Polydonor-Substituted 1-Oxa- and 1-Thia-3,5-diazahexatrienes: Synthesis, Structures, Ring−Chain Tautomerism and Theoretical Calculations[+]

Oliver Maier,[a][++] Roland Fröhlich,[a][+++] and Ernst-Ulrich Würthwein*[a]

Keywords: Density functional calculations / 1-Oxa-3,5-diazahexatrienes / Ring−chain tautomerism / 6*H*-1,3,5-Thiadiazines

Previously unknown 1-oxa-2,4-diazahexatrienes **1a,b** and **c**, substituted with alkoxy groups, have been prepared by carboxylation of *N*-alkylideneisoureas **2** with chloroformates **5**. X-ray analyses of compounds **1b** and **c** show nonplanar, open-chain structures. In contrast, thiocarboxylation of **2** with thiochloroformate **6** leads to the spiro compounds **7-ring**, as verified by spectroscopic data and X-ray analysis. A tetradonor-substituted 1-oxa-2,4-diazahexatriene **1d** was obtained from the reaction of the 1-oxa-3-aza-butadiene **10** with the triply donor-substituted carbenium ion **9**. Attempts at further chain elongation of **1a** by an alkylation/condensation sequence failed because of preferential *N*-alkylation (compound **11**). Quantum chemical calculations (AM1, PM3, RHF/3–21G, B3LYP/6–31+G*) on model systems of **1** predict the predominance, in the gas phase, of twisted, nonplanar chain structures for the oxa systems, and cyclic structures for the corresponding thia system, as found experimentally in the condensed or solid phase. In the series of oxa systems, the barrier towards ring-opening of the cyclic form of the tautomeric equilibrium decreases with increasing number of donor groups; the preference for the chain structures increases simultaneously.

Introduction

In recent years, oligonitriles have received increasing theoretical interest as heteroanalogues of polyacetylenes, due to the unusual electronic and physical properties of the planar-linear structures that have been anticipated for such polymers.[1] In our laboratory, new synthetic routes to variably substituted oligonitriles have been developed, enabling us to investigate their structural properties for the first time. In contrast to the structural assumptions for the calculations nonplanar, highly twisted structures were found in all cases.[2,3] We now also became interested in the chemistry of C=N-polymers bearing functional groups directly bound to the main chain. In this report we present our first results on polydonor-substituted 1-oxa-2,4-diazahexatrienes; the polyalkoxy derivatives among these may be regarded as short oligocyanates originating from a formal oligomerisation of the C≡N triple bonds of ROCN. Furthermore, these highly functionalized carbonic acid derivatives should afford some insight into the substituent effects of π-electron donor groups on the structural and chemical properties of C=N chains.

Until now, donor-substituted oligonitriles have not been the subject of systematic attention in the literature. Formal 1-oxa-3,5-diazahexatrienes have been prepared by Nagano's[4] and Russo's[5] groups, by alkylation of heterocyclic *N*-carboxythiourea derivatives to obtain new 2-alkoxy-4-methylthio-1-oxa-3,5-diazahexatrienes. Bondavalli et al. used the carboxylation of 1,3-diazabutadienes for the synthesis of a 2-phenoxy-1-oxa-3,5-diazahexatriene.[6] Sundaram et al.[7] and Muchowski et al.[8] reported the synthesis of 2-alkoxy-6-dimethylamino-4-methylthio-1-oxa-2,4-diazahexatrienes from isothiourea derivatives; they were used in cycloaddition reactions to form pyrimidines. Stradi et al. observed the ring-opening of an *N*-acyl-4,5-dihydroimidazole to afford a 4-methoxy-1-oxa-3,5-diazahexatriene, which was converted into a pyrimidine.[9] Gertsyuk et al.[10] found that the reaction of an *N*-alkylidenecarbamoyl isocyanate with phosphorous pentachloride resulted in a polyhalogenated oligonitrile. We obtained ω-donor-substituted oligonitriles from alkylation/condensation sequences, starting from *N*-acylimine derivatives.[11−13] The claimed synthesis of 2,4,6,6-tetraethoxy-1-oxa-3,5-diazahexatriene by Bende et al.[14] was later questioned by Jochims et al.;[15] they obtained a tautomer with a bis(imidocarbonic acid) structure from a similar reaction.

Results

1-Oxa-3,5-diazahexatrienes **1** are conveniently synthesized by acylation of 1*H*-1,3-diazabutadienes **2**[6,16] at nitrogen atom N1.[17] For the synthesis of alkoxy-substituted derivatives, this synthetic route requires the preparation of the *N*-alkylideneisoureas **2a**. In an adaptation of a procedure

[+] Unsaturated Hetero Chains, X. − Part IX: Ref.[4]

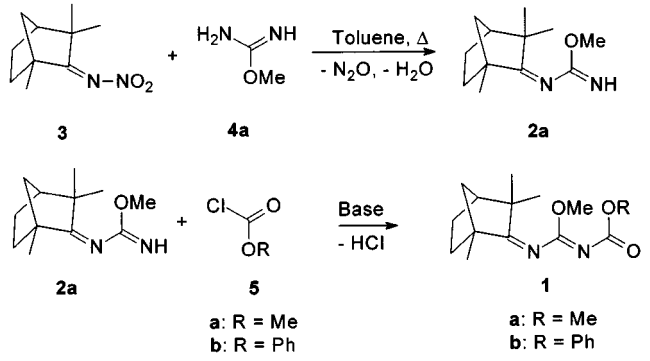
[a] Institut für Organische Chemie der Westfälischen Wilhelms-Universität Münster,
Corrensstrasse 40, 48149 Münster, Germany
Fax: (internat.) + 49-(0)251/83-39772

[++] Taken in part from the Ph. D. Thesis of O. Maier, University of Münster, **1999**.

[+++] X-ray diffraction analyses.

  1434−193X/01/0101−0083 $ 17.50+.50/0

reported by Bondavalli, Schenone et al.,[6] we synthesized such an isourea derivative **2a** from (1*R*)-fenchonnitrimine **3** and the *O*-methylisourea **4a** in 77% yield (Scheme 1). The fenchyl moiety, as a chiral, sterically crowded group, facilitates the isolation of the otherwise rather unstable 1*H*-1,3-diazabutadienes **2**. Acylation using phenyl or methyl chloroformate **5** leads to the 1-oxa-3,5-diazahexatrienes **1a** and **b**, bearing two alkoxy/phenoxy groups, respectively, in 40 to 50% yield as colourless oils. Compound **1b** crystallizes slowly over the course of several weeks.



Scheme 1

The hexatriene structure is easily deduced from the ^{13}C NMR spectra, which show three signals for C=N and C=O groups between δ = 158 and 194. The configuration and conformation of compound **1b** in the crystalline state were established by X-ray diffraction crystallography (Figure 1).

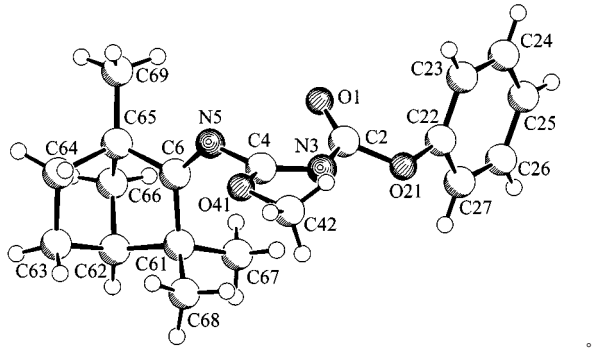
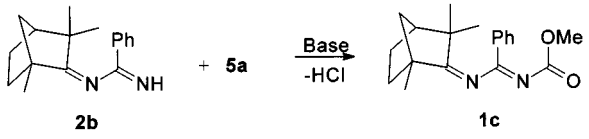


Figure 1. Molecular structure of **1b**; selected bond lengths [A], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.199(2), C(2)−N(3) 1.374(2), N(3)−C(4) 1.286(3), C(4)−N(5) 1.371(2), N(5)−C(6) 1.271(2), C(2)−O(21) 1.351(3), O(21)−C(22) 1.400(2), C(4)−O(41) 1.332(2), O(41)−C(42) 1.446(3); O(1)−C(2)−N(3) 130.2(2), C(2)−N(3)−C(4) 120.23(16), N(3)−C(4)−N(5) 129.21(17), C(4)−N(5)−C(6) 126.49(17), N(5)−C(6)−C(61) 129.64(17), N(5)−C(6)−C(65) 121.93(17), C(22)−O(21)−C(2) 119.29(15), O(21)−C(2)−N(3) 107.18(16), O(21)−C(2)−O(1) 122.52(19), C(42)−O(41)−C(4) 118.45(18), O(41)−C(4)−N(3) 119.88(17), O(41)−C(4)−N(5) 110.60(17); O(1)−C(2)−N(3)−C(4) 21.49, C(2)−N(3)−C(4)−N(5) 1.70, N(3)−C(4)−N(5)−C(6) 92.52, C(4)−N(5)−C(6)−C(65) 174.96, C(4)−N(5)−C(6)−C(61) −2.01, O(1)−C(2)−O(21)−C(22) 5.78, N(3)−C(2)−O(21)−C(22) −171.73, C(2)−O(21)−C(22)−C(23) 63.82, O(21)−C(2)−N(3)−C(4) −161.26, C(42)−O(41)−C(4)−N(3) −2.08, C(42)−O(41)−C(4)−N(5) −176.20, O(41)−C(4)−N(3)−C(2) −171.20, O(41)−C(4)−N(3)−C(6) −94.05

In the solid state, compound **1b** adopts a twisted chain structure [torsion angles: O1−C2−N3−C4 21.49(0.36)°, C2−N3−C4−N5 1.70(0.31)°, N3−C4−N5−C6 92.52(0.27)°]. Thus, the RO−C=O unit displays a *gauche* conformation with respect to the central (*E*)-C=N bond, whereas the N5=C6 moiety is situated perpendicular to this plane; consequently, a helical arrangement of the chain is manifested in the crystalline state. Both the alkoxycarbonyl group and the imidate function, including N3, show *s-cis* conformation, as largely observed in ester-type derivatives.[18] The bonds along the chain alter in length [O1−C2 1.199(2) A, C2−N3 1.374(2) A, N3−C4 1.286(3) A, C4−N5 1.371(2) A, N5−C6 1.271(2) A], but still show considerable conjugative interaction across the single bonds, which are comparatively short. We conclude that polyene-type conjugation is not dominant in this structure, but that interaction of nitrogen lone pairs with adjacent C=N- and C=O bonds (amide-type conjugation) is important in these molecules. Similar structures were observed for oligonitriles without electron donor groups;[3,17] thus, the structural properties of the chain seem only to be influenced a little by donor group substituent effects. Quantum chemical calculations (see below) indicate that the structure found in the solid state belongs to those of low relative energy, although it is not the global minimum structure.

Similarly, a 4-phenyl-substituted 1-oxa-3,5-diazahexatriene **1c** was prepared from the *N*,*N*-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)benzamidine (**2b**, Scheme 2)[6] by acylation with methyl chloroformate **5a** after deprotonation with *n*-butyllithium. The colourless solid was obtained in 80% yield and characterized by X-ray diffraction analysis as the open-chain compound with one perpendicular C=N and one perpendicular C=O functionality about the central, (*Z*)-configured C=N bond [torsion angles along the chain: O1−C2−N3−C4 92.43(0.58)°, C2−N3−C4−N5 9.57(0.57)°, N3−C4−N5−C51 −95.03(0.57)°] (Figure 2). According to quantum chemical calculations, this structure corresponds to the global energy minimum (see below).



Scheme 2

Treatment of *N*-alkylideneisoureas **2** with the chlorothioformate **6** resulted in compounds **7a** (54%) and **7b** (46%, Scheme 3). For these reactions, deprotonation of the isourea **2a** was essential, to increase its nucleophilic reactivity.

At 258 K, the ^{13}C NMR spectra of **7a** and **b** show two closely related sets of signals. Unlike the case of compound **1**, there are only two signals at low field (δ = 157, 175), which are assigned to −O−C=N units. At δ = 89, however, a signal of an sp^3-hybridized carbon atom is observed. These spectra are in agreement with the spiro constitutions of **7a-ring** and **7b-ring**. The two sets of signals are due to mixtures of diastereomers [(*R*,*R*) and (*R*,*S*) with regard to the (*R*)-fenchon moiety and the stereogenic spiro carbon atom] in the ratio of 8−10:1. At room temperature, some signals collapse to single lines. Compound **7a** shows coales-

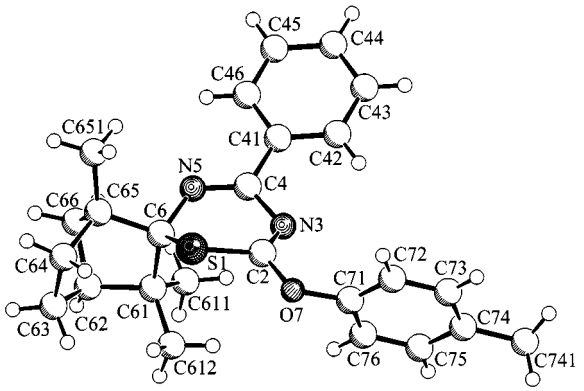
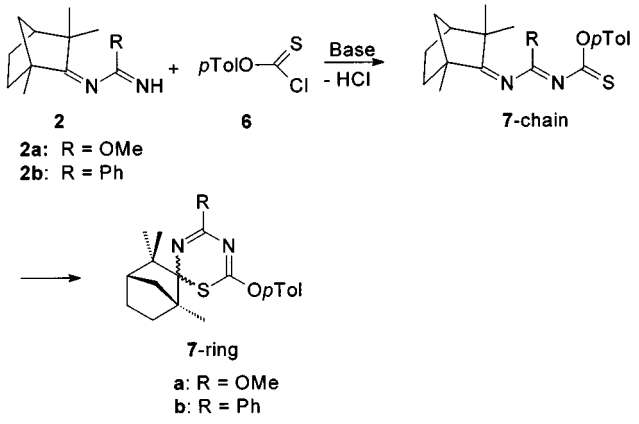


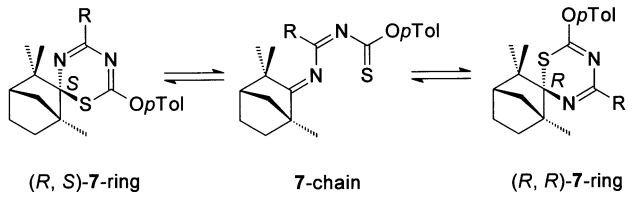
Figure 2. Molecular structure of **1c**; selected bond lengths [A], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.201(5), C(2)−N(3) 1.382(6), N(3)−C(4) 1.287(5), C(4)−N(5) 1.380(5), N(5)−C(51) 1.272(5), C(2)−O(21) 1.333(5), O(21)−C(22) 1.449(6), C(4)−C(41) 1.487(6); O(1)−C(2)−N(3) 124.2(5), C(2)−N(3)−C(4) 118.7(4), N(3)−C(4)−N(5) 123.1(4), C(4)−N(5)−C(51) 129.2(4), N(5)−C(51)−C(52) 120.6(4), N(5)−C(51)−C(56) 131.6(4), C(22)−O(21)−C(2) 115.9(3), O(21)−C(2)−N(3) 112.7(3), O(21)−C(2)−O(1) 122.8(5), C(41)−C(4)−N(3) 118.7(4); O(1)−C(2)−N(3)−C(4) 92.43, C(2)−N(3)−C(4)−N(5) 9.57, N(3)−C(4)−N(5)−C(51) −95.03, C(4)−N(5)−C(51)−C(52) 175.82, C(4)−N(5)−C(51)−C(56) −5.67, C(22)−O(21)−C(2)−O(1) −1.48, O(21)−C(2)−N(3)−C(4) −94.07, C(41)−C(4)−N(3)−C(2) −176.68, C(41)−C(4)−N(5)−C(51) 91.17, C(46)−C(41)−C(4)−N(3) 8.79, C(46)−C(41)−C(4)−N(5) −177.13



Scheme 3

cence phenomena at room temperature; at 313 K, broadening of several signals precludes the observation of individual diastereomers.

Crystals of **7b** were subjected to X-ray analysis. As can be seen from Figure 3, the compound exists in the solid state as ring tautomer **7b-ring**. The central 6*H*-1,3,5-thiadiazine ring adopts a boat conformation. The spiro carbon atom of the crystalline species has (*R*) configuration; PM3 calculations on both diastereomers of **7b-ring** (Scheme 4) indicate an energetic preference of 0.44 kcal/mol in favour of the observed (*R*,*R*) diastereomer over the (*R*,*S*) diastereomer. Equilibration of these diastereomers in solution most probably takes place via an open chain intermediate (**7-chain**). Whereas the phenyl substituent is well in plane with the corresponding C=N bond, the *p*-tolyloxy group is twisted by 109.5° out of the plane of the heterocycle.



Scheme 4

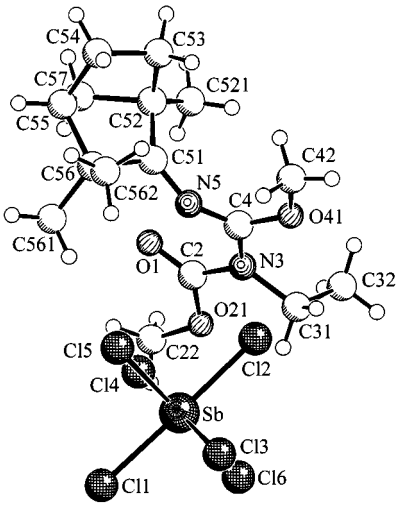
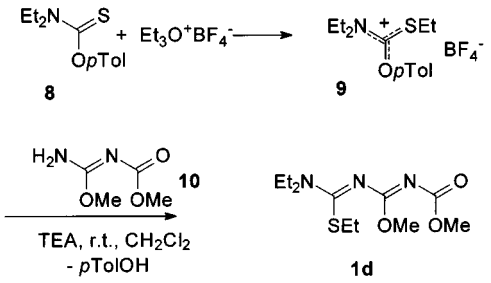


Figure 3. Molecular structure of **7b-ring**; selected bond lengths [A], bond angles [°], and torsion angles [°]: S−C(2) 1.753(3), C(2)−N(3) 1.269(3), N(3)−C(4) 1.403(3), C(4)−N(5) 1.283(3), N(5)−C(6) 1.441(3), S−C(6) 1.859(2), C(2)−O 1.349(3), C(6)−C(61) 1.600(3), C(6)−C(65) 1.570(3); C(2)−S−C(6) 94.23(11), N(3)−C(2)−S 126.7(2), C(4)−N(3)−C(2) 117.1(2), N(5)−C(4)−N(3) 126.5(2), C(6)−N(5)−C(4) 121.5(2), S−C(6)−N(5) 109.0(2), O−C(2)−N(3) 123.1(2), C(65)−C(6)−S 108.2(2), C(61)−C(6)−S 115.5(2), C(61)−C(6)−C(65) 103.5(2); S−C(6)−N(5)−C(4) 40.93, C(6)−N(5)−C(4)−N(3) 1.59, N(5)−C(4)−N(3)−C(2) −28.57, C(4)−N(3)−C(2)−S 3.39, N(3)−C(2)−S−C(6) 31.11, C(2)−S−C(6)−N(5) −48.99, C(4)−N(3)−C(2)−O −176.30, N(3)−C(2)−O−C(71) −2.05, C(2)−O−C(71)−C(72) 109.46, N(3)−C(4)−C(41)−C(46) 0.56, N(5)−C(4)−C(41)−C(46) −178.77

In order to attach even more electron-donating groups to the oligonitrile chain, we used the synthetic potential of *N*-acylamidines for oligonitrile chain elongation.[13] This transformation requires the condensation of activated thiocarbamates **9** with compounds like 4-amino-2,4-dimethoxy-1-oxa-3-aza-butadiene (**10**).[19] Activation of thiocarbamate **8** by alkylation using triethyloxonium tetrafluoroborate produced the onium salt **9**, a stable, though moisture-sensitive, colourless solid. Condensation of this salt with **10** in the presence of triethylamine as base for the removal of tetrafluoroboric acid resulted in the 1-oxa-3,5-diazahexatriene **1d** (yellow oil, 28%) (Scheme 5). As anticipated, of the three donor groups attached to **9**, *p*-cresol acts as the preferred leaving group.

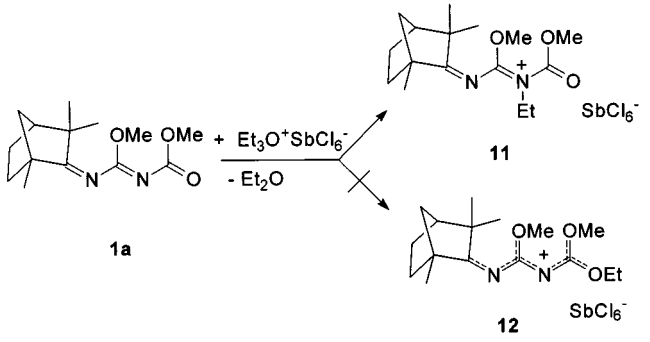
Compound **1d** represents the first example of a 1-oxa-3,5-diazahexatriene substituted with four electron-donating substituents of three different types. Its open-chain structure is evident from the ^{1}H and ^{13}C NMR spectra; the latter is characterized by three low field signals between δ = 160



Scheme 5

and 166, which are attributed to the three quaternary carbon atoms.

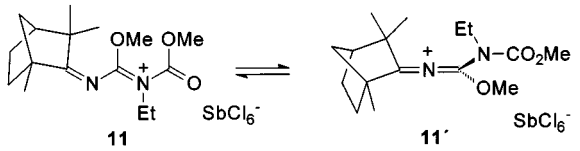
To increase the length of the chain further, a similar activation/condensation sequence starting from **1a** was studied. Treatment of 1-oxa-3,5-diazahexatriene **1a** with triethyloxonium hexachloroantimonate afforded a light brown solid (95%). Its ^{13}C NMR spectroscopic data and an X-ray diffraction study (see below) established the structure of the *N*-alkylation product **11**, which was formed regioselectively. Indications of products **12** of *O*-alkylation, as anticipated,[13] or of attack of the electrophile at nitrogen atom 5 were not observed (Scheme 6). *N*-Alkylations are uncommon in amide chemistry. However, *N*-methylenecarbamates are sometimes attacked by oxonium salts at the nitrogen atom,[20] in contrast to *N*-acylimines.[21] The regioselective



Scheme 6

N-alkylation of **1a** precludes this route for chain elongation.

For compound **11**, the valence-isomeric geometry of a 2-azaallenium cation **11′** (Scheme 7) could also be proposed. The X-ray structure analysis (Figure 4) indicates a compromise between both geometries. Thus, the bond lengths C4−N5 [1.290(6) A] and N5−C51 [1.254(6) A], as well as the bond angle C4−N5−C51 of 146.2(5)°, support the view of a delocalized positive charge and the tendency towards sp hybridization of the nitrogen atom N5. From our earlier work, we know about the influence of donor substituent effects on the 2-azaallylium-2-azaallenium system;[20] uncommon C−N−C bond angles such as in **11** are typical of these flexible molecular moieties.



Scheme 7

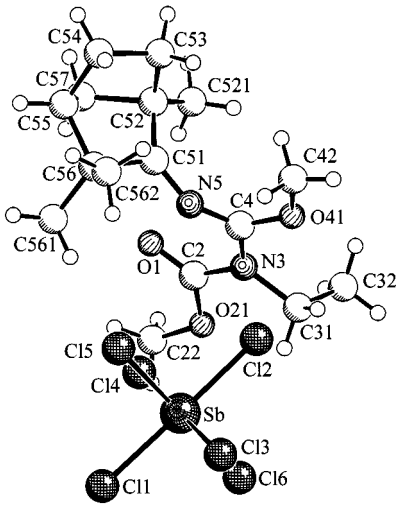


Figure 4. Molecular structure of **11**; selected bond lengths [A], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.188(6), C(2)−N(3) 1.408(6), N(3)−C(4) 1.354(6), C(4)−N(5) 1.290(6), N(5)−C(51) 1.254(6), N(3)−C(31) 1.495(6), C(31)−C(32) 1.492(6), C(51)−C(52) 1.502(9), C(51)−C(56) 1.526(9); O(1)−C(2)−N(3) 124.7(5), C(2)−N(3)−C(4) 119.1(4), N(3)−C(4)−N(5) 124.6(5), C(4)−N(5)−C(51) 146.2(5), N(5)−C(51)−C(52) 131.9(8), N(5)−C(51)−C(56) 119.4(7), C(31)−N(3)−C(4) 119.6(4), O(21)−C(2)−O(1) 125.6(5), O(41)−C(4)−N(5) 121.5(5); O(1)−C(2)−N(3)−C(4) 12.16, C(2)−N(3)−C(4)−N(5) 18.41, N(3)−C(4)−N(5)−C(51) −102.05, O(41)−C(4)−N(5)−C(51) 88.65, C(4)−N(5)−C(51)−C(52) 4.98, C(4)−N(5)−C(51)−C(56) 173.70, C(22)−O(21)−C(2)−O(1) −2.44, C(32)−C(31)−N(3)−C(4) −100.89, C(42)−O(41)−C(4)−N(5) −0.76

Quantum Chemical Calculations

In order to investigate the structural and dynamic properties of the experimentally studied alkoxy-substituted 1-oxa-3,5-diazahexatrienes, quantum chemical calculations were performed at various levels of theory. The semiempirical methods AM1[22] and PM3[23] were used for thorough searches for the best acyclic and cyclic conformations of model compounds; alkoxy groups were generally simulated by methoxy groups and all other substituents were replaced by methyl groups. These replacements prevented direct comparison with the experimentally studied molecules, but gave valuable insights into the intrinsic principal electronic features of these classes of compounds. The performance of the semiempirical methods AM1 and PM3 was checked by RHF/3−21G//RHF/3−21G and DFT method B3LYP/6−31+G*//B3LYP/6−31+G* (Gaussian 98[24]) calculations on all possible open-chain (Table 1, Entry **Ia-c**) and ring (Entry **Id-e**) conformers of 2-methoxy-4,6,6-trimethyl-1-oxa-3,5-diazahexatriene and on 2-methoxy-4,6,6-trimethyl-1-thia-3,5-diazahexatriene (**II**) as model substances.[25] The main emphasis of these calculations was the assessment of the lowest energy structures, and also the thermodynamic and kinetic characteristics of the ring−chain tautomerism frequently observed in these systems. All structures were fully optimized; they correspond to stationary points on the potential energy surface, as confirmed by frequency calculations.

Table 1. Calculated relative energies of various chain and ring isomers for 2-methoxy-2,4,6-trimethyl-6*H*-1,3,5-oxadiazine (**I**) and for 2-methoxy-2,4,6-trimethyl-6*H*-1,3,5-thiodiazine (**II**) [kcal/mol] (AM1, PM3, RHF/3−21G//RHF/3−21, and B3LYP/6−31+G*//B3LYP/6−31+G*); the RHF and B3LYP data include zero point energies; the descriptors for the configurations/conformations follow the chain O=C−N=C−N=C; for the ring tautomers, the conformation of the OMe group with respect to the $C^2=N^3$ bond is given

Entry	Configuration/Conformation	AM1	PM3	RHF/ 3-21G (+ ZPE)	B3LYP/ 6-31+G* (+ ZPE)
Ia	(+)-*gauche*-(*E*)-(−)-*gauche*	[1.66]	[0.67]	[10.10]	[1.17]
Ib	(+)-*gauche*-(*Z*)-(+)-*gauche*	[0.00]	[0.84]	[9.13]	[1.78]
Ic	(+)-*gauche*-(*Z*)-(−)-*gauche*	[0.15]	[0.00]	[7.01]	[0.00]
Id-ring	$CH_3OC^2=N^3$: *s-cis*	[10.04]	[6.54]	[0.00]	[2.71]
Ie-ring	$CH_3OC^2=N^3$: *s-trans*	[12.42]	[10.53]	[3.19]	[5.76]
IIa	(+)-*gauche*-(*E*)-(−)-*gauche*	[15.21]	[11.71]	[6.14]	[6.67]
IIb	(+)-*gauche*-(*E*)-(+)-*gauche*	[14.66]	[11.08]	[5.92]	[6.53]
IIc	(+)-*gauche*-(*Z*)-(−)-*gauche*	[13.97]	[10.34]	[5.76]	[6.15]
IId	(+)-*gauche*-(*Z*)-(+)-*gauche*	[13.78]	[11.39]	[6.20]	[7.13]
IIe-ring	$CH_3OC^2=N^3$: *s-cis*	[0.00]	[0.00]	[0.00]	[0.00]
IIf-ring	$CH_3OC^2=N^3$: *s-trans*	[6.22]	[1.34]	[7.30]	[4.94]

As Table 1 indicates, there is a good agreement in the sequence of relative energies between AM1 and PM3 on one hand and B3LYP/6−31+G* on the other, with some small advantages for PM3 over AM1. These three methods favour open-chain structures for the 2-methoxy-1-oxa-3,5-diazahexatriene system (Entries **Ib** and **Ic**, respectively). In contrast, RHF/3−21G arrives at different predictions regarding the energetic sequence of the isomers and favours the cyclic isomer in ring−chain tautomerism (Entry **Id-ring**). PM3 and the DFT method agree in predicting the (+)-*gauche*-(*Z*)-(−)-*gauche* isomer to be the lowest in energy of all the chain and cyclic isomers (Entry **Ic**; see Figure 5); this structural type is also manifested in the crystalline state (compound **1c**; see above). The structural features of this form allow for optimal bond dipole moment compensation.[3] Helical forms [(+)-*gauche*-*Z*-(+)-*gauche*, Entry **Ib**] and those with central C=N bonds of (*E*) configuration (Entry **Ia**) are slightly higher in energy, as are the two cyclic forms considered. For the 1-thia-3,5-diazahexatriene system **II**, in contrast, all four methods concur in favouring the cyclic form of the isomers (Entry **IIe-ring**). This preference is easily understood in view of the weak C=S bond in the open chain isomers, which is converted into two single C−S bonds in the heterocycle.

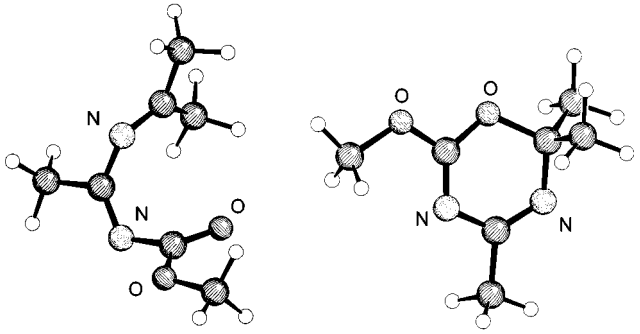
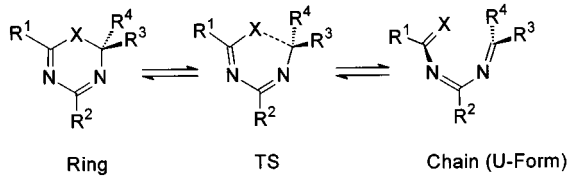


Figure 5. DFT-optimized molecular structures for the lowest energy open-chain isomer **Ic** (left) and for the ring isomer **Id-ring** (right) (B3LYP/6−31+G*//B3LYP/6−31+G*)

The lowest energy structures, as found by AM1 and PM3 optimization, for 1-oxa-3,5-diazahexatrienes substituted with additional methoxy groups in the 4- and 6-positions were further optimized with the DFT method B3LYP/6−31+G* in order to evaluate the influence of the additional donor groups on structure and on ring−chain tautomerism. Table 2 summarizes the relative energies for the best cyclic forms, for the ring-opening process transition states, for the resulting U-shaped forms (Scheme 8) and for the respective lowest energy isomers. It can be seen that the introduction of additional donor groups shifts the tautomeric equilibrium towards the open-chain forms. Within the series of alkoxy-substituted 6*H*-oxadiazines, the activation barrier decreases with increasing number of donor substituents (Table 2, Entry 1−5). At the highest calculational level used (B3LYP/6−31+G*+ΔZPE), the barrier to ring-opening changes from 7.69 kcal/mol for the monoalkoxy system (Entry 2) to 7.80 kcal/mol for the dialkoxy compound (Entry 3), and decreases to 1.86 kcal/mol for the trimethoxy-6*H*-oxadiazine (Entry 4). For the tetramethoxy-6*H*-oxadiazine system, a barrier of only 0.33 kcal/mol is calculated (Entry 5; see Figure 6). The open-chain structures lowest in energy are all nonplanar, showing central (*E*) configurations about the C=N bonds [formally (*Z*) for the 2-methoxy system (Entry 2), due to substituent priority by the Cahn, Ingold, Prelog system], in combination with variable (+)- and (−)-*gauche* conformations of the C−N bonds. In our experience,[3,17] only small barriers to rotation to the best open-chain form should be expected. In summary, for all these compounds, fast equilibration at room temperature is to be expected, with the chain isomers predominating.

Table 2. Ring−chain tautomerism of substituted 6*H*-1,3,5-oxadiazines/1-oxa-3,5-diazahexatrienes; relative energies [kcal/mol] for the best cyclic form, for the ring-opening transition state, for the resulting U-form; for comparison, the relative energy of the respective lowest energy open-chain form is included (B3LYP/6−31+G*//B3LYP/6−31+G*)

Entry	X	R^1	R^2	R^3	R^4	Ring	TS	Chain (U form)	Best chain
1	O	CH_3	CH_3	CH_3	CH_3	0.00	10.72	2.01	2.01
2	O	OCH_3	CH_3	CH_3	CH_3	0.00	7.69	0.26	−2.72
3	O	OCH_3	OCH_3	CH_3	CH_3	0.00	7.80	2.99	−4.34
4	O	OCH_3	OCH_3	OCH_3	CH_3	0.00	1.86	0.95	−8.32
5	O	OCH_3	OCH_3	OCH_3	OCH_3	0.00	0.33	−3.91	−6.88
6	S	OCH_3	CH_3	CH_3	CH_3	0.00	14.68	9.19	6.15



Scheme 8

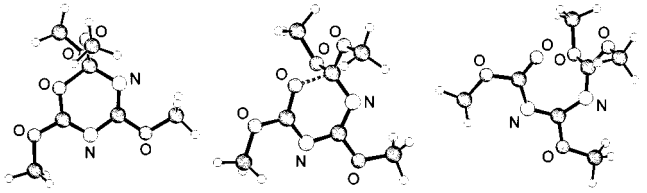


Figure 6. DFT data for the ring−chain tautomerism of 2,4,6,6-tetramethoxy-1-oxa-3,5-diazahexatriene (B3LYP/6−31+G*//B3LYP/6−31+G*)

In contrast, AM1 and PM3 calculations on polymethoxy-substituted 1-thia-3,5-diazahexatrienes **II** show a strong predominance of the cyclic forms; a minor stabilization of the open-chain forms due to mesomeric interactions is observed. The barrier to ring-opening in the 2-methoxythiadiazine **II** (Table 2, Entry 6) is calculated to be significantly higher than that in the corresponding oxadiazine **I**. B3LYP/6−31+G* calculations predict a barrier of 14.68 kcal/mol for this process. Since all open-chain isomers of this heterocycle are higher in energy by more than 6 kcal/mol, fast ring-closure reactions are expected from the calculations. Consequently, both thermodynamic and kinetic reasons prevent the observation of open-chain isomers.

Experimental Section

Materials and Methods: IR: Perkin−Elmer PE298. − ^{1}H NMR: Bruker WM300 (300.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. − ^{13}C NMR: Bruker WM300 (75.47 MHz) and Varian Unity plus (150.85 MHz), internal reference tetramethylsilane or solvent. − MS-EI: Finnigan MAT C312. − MS-CI: Finnigan MAT 8230/SS300 (NH_3). − TOF-MS: Ionisation: N_2 laser 340 nm, 3 ps, acceleration: 1 step 16 kV, resolution m/δm 100−250, accuracy 0.1%, LDI. − CHN: Perkin−Elmer Analysator Dia CHN 240. − Column chromatography: Kieselgel 60 (Merck), 0.063−0.200 mm. − Melting points are uncorrected. − All solvents were rigorously dried by standard methods. All experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique[26]) in glassware that was thoroughly dried by repeated heating under argon and subsequent evacuation. *O*-Methylisourea (**4a**) was obtained by dissolving the hemisulfate in a small amount of water. After adjustment of the pH of the solution to 10 by dropwise addition of 6 N aqueous NaOH, the solution was extracted seven times with dichloromethane. The combined organic extracts were dried with sodium bicarbonate and the solvent was removed at reduced pressure.

***N,N*-(1,3,3-Trimethylbicyclo[2.2.1]hept-2-ylidene)isourea (2a):** A solution of (1*R*)-fenchonnitrimine[6] (**3**) (5.26 g, 26.8 mmol) and *O*-methylisourea (**4a**) (1.99 g, 26.9 mmol) in toluene (25 mL) was stirred under argon for 1 h at 80 °C. The solvent was then removed under reduced pressure. After distillation (kugelrohr apparatus) of the crude material ($1.7\cdot10^{-2}$ mbar, 90 °C), a colourless oil was obtained; this could be used in further reactions. For further purification, the distilled product was dissolved in diethyl ether (20 mL), cooled to 0 °C and extracted twice with ice-cold 1 N hydrochloric acid (20 mL each). The aqueous layer was treated with 6 N NaOH until a pH of 10 was reached, and then extracted with four portions (40 mL each) of a mixture of petroleum ether/diethyl ether (1:1). The combined organic extracts were dried with magnesium sulfate and the solvent was removed at reduced pressure. Colourless oil, 4.30 g (20.6 mmol, 77%). − IR (Film): ν = 3330 cm^{-1} (m, NH), 3280 (m, br, NH), 2970 (s, $CH_{aliph.}$), 2870 (m, $CH_{aliph.}$), 2840 (sh, O−CH_3), 1690 (vs, C=N), 1635 (sh), 1630 (vs, C=N), 1460 (m), 1435 (s), 1380 (m), 1330 (vs, br), 1190 (m). − ^{1}H NMR (600 MHz, $CDCl_3$, 243 K): δ = 1.09, 1.13, 1.17, 1.19, 1.22, 1.30 (s, 9 H, 3 × fenchylidene-CH_3), 1.04−2.04 (m, 7 H, fenchylidene-CH, -CH_2), 3.81, 3.82 (s, 3 H, O−CH_3), 5.79, 5.82 (s, 1 H, NH). − ^{13}C NMR (150 MHz, $CDCl_3$, 243 K): δ = 16.2, 16.4 (CH_3), 23.2, 23.5 (CH_3), 24.4, 24.6 (CH_2), 25.4, 25.6 (CH_3), 33.2, 33.6 (CH_2), 41.6, 44.0 (CH_2), 44.8, 48.2 (CH), 46.2, 46.8 ($C_{quat.}$), 52.4, 53.3 ($C_{quat.}$), 53.7, 53.8 (O−CH_3), 165.9 ($C_{quat.}$, C=NH), 191.1, 191.2 ($C_{quat.}$, C=N). − MS (70 eV); *m/z* (%): 208 (17) [M^+], 193 (22) [$M^+ - CH_3$], 150 (12) [$C_{10}H_{16}N^+$], 136 (17) [$C_{10}H_{16}^+$], 123 (37) [$C_9H_{15}^+$], 81 (100) [$C_6H_9^+$], 71 (75). − $C_{12}H_{20}N_2O$ (208.30): calcd. C 69.19, H 9.68, N 13.45; found C 68.37, H 9.91, N 13.67.

General Procedure for the Synthesis of 4-(1,3,3-Trimethylbicyclo[2.2.1]hept-2-ylidene)amino-1-oxa-3-aza-1,3-butadienes 1 and Spiro Compounds 7. − Method A: A solution of the *N*-alkylidenebenzamidine **2b**[6] in diethyl ether was treated with *n*-butyllithium (1.6 M solution in *n*-hexane) at −78 °C. After stirring for 15−30 min at this temperature, chloroformate was added and the reaction mixture was allowed to warm up slowly to room temperature. After stirring for 16 h, the suspension was treated with petroleum ether. The lithium salt was removed by filtration through Celite and washed with a small amount of petroleum ether. The combined organic extracts were separated from the solvent at reduced pressure. The crude product was purified by column chromatography or recrystallization. − **Method B:** A solution of the *N*-alkylideneisourea **2a** and 2,4,6-collidine in *n*-hexane was treated at 0 °C with the appropriate chloroformate. Subsequently, the reaction mixture was heated under reflux for 1−3.5 h. The precipitate was filtered off and washed thoroughly with warm *n*-hexane. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography.

2,4-Dimethoxy-4-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino-1-oxa-3-aza-1,3-butadiene (1a): From the *N*-alkylideneisourea **2a** (1.00 g, 4.8 mmol) and 2,4,6-collidine (0.90 mL, 0.82 g, 6.8 mmol) in *n*-hexane (30 mL), following method B. The reaction mixture was treated with methyl chloroformate (**5a**) (0.56 mL, 0.69 g, 7.3 mmol; dissolved in 10 mL of *n*-hexane) and then heated under reflux for 3.5 h. The crude material was purified by column chromatography [petroleum ether/ethyl acetate, 5:1, R_f (TLC) = 0.49]. Colourless oil, 0.54 g (2.0 mmol, 42%). − IR (film): ν = 2950 cm^{-1} (s, $CH_{aliph.}$), 2850 (m, O−CH_3), 1710 (vs, C=O), 1680 (s, C=N), 1630 (s, C=N), 1425 (s), 1370 (s), 1320 (m), 1285 (vs), 1250 (vs), 1230 (m), 1180 (m), 1170 (m), 1070 (m), 1055 (m), 1020 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10, 1.13, 1.23 (s, 9 H, 3 × fenchylidene-CH_3), 1.36−2.01 (m, 7 H, fenchylidene-CH, -CH_2), 3.70

(s, 3 H, O−CH_3), 3.83 (s, 3 H, O−CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0 (CH_3), 23.1 (CH_3), 24.8 (CH_2), 25.7 (CH_3), 33.4 (CH_2), 43.4 (CH_2), 46.3 (CH), 46.7 ($C_{quat.}$), 52.8 (O−CH_3), 54.0 ($C_{quat.}$), 54.7 (O−CH_3), 160.7, 164.7 ($C_{quat.}$, C=O, C=N), 192.9 ($C_{quat.}$, fenchylidene-C=N). − MS (70 eV); *m*/*z* (%): 267 (6) [M^+ + 1], 266 (27) [M^+], 251 (98) [M^+ − CH_3], 235 (24) [M^+ − OCH_3], 176 (17) [$C_{10}H_{16}N$−CN^+], 150 (31) [$C_{10}H_{16}N^+$], 123 (28) [$C_9H_{15}^+$], 85 (53), 81 (100) [$C_6H_9^+$], 72 (86), 69 (76), 55 (65) [$C_4H_7^+$]. − $C_{14}H_{22}N_2O_3$ (266.34): calcd. C 63.14, H 8.33, N 10.52; found C 62.98, H 8.95, N 10.47.

4-Methoxy-2-phenoxy-4-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino-1-oxa-3-aza-1,3-butadiene (1b): From the *N*-alkylideneisourea **2a** (1.00 g, 4.8 mmol) and 2,4,6-collidine (0.90 mL, 0.82 g, 6.8 mmol) in *n*-hexane (30 mL), method B. The reaction mixture was treated with phenyl chloroformate (**5b**) [0.91 mL, 1.13 g, 7.2 mmol; dissolved in *n*-hexane (5mL)] and then heated under reflux for 1 h. The crude material was purified by column chromatography [petroleum ether/ethyl acetate, 20:1]; R_f(DC) = 0.57 [petroleum ether/ethyl acetate, 5:1]. Colourless oil, partially crystallizing after a longer time. 0.75 g (2.3 mmol, 48%); m.p. 78−81 °C. − IR (KBr): ν = 3040 cm^{-1} (vw, $CH_{arom.}$), 2950 (s), 2910 (m), 2870 (m, $CH_{aliph.}$), 2850 (m, O−CH_3), 1710 (vs, C=O), 1685 (s, C=N), 1585 (s, C=N), 1560 (vs, C=C), 1475 (s), 1420 (s), 1305 (s), 1290 (vs), 1260 (sh), 1250 (s), 1185 (vs), 1155 (vs), 1030 (s), 1015 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12, 1.14, 1.26 (s, 9 H, 3 × fenchylidene-CH_3), 1.32−1.99 (m, 7 H, fenchylidene-CH, -CH_2), 3.89 (s, 3 H, O−CH_3), 7.12−7.21 (m, 3 H, $CH_{arom.}$), 7.32−7.37 (m, 2 H, $CH_{arom.}$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0 (CH_3), 23.2 (CH_3), 24.8 (CH_2), 25.8 (CH_3), 33.4 (CH_2), 43.4 (CH_2), 46.4 (CH), 46.9 ($C_{quat.}$), 54.2 ($C_{quat.}$), 55.0 (O−CH_3), 121.6, 125.3, 129.2 ($CH_{arom.}$), 151.5 (O−C_{ipso}), 158.6, 165.6 ($C_{quat.}$, C=N, C=O), 193.5 ($C_{quat.}$, fenchylidene-C=N). − MS-CI (NH_3): *m*/*z* (%) = 330 (14) [M^+ + 2], 329 (65) [M^+ + 1], 235 (12) [M^+ − OC_6H_5], 194 (100) [$H_{16}C_{10}$=N−CN·NH_4^+], 177 (24) [$H_{16}C_{10}$=N−CNH^+], 152 (65) [$H_{16}C_{10}NH_2^+$]. − $C_{19}H_{24}N_2O_3$ (328.41): calcd. C 69.49, H 7.37, N 8.53; found C 69.09, H 7.50, N 8.70.

X-ray Diffraction Analysis of 1b ($C_{19}H_{24}N_2O_3$): The colourless single crystals were analyzed with an automatic CAD4 diffractometer (Enraf−Nonius) using Cu-K_α radiation (λ = 1.54178 A) and a graphite monochromator at 20 °C. Crystal system: orthorhombic, space group $P2_12_12_1$ (No. 19) with cell parameters *a* = 8.040(2) A, *b* = 8.752(2) A, *c* = 25.418(6) A, *V* = 1788.6(7) A^3, $\rho_{calcd.}$ = 1.220 g cm^{-3}, *Z* = 4. Crystal size: 0.25 × 0.20 × 0.10 mm. 2104 reflections were collected, resulting in 2104 independent and 1909 observed [$I > 2\ \sigma(I)$] reflections. Absorption coefficient μ = 6.67 cm^{-1}, method of absorption correction: ψ-scan, 222 refined parameters. Non-hydrogen atoms were refined anisotropically. H atoms were geometrically positioned (riding model). $R(F)$ = 0.034, $wR(F^2)$ = 0.092; residual electron density: 0.20/−0.14 e A^{-3}.[27]

2-Methoxy-4-phenyl-4-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)-amino-1-oxa-3-aza-1,3-butadiene (1c): From the *N*-alkylidenebenzamidine **2b**[6] (0.46 g, 1.8 mmol) in diethyl ether (15mL) and *n*-butyllithium (1.6 M solution in *n*-hexane, 1.2 mL, 1.9 mmol), following method A. After stirring for 30 min at −78 °C, methyl chloroformate (**5a**) (0.16 mL, 0.20 g, 2.1 mmol) was added. Purification of the crude product was achieved by recrystallization from *n*-hexane. Colourless crystals, 0.45 g (1.4 mmol, 80%); m.p. 84−85 °C. − IR (KBr): ν = 3040 cm^{-1} (w, $CH_{arom.}$), 2940 (s, $CH_{aliph.}$), 2860 (m, O−CH_3), 1700 (vs, br, C=O), 1675 (vs, C=N), 1595 (vs, C=N), 1560 (s), 1475 (m), 1440 (s), 1425 (s), 1370 (m), 1350 (m), 1300 (s), 1270 (vs), 1210 (vs, br), 1165 (s), 1100 (m), 1080 (m), 1055 (m), 1005 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12, 1.17, 1.18 (s, 9 H, 3 × fenchylidene-CH_3), 1.35−2.04 (m, 7 H, fenchylidene-CH, -CH_2), 3.76 (s, 3 H, O−CH_3), 7.37−7.50 (m, 3 H, $CH_{arom.}$), 7.82−7.86 (m, 2 H, CH_{ortho}). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6 (CH_3), 23.4 (CH_3), 25.0 (CH_2), 26.1 (CH_3), 33.1 (CH_2), 43.8 (CH_2), 46.0 (CH), 46.5 ($C_{quat.}$), 52.7 (O−CH_3), 54.5 ($C_{quat.}$), 128.0, 128.3, 131.8 ($CH_{arom.}$), 134.5 (C_{ipso}), 162.8, 165.0 ($C_{quat.}$, C=N, C=O), 187.4 ($C_{quat.}$, fenchylidene-C=N). − MS (70 eV); *m*/*z* (%): 313 (5) [M^+ + 1], 312 (22) [M^+], 281 (6) [M^+ − OCH_3], 231 (22) [M^+ − C_6H_9], 162 (14) [PhCNCO_2Me$^+$], 118 (100) [PhCNCH_3^+], 103 (21) [PhCN^+], 81 (33) [$C_6H_9^+$], 77 (27) [$C_6H_5^+$], 69 (12) [$C_5H_9^+$]. − $C_{19}H_{24}N_2O_2$ (312.41): calcd. C 73.05, H 7.74, N 8.97; found C 72.94, H 7.74, N 8.95.

X-ray Diffraction Analysis of 1c ($C_{19}H_{24}N_2O_4$):[27] Colourless single crystals were analyzed with an automatic CAD4 diffractometer (Enraf−Nonius) using Cu-K_α radiation (λ = 1.54178 A) and a graphite monochromator at −50 °C. Crystal system: monoclinic, space group $P2_1$ (No. 4) with cell parameters *a* = 7.908(2) A, *b* = 15.863(4) A, *c* = 13.965(4) A, β = 96.78(2)°, *V* = 1739.6(8) A^3, $\rho_{calcd.}$ = 1.193 gcm^{-3}, *Z* = 4. Crystal size: 0.15 × 0.10 × 0.10 mm. 7355 reflections were collected, resulting in 7072 independent and 4328 observed [$I > 2\ \sigma(I)$] reflections. Absorption coefficient μ = 6.16 cm^{-1}, no absorption correction, 423 refined parameters. Non-hydrogen atoms were refined anisotropically. H atoms were geometrically positioned (riding model). $R(F)$ = 0.060, $wR(F^2)$ = 0.150; residual electron density: 0.16/−0.18 e A^{-3}. The asymmetric unit contains two, almost identical, independent molecules.[27]

(1*R*,4*S*)-5′-Methoxy-1,3,3-trimethyl-3′-(4-methylphenoxy)spiro[bicyclo[2.2.1]heptane-2,1′-(2′-thia-4′,6′-diazacyclohexa-3′,5′-diene)] (7a): From *N*-alkylideneisourea **2a** (0.63 g, 3.0 mmol), 2,4,6-collidine (0.56 mL, 0.51 g, 4.2 mmol) and *O*-(4-methylphenyl) chlorothioformate (**6**) (0.69 mL, 0.83 g, 4.5 mmol) in *n*-hexane (15 mL), following method B. After heating the reaction mixture under reflux for 3 h, the crude material was purified by column chromatography [petroleum ether/ethyl acetate, 50:1]; R_f(TLC) = 0.71 [petroleum ether/ethyl acetate, 5:1]. Light yellow oil, 0.58 g (1.6 mmol, 54%). − IR (CH_2Cl_2): ν = 2950 cm^{-1} (m, $CH_{aliph.}$), 2850 (w, O−CH_3), 1640 (s, C=N), 1560 (s), 1490 (s), 1450 (m, br), 1425 (m, br), 1285 (s), 1250 (s, br), 1205 (s), 1180 (vs), 1150 (m), 1065 (s), 1045 (s), 1010 (m), 950 (w). − ^{1}H NMR (600 MHz, $CDCl_3$, 258 K): δ = 0.92, 1.05, 1.07, 1.10, 1.14, 1.16, (s, 9 H, 3 × CH_3), 1.04−1.90 (m, 6 H, CH, CH_2), 2.25−2.26 (m, 1 H), 2.34, 2.36 (s, 3 H, Ph−CH_3), 3.72, 3.73 (s, 3 H, O−CH_3), 6.98−7.02 (m, 2 H, CH_{ortho}), 7.17−7.19 (m, 2 H, CH_{meta}). − ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.96, 1.08, 1.11 (s, 9 H, 3 × CH_3), 1.01−2.30 (m, 7 H, CH, CH_2), 2.32 (s, 3 H, Ph−CH_3), 3.72 (s, 3 H, O−CH_3), 6.98−7.01 (m, 2 H, $CH_{arom.}$), 7.12−7.16 (m, 2 H, $CH_{arom.}$). − ^{13}C NMR (150 MHz, $CDCl_3$, 258 K): δ = 18.2, 18.4 (CH_3), 20.9, 24.1 (Ph−CH_3), 25.4, 25.6 (CH_2), 26.9 (CH_3), 27.8 (CH_3), 29.7, 29.9 (CH_2), 39.9, 40.5 (CH_2), 48.2, 49.2 (CH), 48.6 ($C_{quat.}$), 53.7, 53.8 (O−CH_3), 55.7, 56.9 ($C_{quat.}$), 89.3 (C_{spiro}), 120.7, 121.1 (CH_{ortho}), 129.9, 130.0 (CH_{meta}), 135.7 (C_{ipso}), 149.0 (O−C_{ipso}), 156.4 ($C_{quat.}$, N−C=N), 175.4 ($C_{quat.}$, S−C=N). − ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 18.2 (CH_3), 20.9 (Ph−CH_3), 25.7 (CH_2), 30.1 (CH_2), 40.6 (CH_2), 48.9 (CH, $C_{quat.}$), 53.6 (O−CH_3), 121.3, 130.0 ($CH_{arom.}$), 135.7 (C_{ipso}), 149.5 (O−C_{ipso}), 156.9 ($C_{quat.}$, C=N), 176.0 ($C_{quat.}$, C=N). − MS (70 eV); *m*/*z* (%): 359 (15) [M^+ + 1], 358 (4) [M^+], 343 (9) [M^+ − CH_3], 289 (18), 277 (87) [M^+ − C_6H_9], 251 (100) [M^+ − OC_7H_7], 235 (90), 123 (28), 107 (20) [$C_7H_7O^+$], 91 (65) [$C_7H_7^+$], 65 (34), 41 (52), 39 (43). − $C_{20}H_{26}N_2O_2S$ (358.50): calcd. C 67.01, H 7.31, N 7.81; found C 66.37, H 7.76, N 7.44.

(1*R*,4*S*)-1,3,3-Trimethyl-3′-(4-methylphenoxy)-5′-phenylspiro[bicyclo[2.2.1]heptane-2,1′-(2′-thia-4′,6′-diazacyclohexa-3′,5′-diene)] (7b): From *N*-alkylidenebenzamidine **2b** (0.41 g, 1.6 mmol) in diethyl ether (15 mL) and *n*-butyllithium (1.6 M solution in *n*-hexane, 1.0 mL, 1.6 mmol), following method A. After stirring for 15 min at −78 °C, *O*-(4-methylphenyl) chlorothioformate (**6**) (0.28 mL, 0.34 g, 1.8 mmol) was added. Purification of the crude product was achieved by column chromatography (petroleum ether); R_f(TLC) = 0.49 (petroleum ether/ethyl acetate, 5:1). Light yellow oil, crystallizing after a longer time. 0.30 g (0.7 mmol, 46%); m.p. 125 °C. − IR ($CHCl_3$): ν = 3050 cm^{-1} (sh, $CH_{arom.}$), 3020 (w), 2930 (s, $CH_{aliph.}$), 2860 (m), 1615 (s, C=N), 1545 (s, C=N), 1495 (s), 1440 (m), 1360 (m), 1310 (s), 1290 (s), 1210 (s), 1190 (s), 1160 (s), 1115 (m), 1100 (m). − ^{1}H NMR (600 MHz, $CDCl_3$, 258 K): δ = 0.86, 1.06, 1.12, 1.13, 1.21 (s, 9 H, 3 × CH_3), 1.24−1.94 (m, 6 H, CH, CH_2), 2.33, 2.39 (s, 3 H, Ph−CH_3), 2.46−2.48 (m, 1 H), 7.09−7.12 (m, 2 H, CH_{ortho}), 7.21−7.23 (m, 2 H, CH_{meta}), 7.32−7.35 (m, 2 H, CH_{meta}), 7.37−7.40 (m, 1 H, CH_{para}), 8.01−8.03 (m, 2 H, CH_{ortho}). − ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.88, 1.07, 1.12, 1.21 (s, 9 H, 3 × CH_3), 1.23−1.96 (m, 6 H, CH, CH_2), 2.32, 2.37 (s, 3 H, Ph−CH_3), 2.48−2.50 (m, 1 H) 7.09−7.10 (m, 2 H, CH_{ortho}), 7.19−7.20 (m, 2 H, CH_{meta}), 7.29−7.31 (m, 2 H, CH_{meta}), 7.34−7.36 (m, 1 H, CH_{para}), 7.99−8.01 (m, 2 H, CH_{ortho}). − ^{13}C NMR (150 MHz, $CDCl_3$, 258 K): δ = 18.8, 19.1 (CH_3), 21.0, 24.2 (Ph−CH_3), 25.6 (CH_2), 27.2 (CH_3), 27.9 (CH_3), 29.8, 30.4 (CH_2), 40.6, 40.8 (CH_2), 48.3, 49.8 (CH), 49.2, 49.5 ($C_{quat.}$), 55.8, 56.8 ($C_{quat.}$), 88.8, 89.4 (C_{spiro}), 121.0, 121.4 (CH_{ortho}), 127.6, 127.7 (CH_{ortho}), 127.9 (CH_{meta}), 129.8, 129.9 (CH_{meta}), 130.2 (CH_{para}), 135.5 (C_{ipso}), 136.5, 136.9 (C_{ipso}), 149.4 (O−C_{ipso}), 155.5, 156.2 ($C_{quat.}$, N−C=N), 171.6, 171.9 ($C_{quat.}$, S−C=N). − ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ = 18.7, 19.1 (CH_3), 20.9, 24.2 (Ph−CH_3), 25.7 (CH_2), 27.1 (CH_3), 28.0 (CH_3), 29.8, 30.5 (CH_2), 40.9, 41.0 (CH_2), 48.7, 50.1 (CH), 49.5, 49.8 ($C_{quat.}$), 56.1, 57.1 ($C_{quat.}$), 89.1 (C_{spiro}), 121.0, 121.5 (CH_{ortho}), 127.8 (CH_{ortho}), 127.9 (CH_{meta}), 129.8, 129.9 (CH_{meta}), 130.2 (CH_{para}), 135.4 (C_{ipso}), 136.8 (C_{ipso}), 149.9 (O−C_{ipso}), 155.7, 156.5 ($C_{quat.}$, N−C=N), 171.5, 172.0 ($C_{quat.}$, S−C=N). − MS (70 eV): *m*/*z* (%) = 405 (5) [M^+ + 1], 404 (13) [M^+], 323 (83) [$M^+ - C_6H_9$], 297 (40) [$M^+ - C_7H_7O$], 281 (15) [$M^+ - C_9H_{15}$], 230 (11), 123 (35), 108 (49) [$C_7H_7OH^+$], 107 (36) [$C_7H_7O^+$], 91 (100) [$C_7H_7^+$], 81 (75) [$C_6H_9^+$], 69 (37). − $C_{25}H_{28}N_2OS$ (404.57): calcd. C 74.22, H 6.98, N 6.92; found C 73.30, H 7.24, N 6.69.

X-ray Diffraction Analysis of 7b ($C_{25}H_{28}N_2SO$): The light yellow single crystals were analyzed with an automatic CAD4 diffractometer (Enraf−Nonius) using Cu-K_α radiation (λ = 1.54178 A) and a graphite monochromator at −50 °C. Crystal system: orthorhombic, space group $P2_12_12_1$ (No. 19) with cell parameters *a* = 10.107(1) A, *b* = 10.374(1) A, *c* = 20.816(2) A, *V* = 2182.6(4) A^3, $\rho_{calcd.}$ = 1.231 gcm^{-3}, *Z* = 4. Crystal size: 0.50 × 0.40 × 0.20 mm. 2528 reflections were collected, resulting in 2527 independent and 2371 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 14.45 cm^{-1}, method of absorption correction: ψ-scan, 267 refined parameters. Non-hydrogen atoms were refined anisotropically. H atoms were geometrically positioned (riding model). $R(F)$ = 0.040, $wR(F^2)$ = 0.115; residual electron density: 0.31/−0.24 e A^{-3}.[27]

***O*-(4-Methylphenyl) *N*,*N*-Diethylthiocarbamate (8):** To an ice-cold solution of *O*-(4-methylphenyl) chlorothioformate (**6**) (0.39 mL, 0.47 g, 2.5 mmol) in dichloromethane (20 mL) was added triethylamine (0.35 mL, 0.26 g, 2.5 mmol). After stirring for 16 h, first at 0 °C and later at room temperature, the solvent was removed under reduced pressure. The residue was treated with a little water and extracted several times with *n*-hexane. The organic layer was dried with magnesium sulfate. The light yellow oil was purified by recrystallisation from *n*-hexane. Colourless crystals, 0.47 g (2.1 mmol, 84%); m.p. 65−66 °C. − IR (KBr): ν = 3020 (w, $CH_{arom.}$), 2950 (m, $CH_{aliph.}$), 2900 (m), 2840 (w), 1500 (vs, sh, Amid II), 1490 (vs, C=$C_{arom.}$), 1450 (sh), 1430 (sh), 1415 (s), 1390 (sh), 1370 (s), 1350 (m), 1340 (m), 1305 (s), 1275 (s), 1230 (s), 1205 (vs), 1190 (vs), 1155 (s), 1140 (m), 1120 (s), 1090 (m), 1080 (m), 1065 (s), 1000 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, ^3J = 7.15 Hz, 6 H, 2× N−CH_2CH_3), 2.35 (s, 3 H, Ph−CH_3), 3.67 (q, ^3J = 7.15 Hz, 2 H, N−CH_2CH$_3$), 3.90 (q, ^3J = 7.15 Hz, 2 H, N−CH_2CH$_3$), 6.92−6.96 (m, 2 H, $CH_{arom.}$), 7.15−7.19 (m, 2 H, $CH_{arom.}$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8 (N−CH_2CH_3), 13.5 (N−CH_2CH_3), 20.9 (Ph−CH_3), 44.1 (N−CH_2CH_3), 48.3 (N−CH_2CH_3), 122.3, 129.6 ($CH_{arom.}$), 135.3 (C_{ipso}), 151.7 (O−C_{ipso}), 187.1 ($C_{quat.}$, C=S). − MS (70 eV); *m*/*z* (%): 224 (19) [M^+ + 1], 223 (55) [M^+], 194 (6) [$M^+ - C_2H_5$], 123 (55), 116 (62) [$M^+ - OC_7H_7$], 107 (56) [$C_7H_7O^+$], 100 (79) [$(C_2H_5)_2NCO^+$], 90 (50), 88 (76), 86 (64), 73 (52), 72 (100) [$(C_2H_5)_2N^+$]. − $C_{12}H_{17}NOS$ (223.33): calcd. C 64.54, H 7.67, N 6.27; found C 64.60, H 7.71, N 6.30.

(Diethylamino)(ethylthio)(4-methylphenoxy)methyl Tetrafluoroborate (9): To a solution of triethyloxonium tetrafluoroborate (0.18 g, 0.95 mmol) in dichloromethane (10 mL) was added thiocarbamate **8** (0.17 g, 0.76 mmol). After stirring of the solution for 40 h at room temperature, the salt **9** was slowly precipitated by careful addition of an upper layer of diethyl ether. The solid product was filterd off under argon and dried under reduced pressure. Colourless salt, 0.25 g (0.74 mmol, 97%). − IR (CH_2Cl_2, NaCl): ν = 3040 cm^{-1} (w, $CH_{arom.}$), 2950 (m), 2910 (w), 2850 (m, $CH_{aliph.}$), 1595 (m), 1575 (s), 1550 (sh), 1490 (s), 1310 (s), 1290 (sh), 1230 (m), 1190 (m), 1145 (m), 1100 (vs), 1045 (vs, br). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.39 Hz, 3 H, S−CH_2CH_3), 1.42 (t, ^3J = 7.39 Hz, 3 H, N−CH_2CH_3), 1.51 (t, ^3J = 7.39 Hz, 3 H, N−CH_2CH_3), 2.37 (s, 3 H, Ph−CH_3), 2.87 (q, ^3J = 7.39 Hz, 2 H, S−CH_2CH$_3$), 3.95 (q, ^3J = 7.39 Hz, 2 H, N−CH_2CH$_3$), 4.06 (q, ^3J = 7.39 Hz, 2 H, N−CH_2CH$_3$), 7.18−7.23 (m, 2 H, $CH_{arom.}$), 7.26−7.30 (m, 2 H, $CH_{arom.}$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2, 13.1, 13.7 (3 CH_2CH_3), 20.8 (Ph−CH_3), 28.5 (S−CH_2CH_3), 49.3 (N−CH_2CH_3), 50.5 (N−CH_2CH_3), 117.7 (CH_{meta}), 131.4 (CH_{ortho}), 137.4 (C_{ipso}), 151.5 (O−C_{ipso}), 175.71($C_{quat.}$). − TOF-MS; *m*/*z*: 252 (100) [$C_{14}H_{22}NOS^+$]. − $C_{14}H_{22}NOSBF_4$ (339.20): calcd. C 49.57, H 6.54, N 4.13; found C 49.58, H 6.69, N 4.08.

6-Diethylamino-2,4-dimethoxy-6-ethylthio-1-oxa-3,5-diaza-1,3,5-hexatriene (1d): A solution of triethyloxonium tetrafluoroborate (0.22 g, 1.2 mmol) in dichloromethane (10 mL) was treated with thiocarbamate **8** (0.26 g, 1.2 mmol). After stirring for 16 h at room temperature, 4-amino-2,4-dimethoxy-1-oxa-3-aza-1,3-butadiene (**10**)[19] (0.16 g, 1.2 mmol) and triethylamine (0.19 mL, 0.12 g, 1.2 mmol) were added. Workup followed after 40 h, by treatment of the reaction mixture with a satd. solution of sodium bicarbonate. The aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with magnesium sulfate and solvent was removed under reduced pressure. The crude material was purified by column chromatography (petroleum ether/ethyl acetate, 2:3); R_f (TLC) = 0.1 (petroleum ether/ethyl acetate, 5:1). Yellow oil, 0.09 g (0.3 mmol, 28%). − IR (NaCl): ν = 2970 cm^{-1} (sh), 2950 (m), 2910 (m), 2850 (w, $CH_{aliph.}$), 1730 (s, C=O), 1700 (s, C=N), 1655 (sh), 1645 (sh), 1630 (s, C=N), 1540 (vs), 1495 (sh), 1435 (s, br), 1370 (m), 1350 (m), 1300 (vs), 1245 (s), 1210 (sh), 1195 (m), 1185 (m), 1140 (s), 1095 (s), 1070 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.2 Hz, 6 H, 2× N−CH_2CH_3), 1.28 (t, ^3J = 7.2 Hz, 3 H, S−CH_2CH_3), 2.94 (q,

^3J = 7.2 Hz, 2 H, S−CH_2CH$_3$), 3.58 (q, ^3J = 7.2 Hz, 4 H, 2× N−CH_2CH$_3$), 3.67 (s, 3 H, O−CH$_3$), 3.79 (s, 3 H, O−CH$_3$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.8 (N−CH$_2$*C*H$_3$), 13.9 (S−CH$_2$*C*H$_3$), 26.8 (S−*C*H$_2$CH$_3$), 45.1 (N−*C*H$_2$CH$_3$), 52.5 (O−CH$_3$), 54.9 (O−CH$_3$), 160.7, 161.9, 165.6 (C$_{quat.}$, 2 × C=N, C=O). − MS (70 eV); *m*/*z* (%): 275 (5) [M$^+$], 246 (100) [M$^+$ − C$_2$H$_5$], 244 (48) [M$^+$ − OCH$_3$], 214 (16) [M$^+$ − SC$_2$H$_5$], 200 (26) [M$^+$ − C$_3$H$_7$S], 72 (70) [C$_4$H$_{10}$N$^+$], 58 (15) [C$_3$H$_7$N$^+$], 57 (33). − C$_{11}$H$_{21}$N$_3$O$_3$S (275.37): calcd. C 47.98, H 7.69, N 15.26; found C 48.34, H 7.86, N 14.65. − MS-EI calcd. 275.13037, 275.12813.

1-[Ethyl(methoxycarbonyl)amino]-1-methoxy-2,2-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)-2-azaallenium Hexachloroantimonate (11): To a solution of triethyloxonium hexachloroantimonate (0.57 g, 1.3 mmol) in dichloromethane (10 mL) was added compound **1a** (0.35 g, 1.3 mmol). After stirring of the solution for 20 h at room temperature, the salt **11** was slowly precipitated by careful addition of an upper layer of diethyl ether, first at −78 °C and later at −30 °C. The solid product was filtered off under argon and dried under reduced pressure. Light brown solid, 0.78 g (1.2 mmol, 95%). Single crystals for X-ray analysis could be obtained by dissolving the salt in chloroform and allowing slow evaporation of the solvent. − IR (CHCl$_3$): ν = 2980 cm^{-1} (sh), 2950 (s), 2910 (m, CH$_{aliph.}$), 2850 (m, O−CH$_3$), 1775 (s, C=O), 1725 (sh), 1700 (s, C−N−C), 1575 (m,), 1530 (s, br), 1500 (sh), 1480 (m), 1435 (s), 1375 (s), 1240 (s), 1195 (m), 1150 (s), 1100 (m), 1005 (m), 895 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.16, 1.17, 1.23, 1.28, 1.29, 1.36 (s, 9 H, 3 × fenchylidene-CH$_3$), 1.37 (t, ^3J = 7.15 Hz, 3 H, N-CH$_2$CH_3), 1.55−2.18 (m, 6 H, fenchylidene-CH/CH$_2$), 2.29 (s, 1 H, fenchylidene), 3.97, 3.99 (s, 3 H, O−CH$_3$), 4.11 (q, ^3J = 7.15 Hz, 2 H, N−CH_2CH$_3$), 4.15, 4.16 (s, 3 H, O−CH$_3$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.7 (N−CH$_2$*C*H$_3$), 15.1, 15.4 (CH$_3$), 22.3, 23.5 (CH$_3$), 24.2, 24.4 (CH$_2$), 25.0, 25.9 (CH$_3$), 30.7, 33.4 (CH$_2$), 42.6, 43.8 (CH$_2$), 44.0 (N−*C*H$_2$CH$_3$), 45.7 (CH), 48.3, 48.4 (C$_{quat.}$), 56.0 (O−CH$_3$), 57.4, 57.9 (C$_{quat.}$), 60.56 (O−CH$_3$), 150.2, 150.3, 162.1, 162.2 (C$_{quat.}$, C=N, C=O), 203.5, 205.7 (C$_{quat.}$, fenchylidene-C=N). − TOF-MS; m/*z*: 295 [C$_{16}$H$_{27}$N$_2$O$_3^+$]. − C$_{16}$H$_{27}$N$_2$O$_3$Cl$_6$Sb (629.87): calcd. C 30.51, H 4.32, N 4.45; found C 29.33, H 4.25, N 4.39.

X-ray Diffraction Analysis of 11 (C$_{16}$H$_{27}$Cl$_6$N$_2$O$_3$Sb): The colourless single crystals were analyzed with an automatic CAD4 diffractometer (Enraf−Nonius) using Mo-K_α radiation (λ = 0.71073 A) and a graphite monochromator at 20 °C. Crystal system: monoclinic, space group $P2_1/c$ (No. 14) with cell parameters a = 14.055(1) A, b = 12.581(1) A, c = 15.478(1) A, β = 111.43(1)°, V = 2547.7(3) A^3, ρ$_{calcd.}$ = 1.642 gcm^{-3}, Z = 4. Crystal size: 0.40 × 0.30 × 0.25 mm. 5384 reflections were collected, resulting in 5172 independent and 3933 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 17.31 cm^{-1}, method of absorption correction: ψ-scan, 344 refined parameters. Non-hydrogen atoms were refined anisotropically. The chiral fenchyl group was refined with split positions, refining of occupancy factors gave 0.54(2): 0.46(2). These carbon atoms were also refined anisotropically by using SADI restraints. H atoms were geometrically positioned (riding model). $R(F)$ = 0.044, $wR(F^2)$ = 0.108; residual electron density: 0.63/−0.60 e A^{-3}.[27]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-141427 (**1b**), -141426 (**1c**), -141428 (**7b**) and -141429 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme" and Sonderforschungsbereich 424) and by the Fonds der Chemischen Industrie (Frankfurt) is gratefully acknowledged.

[1] See for example: B. Champagne, D. Jaquemin, J.-M. Andre, B. Kirtman, *J. Phys. Chem. A* **1997**, *101*, 3158−3165; M. Springborg, *Synth. Met.* **1997**, *85*, 1037−1040; J. Del Nero, B. Laks, *J. Molec. Struct. (Theochem)* **1997**, *394*, 209−214; P. Otto, F. L. Gu, J. Ladik, *J. Chem. Phys.* **1999**, *110*, 2717−2726.
[2] J. K. Eberhardt, R. Fröhlich, E.-U. Würthwein, *Eur. J. Inorg. Chem.* **2000**, 1739−1743, and earlier papers in this series.
[3] M. Buhmann, M. H. Möller, U. Rodewald, E.-U. Würthwein, *Angew. Chem.* **1994**, *106*, 2386−2389; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2337−2339.
[4] M. Nagano, T. Matsui, J. Tobitsuka, K. Oyamada, *Chem. Pharm. Bull.* **1973**, *21*, 74−86.
[5] F. Russo, M. Santagati, A. Santagati, *Farmaco, Ed. Sci.* **1978**, *33*, 26−39; F. Russo, M. Santagati, A. Santagati, G. Blandino, *Farmaco, Ed. Sci.* **1983**, *38*, 232−241.
[6] F. Bondavalli, O. Bruno, P. Schenone, W. Filippelli, S. Russo, E. Marmo, *Farmaco, Ed. Sci.* **1987**, *42*, 335−340; F. Bondavalli, O. Bruno, E. Mariani, P. Schenone, M. Lisa, V. Susanna, S. Maione, E. Marmo, *Farmaco, Ed. Sci.* **1987**, *42*, 941−946.
[7] I. Ibnusaud, E. J. P. Malar, N. Sundaram, *Tetrahedron Lett.* **1990**, *31*, 7357−7358.
[8] A. Guzman, M. Romereo, F. X. Talamas, R. Villena, R. Greenhouse, J. M. Muchowski, *J. Org. Chem.* **1996**, *61*, 2470−2483.
[9] L. Citerio, E. Rivera, M. L. Saccarello, R. Stradi, B. Gioia, *J. Heterocycl. Chem.* **1980**, *17*, 97−101; E. Rossi, R. Stradi, *Gazz. Chim. Ital.* **1981**, *111*, 299−307.
[10] N. N. Gertsyuk, V. I. Gorbatenko, L. I. Samarai, *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 1233−1236.
[11] O. Maier, Diplomarbeit, University of Münster, **1996**.
[12] N. C. Aust, R. Fröhlich, J. Hecht, E.-U. Würthwein, *Liebigs Ann./Recueil* **1997**, 1589−1602.
[13] N. Schulte, R. Fröhlich, J. Hecht, E.-U. Würthwein, *Liebigs Ann.* **1996**, 371−380.
[14] Z. Bende, I. Bitter, Z. Csürös, *Acta Chim. Acad. Sci. Hung.* **1977**, *93*, 85−93.
[15] R. Brunnenberg, J. C. Jochims, H. Härle, *Chem. Ber.* **1982**, *115*, 3587−3596.
[16] F. Bondavalli, P. Schenone, A. Ranise, *Synthesis* **1979**, 830−832.
[17] M. Buhmann, M. H. Möller, E.-U. Würthwein, *Chem. Ber.* **1993**, *126*, 957−967.
[18] D. Bond, P. v. R. Schleyer, *J. Org. Chem.* **1990**, *55*, 1003−1013; K. B. Wiberg, M. W. Wong, *J. Am. Chem. Soc.* **1993**, *115*, 1078−1084.
[19] G. Hamprecht, R.-D. Acker, E. Hädicke, *Liebigs Ann. Chem.* **1985**, 2363−2370.
[20] M. Krestel, R. Kupfer, R. Allmann, E.-U. Würthwein, *Chem. Ber.* **1987**, *120*, 1271−1279.
[21] R. Kupfer, E.-U. Würthwein, M. Nagel, R. Allmann, *Chem. Ber.* **1985**, *118*, 643−652.
[22] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.
[23] J. J. P. Stewart, *J. Comp. Chem.* **1989**, *10*, 209−264.
[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98, Revision A.6*, Gaussian, Inc., Pittsburgh PA, **1998**.
[25] Details of the quantum mechanical calculations (MOPAC93

and GAUSSIAN 98 archive entries) are available from E.-U. W. upon request.

[26] T. Durst, in *Comprehensive Carbanion Chemistry*, Part B (Ed.: E. Buncel, T. Durst), Elsevier Amsterdam, **1984**, p. 239f.

[27] Programs used: Data collection: Collect: Nonius B. V., **1994**. − Data reduction: Denzo-SMN: Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326. − Absorption correction: SORTAN: R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; *J. Appl. Crystallogr.* **1997**, *30*, 421−426. − Structure solution: SHELXS-86 and SHELXS-97: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473. − Structure refinement: SHELXL-97: G. M. Sheldrick, Universität Göttingen, **1997**. − Graphics: SCHAKAL: E. Keller, Universität Freiburg, **1997**.

Received June 2, 2000
[O00282]