridised N atoms and a NN bond distance of 141.3(11) Å.



153 : X = O
154 : X = S

The molecule has very nearly C_{2v} symmetry [223]. Surprisingly, **153** is also formed in the reaction of Eq. 56, the open-chained bis(*O*-methyl) compound apparently being instable [217].

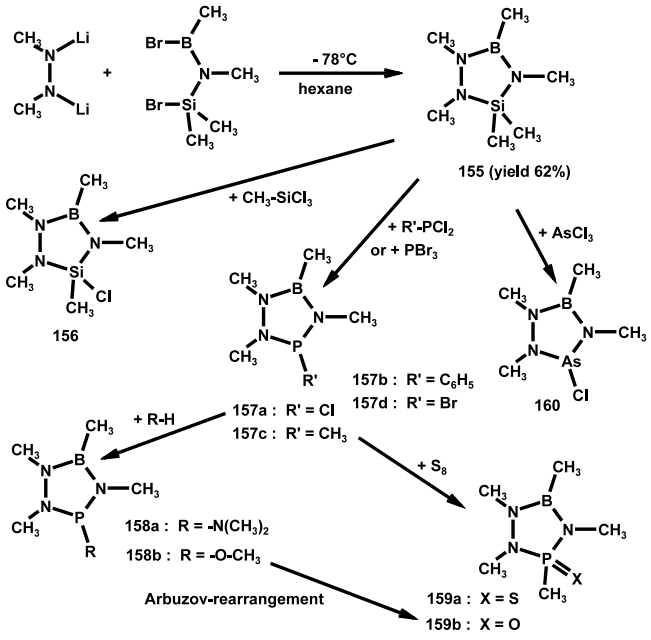


(56)

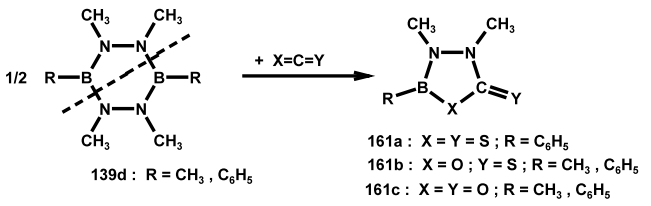
Eq. 57 summarises reactions leading to Si, P, and As containing five-membered rings. An important intermediate is the hexamethyltriaza-3-sila-5-boracyclopentane (**155**) [234].

CS_2, O=C=S, and CO_2 symmetrically cleave six-membered rings such as **139d** yielding the (2+3)-cycloaddition products **161a–c** (Eq. 58). The oxadiazaboracyclopentanones **161c** exist in solution in equilibrium with their dimers. As expected, the rings are planar as shown by an X-ray structure determination of **161a** (monoclinic, $P2_1/c$, $Z=4$; rNN = 144.5 Å) [221].

In our laboratory we mainly focussed on reactions of N-substituted di(hydrazido)thiophosphoric acid phenylester with bifunctional boron compounds



(57)



(58)

such as phenylbordichloride, bis(dimethylamino)phenylborane and or tris(dimethylamino)borane. Transamina-

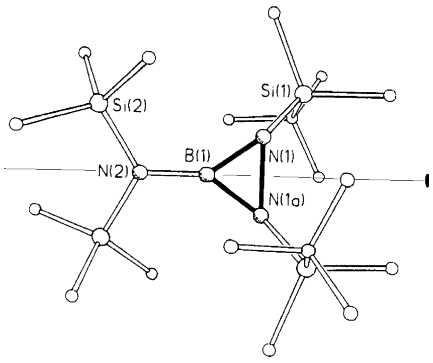
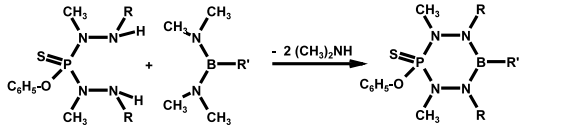


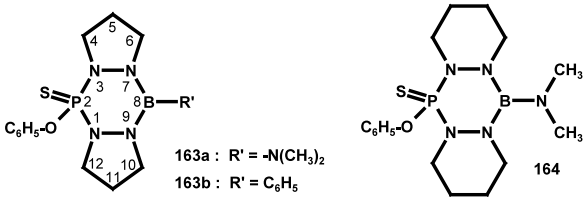
Fig. 37. X-ray structure of the diazaboratricyclopropane system **152b** with its C_2.

tion methods were mainly used (Eq. 59). Analogous reactions with the corresponding di(*N*-pyrazolidino)- or

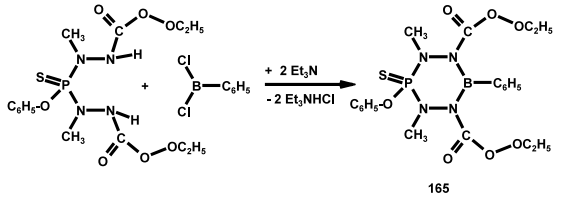


(59)

di(*N*-hexahydropyridazino) derivatives of thiophosphoric acid yielded the tricyclic ring systems **163a**,**b** and **164** [227].



The synthesis of **165** was not feasible by transamination, since the carboethoxy-substituted N atoms are no longer basic or nucleophilic enough (despite of sterical hindrance) to replace the dimethylamino-groups at the boron. But the condensation reaction with dichlorophenylborane in the presence of triethylamine gave the intended ring product in this case (Eq. 60) [227].

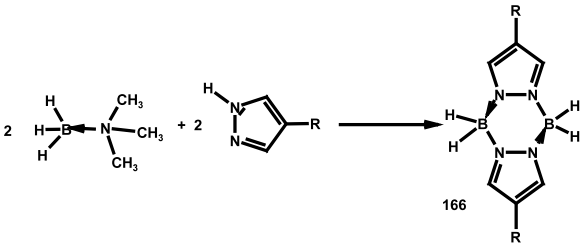


(60)

An X-ray structure analysis of compound **162c** (monoclinic, $P2_1/n$, $Z=4$) revealed a twist-conformation of the ring with a trigonal planar environment at the boron (Fig. 38). The twist-conformation is somewhat distorted into the direction of a half-chair. This means that the right part of the ring containing the boron and including the four N atoms is lying almost in one plane, whereas the phosphorus is tilted downwards [227]. Similar results have been obtained in the molecular structures of **163a** monoclinic, $P2_1/n$, $Z=4$; Fig. 39) and **163b** (orthorhombic, $Pbca$, $Z=8$; Fig. 40) [227].

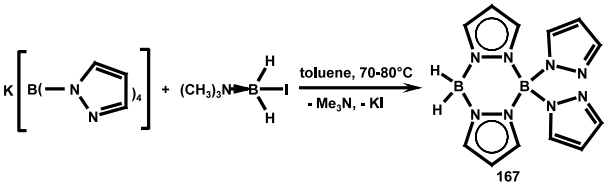
11.3. Cyclic pyrazolo- and triazolo-boranes

Since pyrazole and 1,2,3-triazole have at least two adjacent N atoms in their rings, they might be considered as organically substituted hydrazines. With boron derivatives they form various 'inorganic' ring compounds with only boron and nitrogen in the central ring. A short survey will be given below.

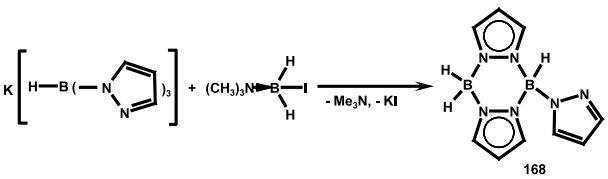


(61)

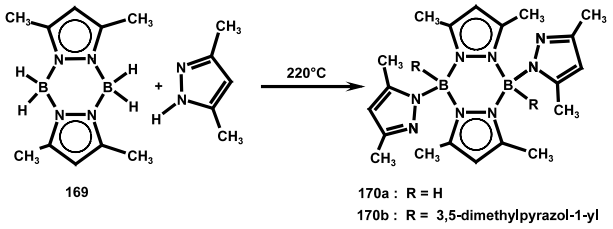
Trofimenko published his first investigations on cyclic pyrazolyl-boron compounds as early as 1966 (Eq. 61) [235–237]. Later at the boron or at the pyrazole differently substituted compounds followed [238–240]. A survey with 866 references has been compiled by Trofimenko himself in 1986 dealing mainly with transition metal complexes of the famous tris(pyrazolo)hydridoborate ligand. They may be considered as 'hydrazine'-chelate rings also, but will not be discussed here in detail [241]. Later, Niedenzu and co-workers prepared a variety of molecules similar to **166** partly in collaboration with Trofimenko and Nöth and co-workers. Eqs. 62, 63 and 64 give examples [242–244].



(62)

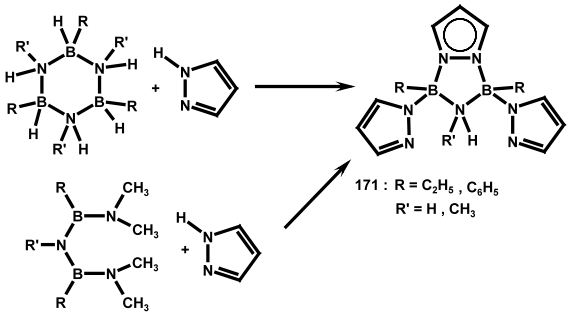


(63)



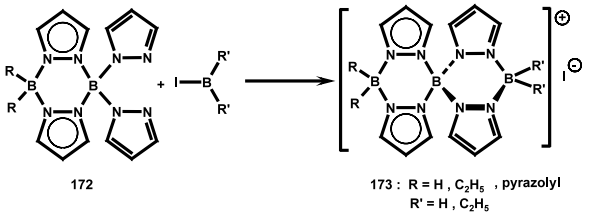
(64)

The reaction of **166** with BF_3, Cl_2, BBr_3 or Br_2 leads to halogen-substituted products [243]. Starting materials for the synthesis of cyclic pyrazoloboranes may also be alkylamino-derivatives of boron or substituted 1,3,5-triazatribora-cyclohexanes. Here also five-membered rings may result (Eq. 65) [245].



(65)

Spiro- and dispiro-compounds can also be synthesised (Eq. 66) [246].



(66)

The compounds **173** usually are crystallised as hexafluorophosphates in aqueous solutions (reaction of the iodides with ammoniumhexafluorophosphate). Compound **172** (R = pyrazolyl) reacts with two molecules

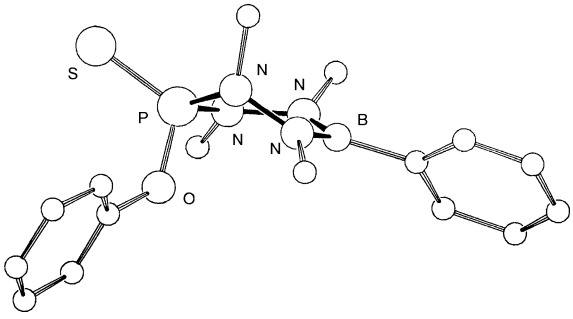


Fig. 38. Molecular structure of **162c** (1,2,4,5-tetramethyl-3-phenoxy-6-phenyl-1,2,4,5-tetraaza-3λ^5-phospha-6-boracyclohexane-3-sulfide).

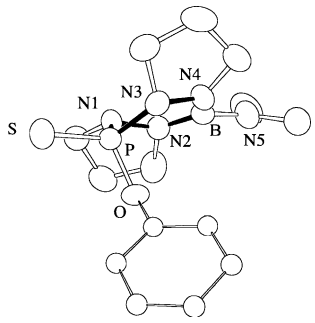


Fig. 39. Structure of the tricyclic molecule **163a** (8-dimethylamino-2-phenoxy-1,3,7,9-tetraaza-2λ^5-phospha-8-boratricyclo[7.3.0.0^{3,7}]dodecane-2-sulfide).

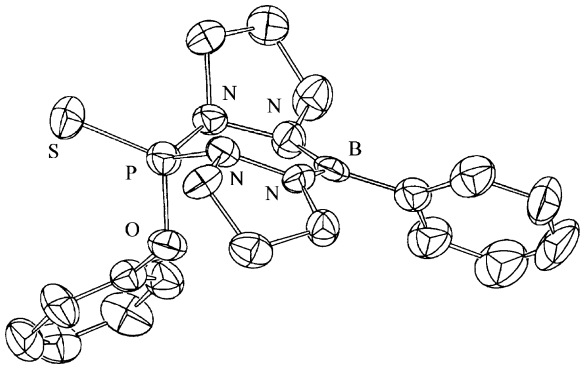
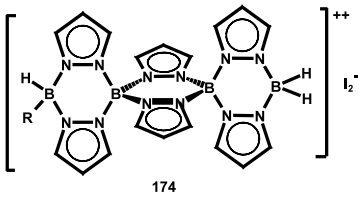


Fig. 40. Structure of **163b** (the corresponding 8-phenyl-compound).

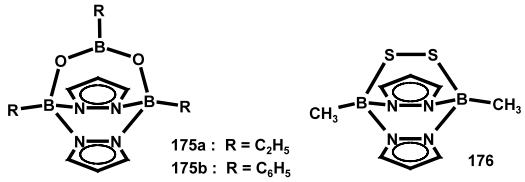
of $(CH_3)_3N->BH_2I$ to the dispiro-compound **174** [230].



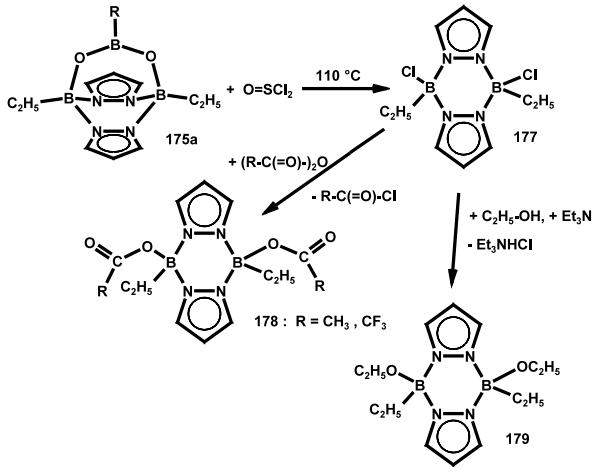
Many X-ray structures have been determined. The basic molecule **166** (orthorhombic, *Pbca*, $Z = 8$; Fig. 41) as well as many others have boat conformations of the six-membered B_2N_4 ring [243]. Yet the rings are very flexible and planar structures as in the corresponding tetrabromo-compound (monoclinic, $C2/m$, $Z = 4$) and also flat chair conformations may occur [243,244,247–249].

Interestingly in one case, **170**, R = C_2H_5, a *cis*- and a *trans*-isomer could be isolated. The *cis*-isomer (tetragonal, $I4_1/acd$, $Z = 16$) has a boat conformation, the *trans*-isomer (monoclinic, $P2_1/c$, $Z = 2$) a flat chair conformation [245].

Molecules with an additional bridge such as **175** (monoclinic, $P2_1/c$, $Z = 4$) and **176** (orthorhombic, *Pbcn*, $Z = 4$) of course adopt boat conformations of the six-membered ring [250–252]. Compounds **175a** and **175b** have been synthesised by reacting



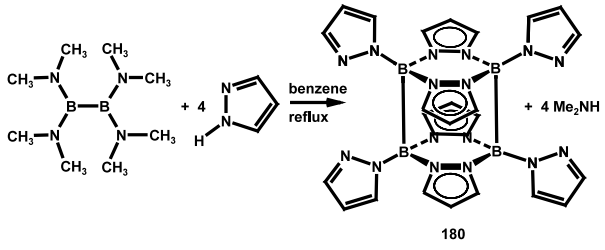
the corresponding cyclotri(boroxene) with pyrazole [250]. Compound **175a** reacts with thionylchloride to form the chloro-substituted compound **177**, that reacts further with carbonic acid anhydrides or ethanol to yield the substituted products **178** or **179** (Eq. 67). Isomers could not be separated in this case [251].



(67)

For the preparation of molecule **176**, 3,5-dimethyl-5-phenyl-1,2-dithia-5-aza-3,5-diboracyclopentane has been used as starting material in the reaction with pyrazole [252].

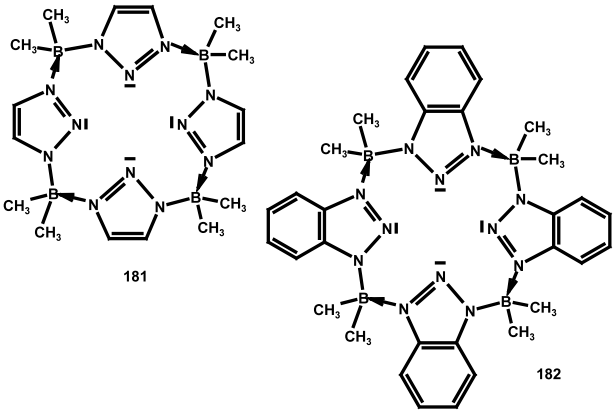
Larger rings containing pyrazoloboranes are also known. An example is compound **180** obtained accord-



(68)

ing to Eq. 68 [253].

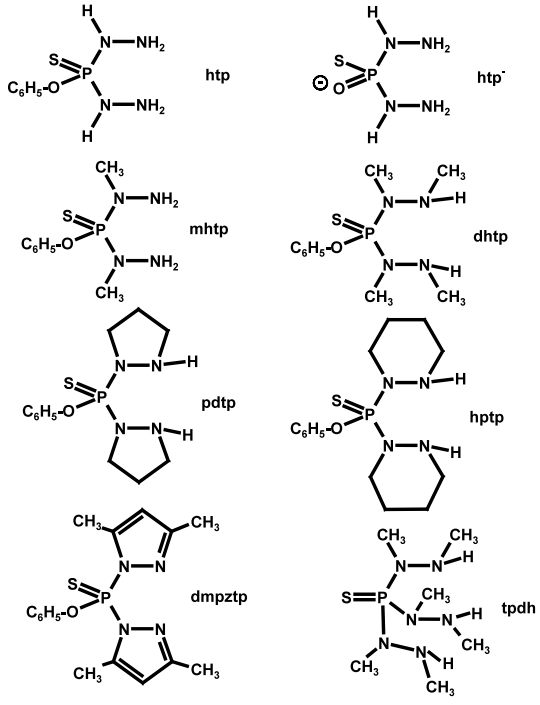
Attempts to synthesise porphine-like molecules led to the products **181** and **182** using 1,2,3-triazole or benztriazole and trimethylamino-dimethylborane, $(CH_3)_3N->BH(CH_3)_2$, as starting material [254]. Both molecules have strongly puckered structures and are no analogues of porphines [255].



12. Metal complexes of thiophosphoric acid hydrazine derivatives with hydrazine chelate rings

The great number of known metal complexes of hydrazine, of substituted hydrazines (see for instance Ref. [256]) and acid hydrazides, especially hydrazido carbonates, would exceed by far the scope and limits of this survey. Therefore, only some results of our investigations pertaining to the title compounds will be presented here.

The complexing properties of the following hydrazido derivatives of thiophosphoric acid have been tested (abbreviations used in complex formulas are in parentheses):



The first seven molecules could possibly function as tri-dentate S,N,N ligands, the trihydrazide even as up

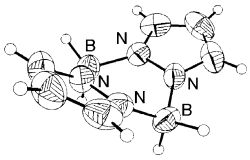


Fig. 41. The boat conformation of the cyclic pyrazolo-boron compound **166**.

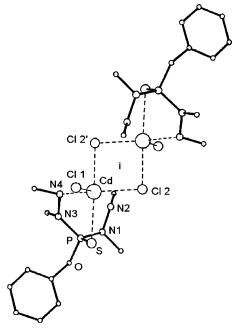


Fig. 42. The dimeric complex of di(1,2-dimethylhydrazido)thiophosphoric acid *O*-phenylester, dhtp, with $CdCl_2$.

to four-dentate S,N,N,N ligand. Our first attempts to synthesise complexes with first-row transition metals and htp led to compositions $[M(htp)_2]Cl_2$ with M = Ni^{2+}, Zn^{2+}, Cd^{2+}. UV–vis spectra in the solid state—the compounds are not soluble except in coordinating solvents, that destroy the complexes—showed the Ni complex to have an octahedral geometry at the central atom. No single-crystals could be obtained. Solvolysis with methanol in water under slightly basic conditions gave a dark-blue product, that no longer had chlorine nor phenyl-groups in the molecule (Eq. (69)). Compound **183** also is an octahedral complex, but no information is available, if it is a monomer or a polymer, though from the analytical composition it can be concluded that htp^- is a three-dentate ligand [257]. Similar results have been obtained with Mn(II) and Fe(II) complexes [258]. In contrast to these findings X-ray structure determinations of Ni(II)

$$[Ni(htp)_2]Cl_2 + 2OH^- \xrightarrow{H_2O/CH_3\text{–}OH,\ NH_3} \times \underset{\mathbf{183}}{[Ni(htp^-)_2]} + 2Cl^- + 2C_6H_5\text{–}OH \qquad (69)$$

with monohydrazido-thiophosphoric acid diesters (possible bi-dentate S,N ligands?) revealed these ligands to function only mono-dentate binding through the βN atoms of the hydrazido group. No chelate rings are formed [259–261].

The cadmium complex with dhtp is soluble in methanol and can be crystallised (monoclinic, $P2_1/c$, $Z = 2$). Fig. 42 shows the centrosymmetric dimeric structure of the complex molecule. Two Cd^{++} ions are bridged by two Cl^- anions. The Cd central units are in the centers of two distorted tetragonal pyramids. The

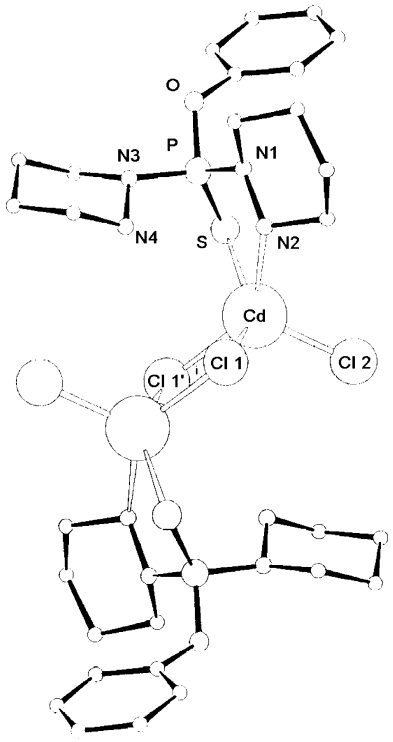


Fig. 43. The centrosymmetric complex molecule of [ClCd(hptp)(μ-$Cl)_2$(hptp)CdCl], N4 does not bind to the Cd: rCd–N = 364.6(4) Å.

dhtp ligands coordinate through S and one of the terminal βN atoms. The other approaches the Cd atom from the base of the pyramid but is too far (328.0(6) Å) to be considered 'coordinated' [262].

The structural variety of Cd complexes is surprising. The complex of $CdCl_2$ with the di(hexahydropyridazido) compound hptp also dimerises over two Cl bridges. The ligand again coordinates through S and one of the βN atoms (Fig. 43) (triclinic, $P\bar{1}$, $Z = 1$) [263,264]. But the corresponding ligand with five-membered pyrazolidine rings behaves quite differently. The X-ray structure (monoclinic, $P2_1/c$, $Z = 4$) reveals polymeric helices The subunits are linked by Cl bridges and the pdtp ligands coordinate through S and through both βN atoms to the same Cd (Figs. 44 and 45) [263,265,266].In a complex with mhtp, where the hydrazido-groups are only αN-methylated, the mhtp functions three-dentate as S,N,N ligand forming five-membered chelate rings. But here one βN atom bridges to a second Cd building up a polymeric chain in the direction of the *b*-axis (Fig.

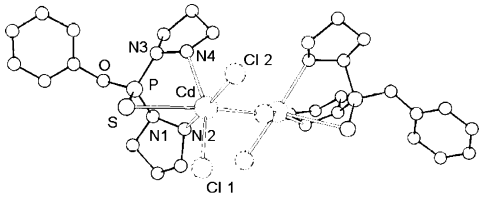


Fig. 44. Asymmetric unit of the polymeric complex [Cl(pdtp)Cd(μ-$Cl)_2$Cd(pdtp)$Cl]_n$.

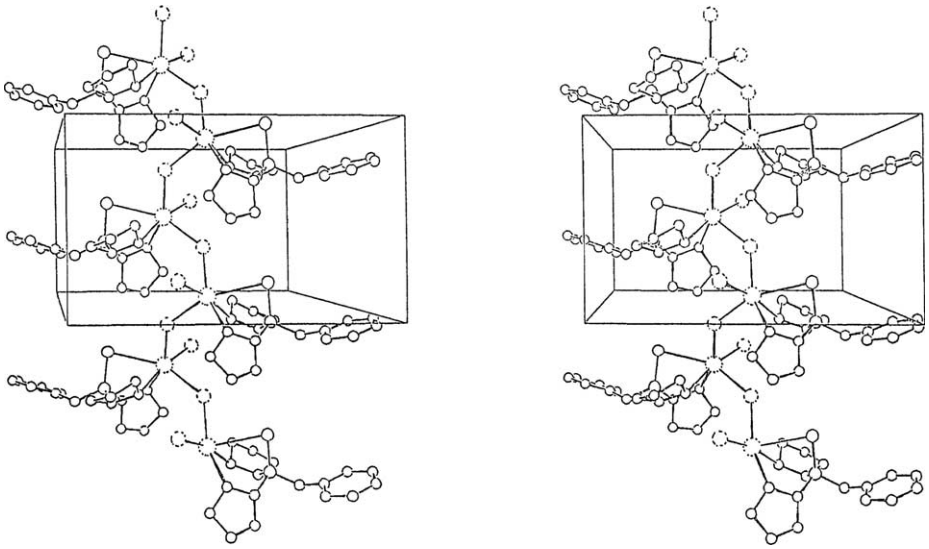


Fig. 45. Stereoplot of one of the two polymeric helices in the unit cell of the complex of Fig. 44.

46) (monoclinic, $P2_1/c$, $Z=4$). The coordination sphere around the Cd is best described as a tetragonal pyramid with Cl1, Cl2, N2 and S in the basal positions and $N4^{i}$ in the apical position. $Cl2^{ii}$ of a second chain (not shown in Fig. 46) is too far away, 329 Å, to be interpreted as coordinated [263].

Very surprising was the result of an X-ray structure analysis of the complex [Cl(tpdh)Cd(μ-Cl)$_2$Cd(tpdh)Cl] (monoclinic, $P2_1/c$, $Z=4$). The thiophosphoryltri(1-methylhydrazide) tpdh binds to the Cd via two βN atoms and one αN atom. The S atom does not participate in the coordination. Two symmetry-independent units are bridged by two Cl^- anions. The coordination at the Cd is nearly octahedral (Fig. 47) [263,266].

13. Conclusions

The presented review shows, that research in the field of inorganic heterocycles also can contribute to general aspects of ring structures and especially of ring conformations. Some light is brought into effects that determine the conformations of six-membered rings and that can stabilise unusual twist-conformations. Once more the versatility of hydrazine and substituted hydrazines as bifunctional ring building entities has been demonstrated.

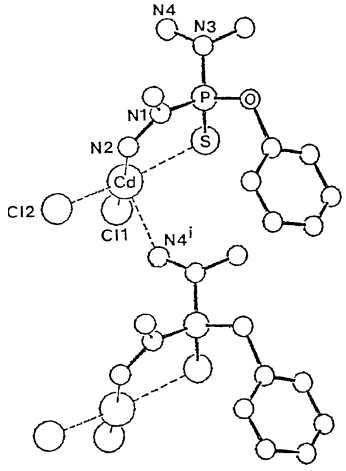


Fig. 46. Asymmetric unit of the polymeric complex [$Cl_2Cd(m$-S,N-mhtp-N-)]$_n$.

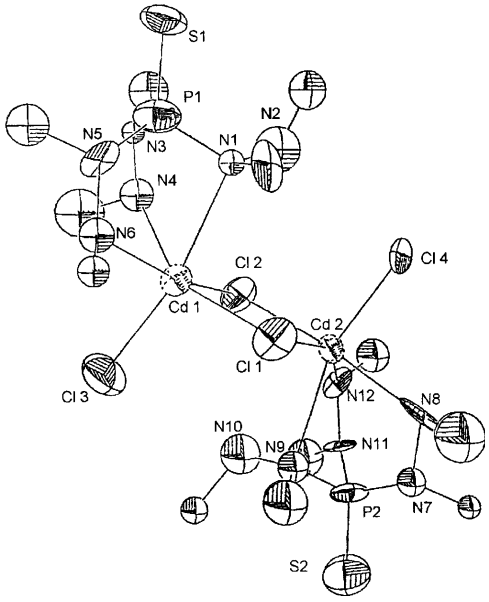


Fig. 47. The dimeric molecule of the complex of $CdCl_2$ with thiophosphoryltri(1,2-dimethylhydrazide) (tpdh).

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