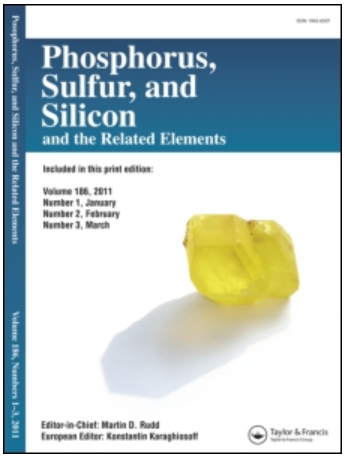

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Synthesis Structure and Conformational Behaviour of Inorganic Phosphorus-Hydrazine Heterocycles With Organic Fused Sixmembered Rings

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SYNTHESIS STRUCTURE AND CONFORMATIONAL BEHAVIOUR OF INORGANIC PHOSPHORUS-HYDRAZINE HETEROCYCLES WITH ORGANIC FUSED SIXMEMBERED RINGS.

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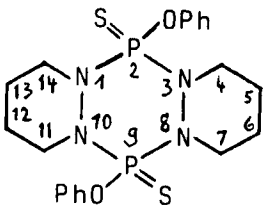
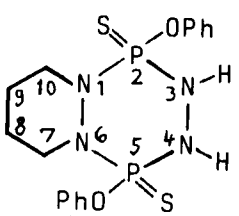
Abstract The title compounds Ia, Ib and IIa are prepared starting with Ph-O-P(=X)Cl_2 and hydrazine and/or hexahydropyridazine. Ia and IIa can be separated into cis- and trans-isomers. Ib is only isolated as trans-isomer. X-ray structures and NMR-spectra in solution show that both trans-isomers have a normal chair-conformation of all fused saturated sixmembered rings. The cis-isomer of Ia adopts a twist-conformation of the central inorganic ring, the fused hexahydropyridazine rings having chair-conformations. Temperature dependent NMR-spectra reveal hindered interconversions of twist-forms of cis-Ia and cis-IIa.



Ia: X = S Ib: X = O



IIa

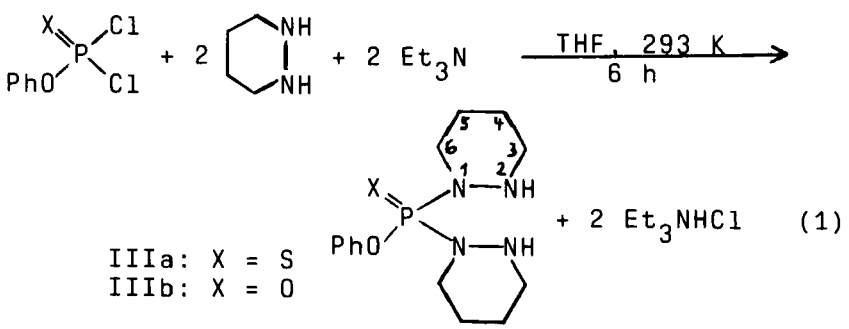
INTRODUCTION

In the past several reports on unusual ring conformations of cyclic phosphoric acid derivatives, i.e. esters, amides and hydrazides have been issued from our laboratory and from other groups.[1-9] Interest in this field is stimulated by the use of some of these compounds (cyclophosphamide) as antitumor drugs and by

the more theoretical intent to find reasons and effects that cause deviations from the "normal" chair-conformation of saturated sixmembered rings especially in phosphorus-hydrazine heterocycles. The title compounds have been synthetized to enlarge our knowledge about the effect of torsion angles arround N-N bonds on ring conformations.

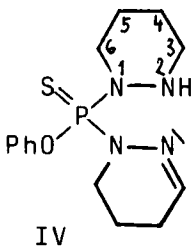
RESULTS

Hexahydropyridazine used in excess reacts with phenoxythiophosphoryldichloride or with phenoxyphosphoryldichloride in the presence of triethylamine to the corresponding "dihydrazide" bis(hexahydro-1-pyridazinyl)-thiophosphoric acid O-phenylester IIIa or bis(hexahydro-1-pyridazinyl)phosphoric acid phenylester IIIb according to Eq. (1). IIIa is obtained in two crystal modifications, that differ in melting point (336 and 341 K) and slightly in their IR- and Raman-spectra.

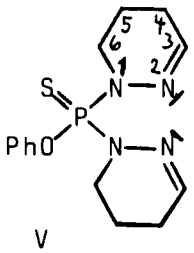


NMR-spectra in solution are identical. The ^{1}H-NMR is of higher order (complex multiplets). Table I gives the data of proton-decoupled ^{13}C- and ^{31}P-NMR-spectra.[10]

IIIb is also obtained in two different crystal forms (melting points 379 and 369 K). Both forms give identical mass spectra and NMR-spectra (see Table I). In the table the NMR-data of two compounds IV and V are included, that appear as impurities, if the hexahydropyridazine prepared from pyridazine by catalytic hydration contains some 2-tetra hydropyridazine as impurity. Compound V cannot react further in the following reaction steps with dichloroderivatives of phosphoric acid and thus accumulates in the reaction mixtures. The ^{1}H-NMR-spectra of all four hydropyridazine derivatives consist of hihger order multiplets for the aliphatic ring protons as well as the usual pattern for the phenyl-protons.



IV



V

The tricyclic compound Ia was prepared from the corresponding "dihydrazide" IIIa using a procedure already established with N,N'-dimethylhydrazides in our laboratory according to Eq. (2).[1,11] Two crystal forms

$$\text{IIIa} + \text{PhO-P(=S)Cl}_2 + 2\ \text{Et}_3\text{N} + \text{Al}_2\text{Cl}_6 \xrightarrow{\text{THF, 323 K, 48 h}} \text{Ia} + 2[\text{Et}_3\text{NH}]\text{AlCl}_4 \quad (2)$$

are obtained from n-hexane: hexagons m.p. 457 K and small needles m.p. 436 K. Since a separation of the two compounds assumed to be the expected trans- and cis-isomers of Ia could not be achieved by chromatographic methods, crystals were separated mechanically under a microscope and then recrystallized from n-hexane.

tetrahydropyridazine: δ (ppm), J (Hz); standards TMS resp. 85% H_3PO_4 ,
solvent $CDCl_3$; * tetrahydropyridazine ring, u. = unresolved.

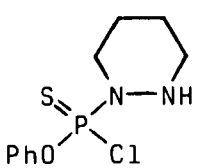
mpound	δ:	C3	C4	C5	C6	$^2J_{PC6}$	$^3J_{PC5}$	$^3J_{PC3}$	$^4J_{PC4}$
a		47.7	25.8	24.1	48.0	7.3	7.3	7.3	---
b		47.3	25.8	24.2	47.6	5.3	4.8	6.6	---
		47.6	25.4	24.3	47.9	7.3	7.3	7.3	---
	*	143.2	17.3	23.1	42.3	6.1	u.	14.7	6.1
		143.3	17.8	23.4	43.0	6.9	1.9	13.8	5.7
ahydro-idazine		47.7	24.5	24.5	47.7	---	---	---	---
trahydro-ridazine		137.7	18.4	21.9	40.8	---	---	---	---

^{13}C-data for the phenoxy-rings: C1 150.6±0.3, C2/C6 121.3±0.4 (IIIb 1
/C5 129.1±0.1, C4 124.6±0.2 (IIIb 123.8), $^3J_{PC}$ 4.9 (V 4.4), $^2J_{PC}$ 6.1 (V

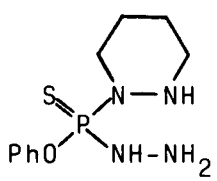
Mass spectra of the pure compounds are almost identical and show the mole peak in high intensity. ^{1}H-NMR-spectra are of higher order. Considerable broadening is observerd with the lower melting isomer. In the $\{^{1}H\}^{13}C$-NMR of the other isomer a sharp singlet and doublet are seen for methylene C-atoms α resp. ß to N. In contrast to this the spectrum of the 2nd isomer consists of four broad signals. Coupling to phosphorus is not resolved. Shifts and J-values are given in TABLE II. Spectra at different temperatures are displayed in FIGURE I and are discussed below.

Analogous reactions of IIIb with phenoxyphosphoryldichloride gave only one compound Ib. An X-ray structure analysis showed this to be the trans-isomer.[11] Relevant NMR-data are included in TABEL II.

If the reaction according to Eq. (1) with the thiodichloride and pyridazine is carried out in a 1:1 molar ratio and at low temperature or with an excess of the dichloride for only a few hours at room temperature, a monosubstitution product VI is obtained besides some IIIa. VI reacts with absolute hydrazine to the mixed "dihydrazide" VII that can be isolated as a colourless oil. Since separation from impurities, mainly IIIa and some PhO-P(=S)(NH-NH_2)$_2$, could not be easily achieved, raw VII was reacted directly with phenoxythiophosphoryldichloride according to Eq. (2) but without Al_2Cl_6 to give the partly N-substituted ring IIa in about 14% yield. IIa was purified by preparative thinlayer chromatography on silicagel plates with a mixture THF:CCl_4 1:9. Two com-



VI



VII

pounds with Rf-values of 0.49 and 0.42 give identical mass spectra with correct mole peaks for IIa. The ^{1}H-NMR spectra of both compounds show broad undissolved multiplets for the methylene protons. Other NMR-data are included in TABLE II and will be discussed below.

TABLE II $\{^{1}H\}^{13}C$- and ^{31}P-NMR data of the trans- and cis-isomers of the tricyclic compounds Ia and Ib and of the bicyclic compound IIa : δ (ppm), J (Hz); standards and solvent as in Table I ; u. = unresolved, D doublet and Q quadruplet collaps to singlets on decoupling of protons.

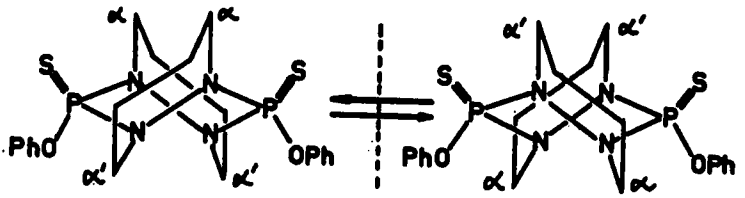
compound	δ: C7/14	C4/11	C5/12	C6/13	$^{2}J_{PC}$	$\delta^{31}P$
trans-Ia	45.3		23.8		7.3	62.6
cis-Ia	45.2	44.8	25.1	21.7	u.	D: 71.1
trans-Ib	44.6		23.7		6.1	1.7
	δ: C7/10		C8/9			
trans-IIa	44.9		23.7		u.	62.5
cis-IIa	45.3	44.4	24.8	22.3	u.	D: 72.9 Q: 68.5

DISCUSSION

As expected the tricyclic system Ia is formed as a pair of cis/trans-isomers. The attribution can be made using the ^{31}P-NMR-shifts, since in all known cases of similar molecules the trans-isomer has the upfield shift value.[12-14] This classification of isomers could be confirmed by X-ray structure determinations.[15] Trans-Ia adopts a centrosymmetric chair-conformation of the

central phosphorus-hydrazine ring in the crystal. The $\{^1H\}^{13}C$-NMR data are consistent with the assumption of a similar structure of the molecule in solution: sharp signals are observed for only two types of methylene C-atoms α to nitrogen (doublet by coupling to P) and ß to nitrogen (singlet). These features of the spectrum do not change in a temperature range from 193 - 323 K. This and the observed singlet in the ^{31}P-spectrum support the conclusion, that mainly one centrosymmetric chair-conformation (with S equatorial as in the crystal) is present in solution, which does not interconvert quickly to other less favourable forms. In cis-Ia the central ring has a twist-conformation, whereas the fused hexahydropyridazine rings possess normal chair conformations in the crystal. The molecule has a twofold axis of symmetry, leaving only the α-C-atoms C4 and C11 respectively the α'-C-atoms C7 and C14 symmetry-equivalent. Analogously the same is true for the corresponding ß- and ß'-C-atoms (FIGURE 1). In accordance the spektrum in solution shows signals for four different C-atoms, α-, α', ß and ß'. Coupling to the phosphorus is not resolved due to a remarkable broadening of the lines at 293 K. Apparently the interconversion of the two enantiomeric twist-conformations is comparable to the NMR-time scale at ambient temperature. On heating to 323 K the two peaks for the α-C-atoms almost collaps to one signal, whereas still two very broad peaks are observed for the ß-C-atoms. By lowering the temperature to 193 K, on the other side, all four signals become narrow lines. The hindered interconversion is now slower than the NMR-time scale. The free energy of activation can be roughly estimated as 68 ± 5 kJmol^{-1}, which is a remarkable high value for an interconversion of enantiomeric twist-

-conformations. But it has to be taken into considera-
tion that the central ring is highly substituted and



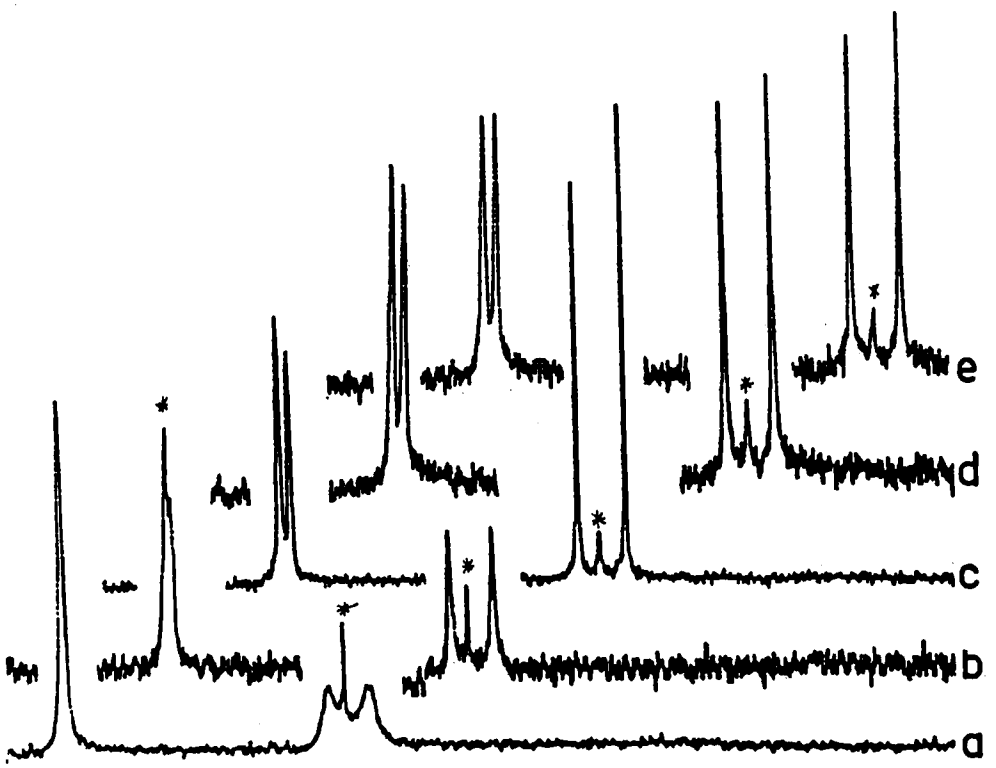


FIGURE 1 $\{^1H\}^{13}C$-NMR-spectra of cis-Ia, region of methylene C-atoms, at : a 323, b 293, c 233, d 213, e 193 K; * impurity of trans-Ia.

the usual interconversion over boat-conformations in the so-called pseudorotation cycle must be highly hindered by steric interactions of the substituents at P- and N-atoms. A significantly lower value of 53 ± 2 kJmol^{-1} was found in 1,2,4,5-tetramethyl-3-phenoxy-6,6-diphenyl-1,2,4,5-tetraaza-3-phospha-6-silacyclohexane-3-sulfide, a ring compound, where one PhO-P(=S)< - unit is replaced by a $Ph_2Si<$-unit and the outer rings by four methylgroups at the four N-atoms.[1] The corresponding rings similar to Ia but with four methylgroups insted of the outer rings have $\Delta G^{\#}$-values between 47 ± 1 (trans-) and 63 ± 1 kJmol^{-1} (cis-isomer).[12] Considerably lower values between 40 and 50 kJmol^{-1} are observed for analogous compounds with only two methylgroups at ring N-atoms.[16]

The only isolated isomer of Ib has the trans-configuration (X-ray structure determination).[11] In solution the features of the NMR-spectra are very similar to those of trans Ia (TABLE II), so that again a rather rigid chair-conformation is assumed in solution.

The two isomers of the bicyclic compound IIa separated by thin-layer chromatography can be attributed to trans- and cis-configuration from Rf-values, the more polar cis-isomer having the lesser Rf, and in addition from ^{31}P-shifts (TABLE II). Only one signal for α-C-atoms and one signal for ß-C-atoms in the pyridazine ring (^{13}C-NMR) and one broad singlet for phosphorus (^{31}P-NMR) again lead to the conclusion that only one distinguishable conformation exists in the solution of trans-IIa, that should have C_2-symmetry as chair-(or twist-)-conformation with magnetically equivalent pairs of P- and ring-C-atoms. Between the higher order multiplets for phenyl- and pyridazine methyleneprotons a distinct doublet is found for the NH-protons in the

^{1}H-NMR at 5.06 ppm, $^2J_{PNH}$ = 32 Hz. Though no suitable crystals for an X-ray structure analysis could be obtained so far, we assume a chair-conformation analogous to trans-Ia. Due to the lower symmetry of IIa a racemate of two configurational enantiomers - P(R)P'(R) and P(S)P'(S) is expected. Both enantiomers give identical NMR-spectra of course.

In contrast to these findings molecules of cis IIa apparently have no symmetry-equivalent pairs of either P- or C-atoms in solution (TABLE II). Peaks in the $\{^1H\}^{13}$C-NMR are broad at ambient temperature. Coupling to phosphorus is unresolved. ^{31}P-NMR spectra show two groups of signals at 293 K: a doublet and a doublet of doublets. The lines collaps to two singlets on decoupling of protons. The rather broad lines at ambient temperature grow sharp at 233 K. These features of the spectra obviously are due to a beginning, strongly hindered interconversion process. The most probable model is the existence of two enantiomeric twist-conformations. Only fast interconversions, that obviously do not occur, would render both pairs to a time-averaged meso-form with a plane of symmetry and magnetically equivalent pairs of P(R)P'(S) and α - and ß-C-atoms. Coalescence of signals is indicated but not quite complete at 323 K (experimental limit).

EXPERIMENTAL

Bis(hexahydro-1-pyridazinyl)thiophosphoric acid-O-phenylester, $C_{14}H_{23}N_4OPS$: hexahydropyridazine was prepared from hydrazodicarbonic acid diethylester via the corresponding azo compound, Diels-Alder addition of butadien, decarboxylation and catalytic hydration according to

the literature.[17-19] A solution of 11.35 g (0.05 mole) phenoxythiophosphoryldichloride in 100 mL abs. THF was given dropwise to a stirred solution of 10 g (0.116 mole) hexahydropyridazine and 30 mL triethylamine in 400 mL abs. THF during a period of 3 h. After additional 3 h stirring the solution was filtered from triethylammoniumhydrochloride under dry nitrogen. Solvent and excess triethylamine were removed under reduced pressure. The residue was agitated with 100mL n-hexane. The decanted solution was cooled to 248 K, colourless cristals, m.p. 341 K (form A). A 2nd extract with 200 mL n-hexane gave crystals, m.p. 336 K (form B) combined yield 76%. Recrystallisation from n-hexane of both forms in most cases gives crystals of form A. Form B transforms slowly to A under the mother solution. MS of A and B: m/z 326(30%) M^+, 327(16%) M^++1, 149(20%) M^+-177(C_6H_5O, $C_4H_9N_2$), 148(18%) M^+-178, 86(30%) $C_4H_{10}N_2^+$, 85(100%) $C_4H_9N_2^+$; Anal.: form A C 51.76%(theor. 51.52%), H 7.11%(7.10), N 17.14%(17.16); form B 51.43%, H 7.09%, N 17.14%. IR (cm^{-1})(only some characteristically different bands) form A: 3235w, 3202w, 3055m, 2945vs, 2864s; form B: 3235m, 3080w, 3055w, 2958vs, 2935vs, 2850s. Raman form A: 3222vs, 3189vs, 639m; form B: 3223vs, 3180vw, 639m.

Bis(hexahydro-1-pyridazinyl)phosphoric acid phenylester, $C_{14}H_{23}N_4O_2P$, IIIb : A solution of 4.22 g (0.02 mole) phenoxyphosphoryldichloride in 100 mL abs. THF was dropped to a solution of 3.44 g (0.04 mole) hexahydropyridazine and 6 mL triethylamine in 300 mL THF under stirring in a period of 6 h. The filtered solution was evaporated under reduced pressure. The residue was extracted with n-hexane/toluene mixtures 1:1 in several 100 mL portions. On cooling to 248 K the 1st

three extracts gave crystal form A, m.p. 379 K, the next two extracts crystal form B, m.p. 369 K, combined yield 66%. MS of A and B : m/z 310(100%) M^+, 311(18%) M^++1, 308(12%) M^+-2H, 86(44%) $C_4H_{10}N_2^+$, 85 (57%) $C_4H_9N_2^+$, 56(18%) $C_4H_8^+$; Anal.: form A C 54.05% (theor. 54.18%), H 7.22%(7.47), N 17.59%(18.05); form B C 54.03%, H 7.26%, N 17.69%. IR (cm^{-1}) A and B 3214s; Raman A: 3283w, 3218m, 3209 shoulder, B 3218vs.

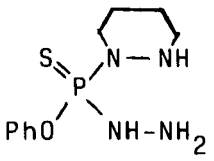
2,9-Diphenoxy-1,3,8,10-tetraaza-2λ^5,9λ^5-diphospha-tricyclo[8.4.0.$0^{3,8}$]tetradecane-2,9-disulfide, $C_{20}H_{26}N_4O_2P_2S_2$, Ia : 4.77 g (0.021 mole) phenoxy-thiophosphoryldichloride in 100 mL THF were dropped to a stirred solution of 6.53 g (0.02 mole) of the "dihydrazide" IIIa, 6.67 g (0.05 mole) anhydrous $AlCl_3$ and 8.3 mL (0.06 mole) triethylamine in 300 mL THF held at 323 K. The solution was heated and stirred for two days. The precipitate of triethylammoniumtetra-chloroaluminate was filtered from the brown solution. Solvent and other volatile produkts were removed under vacuum. The brown oily residue was extracted with 300 mL dry n-hexane at 303 K. This procedure was repeated several times. Crystallisation at 248 K gave two different crystal forms, yield 9%. Crystals of both forms were selected separately under a microscope and then recrystallized from n-hexane: cis Ia m.p. 436 K, trans-Ia m.p. 457 K. MS (cis- and trans-Ia identical) m/z 480(100%) M^+, 481(27%) M^++1, 482(12%) M^++2, 411 (22%) M^+-69(C_4H_7N), 318(20%) M^+-93-69 (C_6H_5O, C_4H_7N), 303(24%) M^+-93-84 (C_6H_5O, $C_4H_8N_2$), 147(61%) ?, 85(56%) $C_4H_9N_2^+$, 70(51%) $C_4H_8N^+$, 56(41%) $C_4H_8^+$. Anal.: trans-Ia C 49.89%(theor. 49.99%), H 5.42%(5.45), N 11.60%(11.65) cis-Ia C 49.95, H 5.56, N 11.64, S 13.30%(13.34);

IR (cm^{-1}, solid in KBr) trans-Ia (cis-Ia): 2938s(2948w) 2855w(2905w, 2855w), 1588s(1596s), 1488vs(1495vs) 1198vs, 1190shoulder (1225shoulder, 1212vs), 1140s (1142s), 1965s(1098m), 1058s(1025s), 1005s, 939s, 921vs 904s (934s, 916vs, 898s), 798vs, 773vs (791vs, 780vs), 690m, 650s (745m, 690s, 638s).

trans-2,9-Dioxo-2,9-diphenoxy-1,3,8,10-tetraaza-2λ^5, 9λ^5-diphosphatricyclo[8.4.0.0^{3,8}]tetradecane, $C_{20}H_{26}N_4O_4P_2$, trans-Ib : 7.60 g (0.036 mole) phenoxy-phosphoryldichloride in 200 mL abs. THF were given to a solution of 11.16 g (0.036 mole) of the "dihydrazide" IIIb, 13.34 g (0.10 mole) anhydrous $AlCl_3$ and 16.6 g (0.12 mole) triehtylamine in 600 mL THF. The mixture was boiled under reflux for two days. After filtration under vacuum the solvent was removed together with excess triethylamine and other volatile products and the residue extracted with several portions of n-hexane and n-hexane/toluene mixtures 1:1. Evaporation of the extraction solvent and recrystallisation from n-hexane gave colourless crystals m.p. 504 K; yield ca. 8%. MS m/z 448(100%) M^+, 449(26%) M^++1, 450(4%) M^++2, 85 (5.8%), 77(4.9%), 43(5.6%). Anal.: C 53.29%(theor. 53.57%), H 5.87%(5.85), N 12.30%(12.49). IR (cm^{-1}, solid in KBr) 2968m, 2944s, 2924s, 2871m, 2854m, 1593s, 1588s, 1488vs, 1441s, 1317s, 1273vs, 1220s, 1197vs, 1162vs, 1144vs, 1101s, 1067vs, 1026vs, 923vs, 781vs, 766s, 693vs, 586s, 520s, 490s, 470s.

2,5-Diphenoxy-1,3,4,6-tetraaza-2λ^5,5λ^5-diphospha bicyclo[4.4]decane-2,5-disulfide, $C_{16}H_{20}N_4O_2S_2$, IIa : 1.73 g (0.02 mole) hexahydropyridazine in 100 mL THF and 4.54 g (0.02 mole) thiophosphoryldichloride in another 100 mL THF were dropped simultanously to a solution of 4.1 mL (0.03 mole) triethylamine in 400 mL

abs. THf held at 238 K. After 5 h triethylammoniumhydrochloride was filtered and the resulting clear solution was dropped to a solution of 1.5 g (0.047 mole) of abs. hydrazine in 200 mL THF during a period of 5 h at 293 K. After filtration and removal of volatiles and solvent under reduced pressure a colourless oil remained that mainly contained the mixed "dihydrazide" :



and some IIIa and traces of bis(hydrazido)thiophosphoric acid phenylester. This oil was mixed with 400 mL THF and 8.3 mL (0.05 mole) triethylamine and then reacted directly with 4.77 g (0.021 mole) phenoxythiophosphoryldichloride in 100 mL THF at 328K for two days. After filtration and evaporation of the solvent under vacuum the residue was extracted with several 100 mL portions of n-hexane and n-hexane/toluene 1:1 . The solvent from the combined extracts was removed under reduced pressure and the colourless reaction products were separated on preparative Silicagel-plates (Schleicher&Schüll DC G 1510/LS254, 1mm layer) with a mixture of THF/CCl_4 1:9 as eluent. Zones with Rf 0.49 and 0.42 containing trans- and cis-IIa were scapped off the plates and extracted with $CHCl_3$ separately: trans-IIa m.p. 364 K, yield 860 mg = 8%; cis-IIa m.p. 352 K, yield 500 mg = 5.9%. MS m/z (trans- and cis-IIa identical) 426(100%) M^+, 427(23%) M^++1, 428(13%) M^++2, 85(54%) $C_4H_9N_2^+$. Anal.: trans-IIa C 46.02%(theor. 45.07%), H 5.09%(4.73), N 12.04%(13.14) cis-IIa C 45.90%,H 5.03%, N 11.92%. IR (cm^{-1}, solid in KBr) trans-IIa (cis-IIa): 3420 shoulder, 3360m, 3250m (3420m, 3350m, 3250m), 3050w (3050w), 2905m (2905m), 2850m (2850m), 1590vs (1588vs), 1488vs (1485 vs), 1455w, 1442w, 1438 sh. (1450w, 1440w, 1438 sh.),1198vs

(1198vs), 1159s (1158s), 1020m, 1006w (1020m, 1002 sh.) 938vs, 922vs, 898s (936vs, 921vs, 894s), 785vs, 766vs (780vs, 770 sh., 742 sh.), 686s, 668s (705w, 686s, 658m).

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