Transannular Interactions in Difunctional Medium Rings, 8[≠]

Spectroscopic and Theoretical Investigations of Monocyclic Dioximes and Dimethoximes with Six-, Eight-, and Ten-Membered Rings

Andrea Strenge[a] **and Paul Rademacher,***[a]

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

Keywords: Photoelectron spectroscopy / Conformation analysis / Ab initio calculations / Through-space interactions / NMR spectroscopy

The dioximes **4–6** and the dimethoximes **7–9**, which contain the functional groups in opposite positions of a six-, eight-, or ten-membered ring, were synthesized. Their conformational properties and transannular interactions were investigated by spectroscopic (PE, ^{13}C NMR) and theoretical (MMX, AM1, ab initio HF, and B3LYP) methods. While the cyclooctane derivatives **5** and **8** have conformations favourable for through-space interactions of the $\pi(C=N)$ orbitals, in the other compounds no such interactions can be ascertained. Through-space orbital interactions in the molecules with an eight-membered ring lead to a splitting of the $\pi(C=N)$ MOs of 0.4 eV.

1. Introduction

It has convincingly been shown that difunctional medium rings can serve as models for bimolecular reactions.[1] The *intra*molecular transannular interactions of the functional groups are comparable to the *inter*molecular interactions at distances close to the transition state of the analogous monofunctional compounds in a reaction. Spectroscopic methods like IR, NMR, and photoelectron (PE) spectroscopy are well suited to analyse the homoconjugative interactions. For this purpose, the spectroscopic parameters of the difunctional compound are compared with those of the two monofunctional compounds of the same ring size or skeleton structure. PE spectroscopy in combination with quantum chemical calculations allows for the direct determination of through-space orbital interactions (OITS) between functional groups. We have so far investigated amino ketones[2–5] and aminoalkenes[2] as models for nucleophilic additions, and boraalkenes[6] and aminoboranes[7] as models for electrophilic additions. On the other hand, also interactions of two functional groups of the same type in diketones,[8–11] dialkenes[8,12,13] and diamines[14–18] have been studied with various techniques by several authors. We now turn to functional groups with C=N double bonds, and in this and the succeeding paper[19] we report our results for dioximes and dimethoximes. The bimolecular analogue of this intramolecular interaction would be the thermally forbidden [2+2] cycloaddition of two oxime molecules. Oximes are well-known compounds of synthetic use that can undergo a number of unique reactions like the Beckmann rearrangement and the Barton reaction.[20–23] Many compounds with C=N double bonds are of biological and pharmacological interest, and *N*-oxidative transformations of C=N groups are important as means of toxification and detoxification in drug metabolism.[24]

Transannular interactions and reactions are characteristic features of medium rings because puckering can lead to conformers in which opposite ring atoms that are constitutionally far apart approach each other to a rather short distance.[25–28] Most frequently, transannular interactions are found in saturated eight-membered rings[1] because the prevailing CC and BC conformations (see below) presents optimal conditions for the "contact" of substituents in the positions 1 and 5. Often, although usually to a lesser extent, such interactions are also found in ten-membered rings with functional groups in the 1,6-positions. On the other hand, the corresponding twelve-membered ring derivatives populate no conformations that would allow for transannular interactions.[1] In studying the influence of the ring size on such effects, it is appropriate to include six-membered rings for comparison.[1] Transannular interactions in medium-sized heterocycles can also be an important property in drug design.[29] In this paper, we report on our investigations on monocyclic dioximes and dimethoximes with six-, eight-, and ten-membered rings, and in the next communication[19] the results for bicyclic dioximes and dimethoximes are described in which the two functional groups are in 1,5-positions of eight-membered rings.

2. Syntheses

Starting materials for the synthesis of the dioximes **4−6** and the dimethoximes **7−9** were the diketones **1−3**. Cyclo-

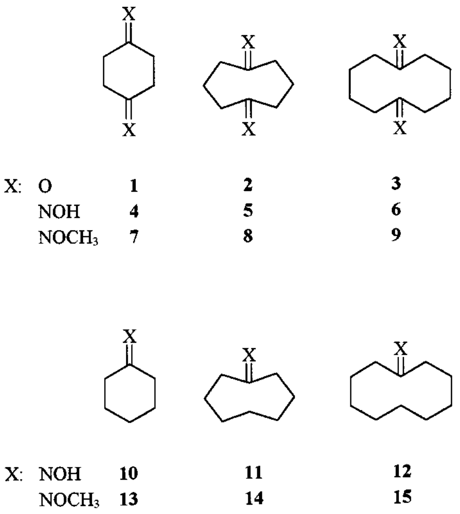
---

[≠] Part 7: Ref.[1]

[a] Institut für Organische Chemie, Universität GH Essen,
D-45117 Essen, Germany
Fax: (internat.) + 49(0)201/183-4252,
E-mail: radem@oc1.orgchem.uni-essen.de

1434−193X/99/0707−1601 $ 17.50+.50/0

octane-1,5-dione (**2**) was obtained as described in the literature[30][31] starting from cycloocta-1,5-diene. Cyclodecane-1,6-dione (**3**) was prepared according to the method of House et al.[32] The diketones were treated with hydroxylamine hydrochloride or with *O*-methylhydroxylamine hydrochloride to generate the dioximes **4−6** or the dimethoximes **7−9**, respectively. The solid dioximes were recrystallized from ethanol, and it was possible to enrich or isolate ***4E***, ***5Z***, ***6E*** as single configurational isomers. Compounds **7−9** were purified by distillation in vacuo, and in all cases mixtures of (*E*) and (*Z*) isomers were obtained. The geometrical isomers could not be separated by column chromatography.[19] Prevailing isomers are ***7E***, ***8E*** and ***9E***. For the eight-membered ring compounds (**5**, **8**), (*E*) and (*Z*) isomers are easily identified by ^{13}C-NMR spectroscopy. The (*Z*) isomers are of lower symmetry than the (*E*) isomers and therefore the former have more ^{13}C signals than the latter. For the other compounds (**4**, **6**, **7**, **9**) a similar identification of configurational isomers is not possible since both have the same number of signals in the ^{13}C-NMR spectra. In these cases decisions are based on relative thermodynamic stablities calculated by MMX and AM1, and on spectral analogies. The dioximes **4**,[33][34] **5**,[35] and **6**[36] were synthesized earlier. Both (*E*)- and (*Z*)-cyclohexane-1,4-dione bis(*O*-methyloxime) (***7E***, ***7Z***) were prepared by Shatzmiller and Lidor[37] on a different way. To our knockledge, the dimethoximes **8** and **9** have not been described previously in the literature.



Scheme 1. Formulas of compounds **1−15**

The monoximes **10−12** and the monomethoximes **13−15** were synthesized in an analogous manner from the corresponding cyclic ketones. The syntheses of **11−13** have been reported in the literature.[38][39]

3. Results

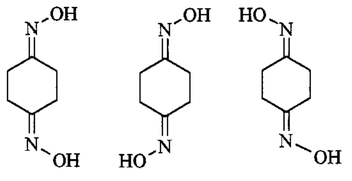
3.1 Structures

The molecular structures of some simple oximes like formaldoxime,[40] (*E*)- and (*Z*)-acetaldoxime,[41][42] (*E*)- and (*Z*)-propionaldoxime,[43−46] acetone oxime,[47] (*E*)- and (*Z*)-chloroacetaldoxime,[48−50] and (*Z*)-acrylaldehyde oxime[51] have been determined by gas-phase electron diffraction or microwave spectroscopy in combination with ab initio calculations. The conformational properties of medium rings have been investigated by experimental and theoretical methods.[25−28,52] For all molecules studied here, several conformations have to be considered. For a first orientation the corresponding diketones were used. Most simple are the two six-membered ring compounds, cyclohexane-1,4-dione dioxime (**4**) and cyclohexane-1,4-dione bis(*O*-methyloxime) (**7**), for which only two low-energy conformations, chair (C) and twist-boat (TB), are possible. For cyclohexane-1,4-dione (**1**) nonuniform results were obtained depending on method and state of aggregation: In the crystalline state, the molecules adopt an unsymmetrical TB conformation with a dihedral angle of $\varphi = 154°$ between the two carbonyl groups,[53] whereas in solution a TB form with D_2 symmetry ($\varphi = 180°$) is present.[54] Based on dipole moment measurements, the C conformation was deduced by Dowd et al.[55] for the gas phase. Molecular mechanics studies indicated that the energy of the C form is only 0.54 kJ mol^{-1} above that of the TB form,[52][56] and all experimental data can be interpreted in terms of a flexible, rapidly pseudorotating D_2 TB form.

The conformational complexity grows rapidly with ring size, and for the saturated eight-membered ring already ten conformers have to be considered which belong either to the boat-chair, the chair-chair, or to the boat-boat family.[52,57,58] In addition, for the functional groups different positions on the ring atoms have to be distinguished. Cyclooctane and most of its simple derivatives populate primarily the boat-chair (BC) and to a lesser extent the crown conformation (CC = chair-chair). For cyclooctane-1,5-dione (**2**) mainly two conformers (CC-3,7 and BC-3,7) seem to be favoured.[54]

The number of conformations possible for a saturated ten-membered ring is so large that no systematic investigation of all of them has been reported.[52] The most stable conformer is the boat-chair-boat (BCB) form that is a distorted part of the diamond lattice.[59−62] For cyclodecane-1,6-dione (**3**), the expected BCB-3,8 conformation was found by X-ray analysis and by molecular mechanics investigations.[60] On the other hand, NMR- and IR-spectroscopic as well as dipole measurements indicated that in solution there is a mixture of several conformers in which the crown-like, highly symmetrical twist-chair-chair-chair (TCCC) form plays the main part.[54][63]

The stereochemical problem of the dioximes **4−6** and the dimethoximes **7−9** becomes even more complicated since these compounds can adopt (*E*) and (*Z*) configurations.[20][21] For each compound, there are three configurational isomers, one (*Z*) and two (*E*) forms. These are shown, as a representative example, for compound **4** in Scheme 2. The latter two isomers are enantiomers and as such will not differ in their electronic structures and their transannular interactions. The (*Z*) and (*E*) isomers are stable and can − at least in principle − be separated.



4Z **4E** **4E'**

Scheme 2. Configurational isomers of dioxime **4**

We have investigated the structures of compounds **4–9** by various theoretical methods. The molecular mechanics method MMX[64] was used to establish the main conformational and configurational features. For the more stable conformers, AM1[65] calculations were performed, and selected conformers were also investigated by ab initio calculations (Hartree–Fock[66] [HF], B3LYP[67–70]) with different basis sets. The results[71] are far too manifold in order to give a complete account in this paper where only those which seem to be most important are presented. In particular, for the difunctional compounds this concerns the (*E*)/(*Z*) isomers of which only the prevailing is considered.

As representative examples, the conformers of the dimethoximes **7–9** and their strain energies as calculated by the MMX method are displayed in Figures 1–3. In Table 1, the results of different methods for the two most important conformers of the dioximes **4–6** and the dimethoximes **7–9** are summarized. In each case, the enthalpies of formation or the total energies of the conformers are given together with the transannular N=C···C=N distance that is the most relevant parameter with respect to transannular interaction.

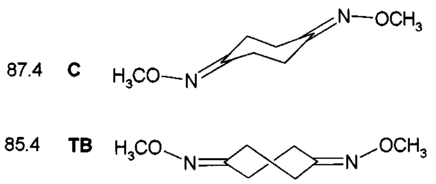


Figure 1. Conformers of dimethoxime **7** with MMX strain energies [kJ mol^{-1}]

With regard to the relative stabilities of the conformers, only the results for compounds **6** and **9** are uniform so that a single prevailing conformer can be assumed. For the other compounds, at least one method favours the other of the two conformers. If, however, we give less confidence to the AM1 results than to those of the other methods, then also for **4** and **7** the same conformers become probable. Finally, for **5** and **8** the HF and B3LYP results are at variance with those of MMX and AM1 so that no decision is possible. For the eight-membered ring compounds **5** and **8** transannular distances *d* of less than 300 pm were computed (MMX) for both conformers indicating that sizeable OITS is possible. On the other hand, rather large *d* values were found for the most stable conformers of **6** and **9** that can be expected to be too large for detectable transannular interactions of the functional groups.[1]

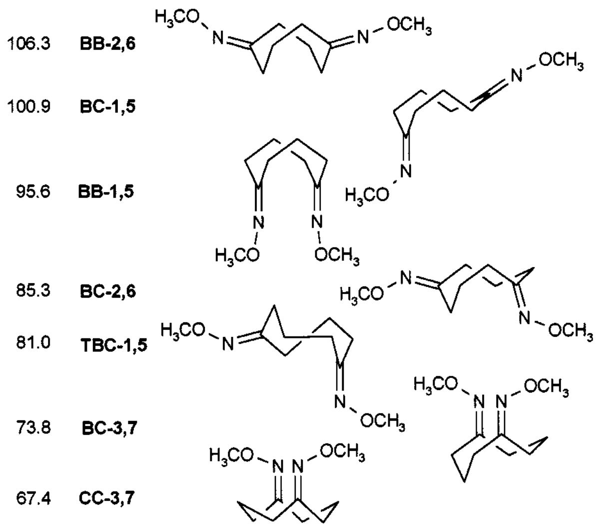


Figure 2. Conformers of dimethoxime **8** with MMX strain energies [kJ mol^{-1}]

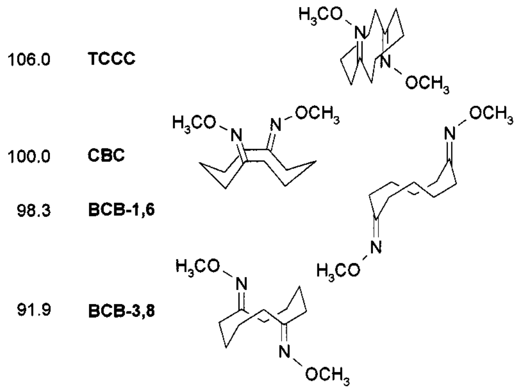


Figure 3. Conformers of dimethoxime **9** with MMX strain energies [kJ mol^{-1}]

3.2 Electronic Structures

The electronic structure of the simplest oxime, formaldoxime,[72–74] has been investigated meticulously by quantum chemical methods. Such calculations have also been performed for some other oximes and dioximes in connection with the interpretation of their PE spectra (see section 3.3).

The electronic structure of the oxime functional group is characterized by the C=N double bond and three electron lone-pairs, one on the N atom and two on the O atom. In a planar arrangement of the >C=N–OH unit, the $n_\pi(O)$ orbital will interact with the $\pi(C=N)$ orbital leading to two π-type MOs that are spread over these three atoms. On the other hand, the interaction of the $n_\sigma(O)$ with the n(N) orbital will lead to two σ-type MOs. For simplicity reasons, these four oxime MOs will be termed according to their origin and their prevailing characteristics as $\pi(C=N)$, n(N), $n_\pi(O)$, and $n_\sigma(O)$. The given sequence corresponds to their relative energy. Dioximes and dimethoximes have two sets of such MOs, that can pairwise be described as symmetric and antisymmetric combinations of the basic MOs of the

Table 1. Enthalpies of formation ΔH_f [kJ mol^{-1}], total energies E [au] and transannular N=C···C=N distances d [pm] of cyclohexane-1,4-dione dioxime (**4**), cyclohexane-1,4-dione bis(*O*-methyloxime) (**7**), cyclooctane-1,5-dione dioxime (**5**), cyclooctane-1,5-dione bis(*O*-methyloxime) (**8**), cyclodecane-1,6-dione dioxime (**6**), cyclodecane-1,6-dione bis(*O*-methyloxime) (**9**)

		MMX		AM1		HF/6-31+G*		B3LYP/6-31+G*	
		ΔH_f	*d*	ΔH_f	*d*	*E*	*d*	*E*	*d*
4*E*	C	56.1	285.8	−81.8	287.9	−491.5428464	287.3	−494.520947	287.8
	TB	54.4	293.8	−81.3	294.6	−491.5432791	288.0	−494.5212511	288.3
	Δ[a]	−1.7		0.5		−1.14		−0.80	
7*E*	C	57.9	286.0	−11.1	287.8	−569.599602	287.5	−573.136864	288.1
	TB	55.9	292.6	−10.7	295.2	−569.600107	288.1	−573.137237	288.5
	Δ[a]	−2.0		0.4		−1.32		−0.98	
5*Z*	CC-3,7	−7.2	299.8	−117.1	324.3	−569.601883	321.2	−573.141527	322.2
	BC-3,7	−2.8	291.1	−112.7	291.0	−569.604931	304.4	−573.144309	304.5
	Δ[a]	4.4		4.4		−8.00		−7.30	
8*E*	CC-3,7	−10.3	293.5	−46.2	332.7	−647.659387	328.2	−651.7580931	328.4
	BC-3,7	−3.8	287.1	−42.1	289.6	−647.660056	311.4	−651.758834	312.8
	Δ[a]	6.5		4.1		−1.75		−1.94	
6*E*	BCB-3,8	−32.9	347.5	−150.3	357.6	−647.663705	355.9	−651.764146	355.6
	BCB-1,6	−26.1	424.4	−146.9	423.1	−647.661840	434.7	−651.763156	435.5
	Δ[a]	6.8		3.4		4.89		2.60	
9*E*	BCB-3,8	−33.9	347.0	−78.8	358.5	−725.720185	356.9	−730.379571	357.2
	BCB-1,6	−27.2	424.1	−75.8	424.0	−725.718419	434.8	−730.378853	436.0
	Δ[a]	6.7		3.0		4.63		1.88	

[a] kJ mol^{-1}.

monofunctional molecules, and their energy separation depends on the interaction of the functional groups.

The electronic structures of dioximes **4−6** and dimethoximes **7−9** as well as that of the corresponding monoximes **10−12** and the monomethoximes **13−15** have been investigated by quantum chemical methods. The results for the most important conformer of the molecules are summarized in Table 2. For the difunctional compounds only one (*E*)/(*Z*) isomer is considered. We will restrict the data to the two highest occupied oxime MOs, π(C=N) and n(N), that are of greatest relevance for the interpretation of the PE spectra (see below). In the difunctional compounds, the MOs are named π^-(C=N), π^+(C=N), n$^-$(N), and n$^+$(N). These MOs are plotted in Figure 4 for compound **8*E***.

The data in Table 2 indicate that the orbital sequence for the cyclohexane derivatives, dioxime **4** and dimethoxime **7**, is π^+(C=N) > π^-(C=N) > n$^+$(N) > n$^-$(N). The two π(C=N) and the two n(N) orbitals are separated by 0.1−0.5 eV (depending on the method of calculation) which can be attributed to through-bond interactions. While − according to the AM1 results − the higher π(C=N) and the higher n(N) orbital have nearly the same energy as that calculated for the monofunctional compounds **10** and **13**, the lower π(C=N) and n(N) orbitals are stabilized by the above given energy values. The centres of the π(C=N) and the n(N) MOs of the difunctional compounds are thus stabilized relative to the monofunctional molecules which can be ascribed to their mutual inductive interaction.

In the difunctional compounds with an eight-membered ring (**5**, **8**), the natural sequence of the π orbitals is found, i.e., π^-(C=N) > π^+(C=N). Compound **5** shows the inverted sequence for the n orbitals, n$^+$(N) > n$^-$(N), because of the (*Z*) configuration, while in **8** also these orbitals appear in the natural sequence in accord with the (*E*) configuration. The π(C=N) as well as the n(N) orbitals are split approximately symmetrically relative to the values calculated for the monofunctional compounds **11** and **14**. These findings indicate that orbital interactions in the difunctional

Table 2. Negative orbital energies [eV] of the most important conformers of dioximes **4−6**, dimethoximes **7−9**, monoximes **10−12** and monomethoximes **13−15** (AM1, HF/6-31+G* and B3LYP/6-31+G* results)

		π^+(C=N)			π^-(C=N)			n$^+$(N)			n$^-$(N)		
		AM1	HF	B3LYP	AM1	HF	B3LYP	AM1	HF	B3LYP	AM1	HF	B3LYP
4*E*	C	9.90	10.23	6.93	10.31	10.74	7.29	10.73	11.42	7.63	11.13	11.69	7.72
7*E*	C	9.66	9.92	6.58	10.02	10.36	6.88	10.57	11.24	7.45	10.89	11.48	7.53
10	C	9.89[a]						10.66[b]					
13	C	9.67[a]						10.54[b]					
5*Z*	BC-3,7	10.08	10.57	7.12	9.62	9.81	6.60	10.53	11.16	7.54	10.87	11.53	7.39
8*E*	BC-3,7	9.83	10.17	6.70	9.41	9.62	6.36	10.61	11.32	7.38	10.43	11.02	7.24
11	BC-3	9.76[a]						10.62[b]					
14	BC-3	9.57[a]						10.51[b]					
6*E*	BCB-3,8	9.94	10.33	6.95	9.71	10.06	6.75	10.58	11.10	7.33	10.76	11.33	7.48
9*E*	BCB-3,8	9.70	10.02	6.87	9.51	9.79	6.52	10.44	10.95	7.26	10.61	11.16	7.28
12	BCB-3	9.75[a]						10.61[b]					
15	BCB-3	9.57[a]						10.48[b]					

[a] π(C=N). − [b] n(N).

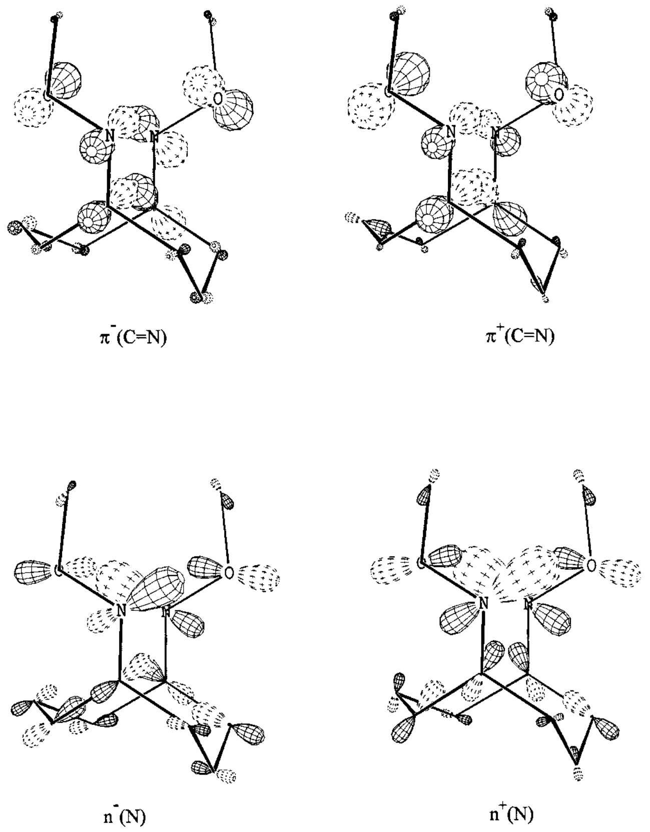


Figure 4. π(C=N) and n(N) MOs of dimethoxime **8*E*** (AM1 results); hydrogen atoms are omitted for clarity reasons

compounds occur predominantely by the through-space mechanism.

In the cyclodecane derivatives **6** and **9**, the π(C=N) orbitals again have the natural sequence, but for the n(N) orbitals the inverted order is found with considerably smaller splittings than in the other ring systems. Comparison with the results for the monofunctional compounds **12** and **15** (AM1 results only) indicates again that the splitting is unsymmetrical. These results can be explained by weak through-bond interactions of the orbitals.

3.3 Photoelectron Spectra

The PE spectra of some oximes and methoximes have already been studied.[75–83] In particular, the spectrum of formaldoxime was analysed by several authors.[75,77,78] Stunnenberg et al. have investigated the PE spectra of 3,3,4,4-tetramethyl-1,2-bis(methoxyimino)cyclobutane[80] and of 3,3,5,5-tetramethyl-1,2-bis(methoxyimino)cyclopentane[79] which have vicinal functional groups. They found that the three geometric isomers of the compounds differ only in a limited way in the ionization potentials of the various π levels but that there is a significant effect on the order of the n^+ and n^- levels. The variations are discussed in terms of through-bond and through-space interactions.

We have measured the PE spectra of the dioximes **4–6**, the dimethoximes **7–9**, the monoximes **10–12** and the monomethoximes **13–15**. The spectra of the dimethoximes and the monomethoximes are depicted in Figures 5–7. The observed ionization potentials are listed in Table 3. The spectra of **7–9** were recorded from mixtures of (*E*)/(*Z*) isomers since these could not be separated. It is assumed that the relevant IPs are not significantly dependant on the configuration. The spectra of the dioximes and dimethoximes were inspected for splittings of the characteristic ionization bands, and for this purpose the spectra of the monoximes and monomethoximes were used for comparison. The ionization potentials were assigned to MOs making use of the Koopmans theorem,[84] $IP_i = -\varepsilon_i^{SCF}$, which relates vertical ionization potentials IP_i with orbital energies ε_i^{SCF} obtained by SCF MO calculations.

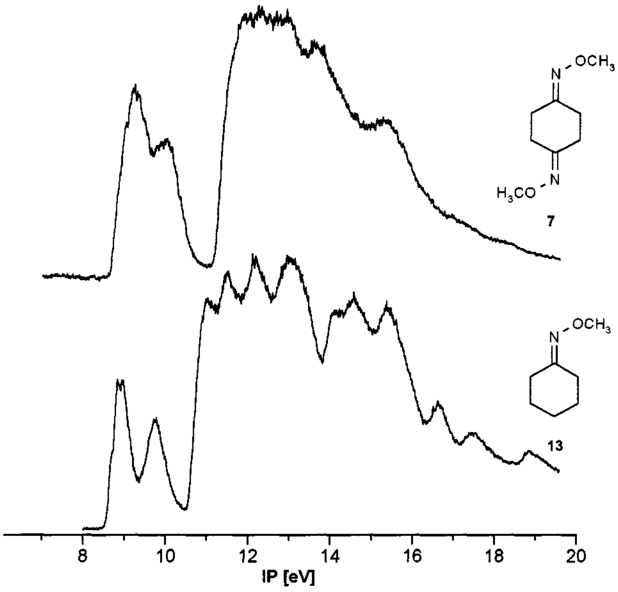


Figure 5. PE spectra of cyclohexane-1,4-dione bis(*O*-methyloxime) (**7**) and cyclohexanone *O*-methyloxime (**13**)

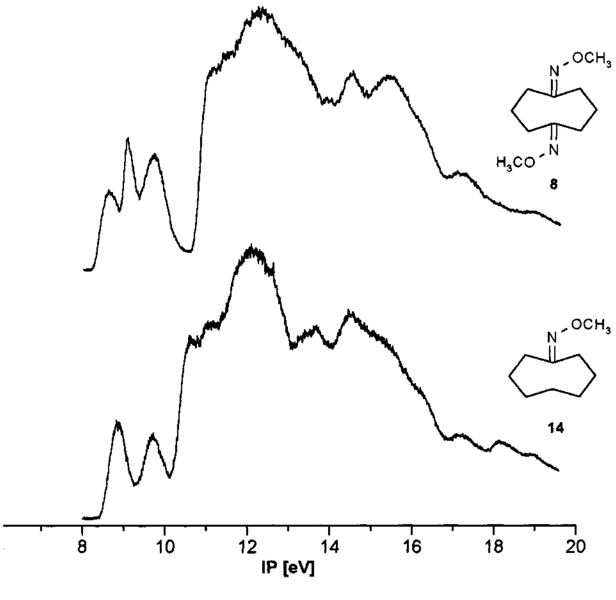


Figure 6. PE spectra of cyclooctane-1,5-dione bis(*O*-methyloxime) (**8**) and cyclooctanone *O*-methyloxime (**14**)

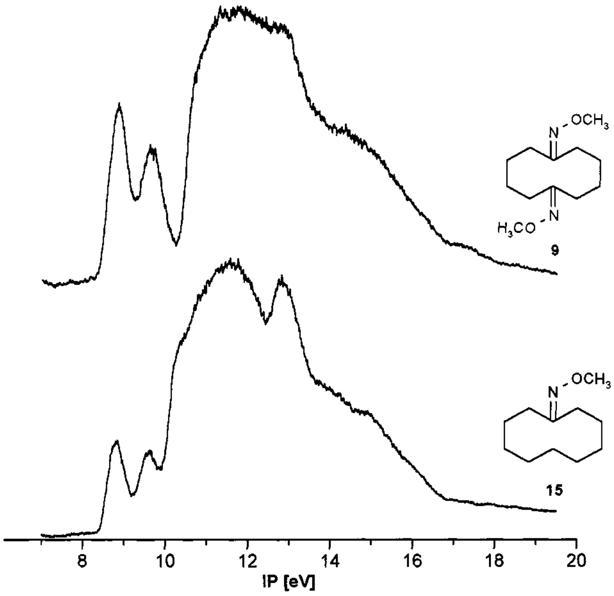


Figure 7. PE spectra of cyclodecane-1,6-dione bis(*O*-methyloxime) (**9**) and cyclodecanone *O*-methyloxime (**15**)

Table 3. Vertical ionization potentials [eV] of dioximes **4−6**, dimethoximes **7−9**, monoximes **10−12**, and monomethoximes **13−15**

	π^-(C=N)	π^+(C=N)	n^-(N)	n^+(N)
4*E*		9.72		10.20
7[a]		9.18		9.97
10	9.40[b]		9.95[c]	
13	8.92[b]		9.74[c]	
5*Z*	9.23	9.60		9.96
8[a]	8.61	9.07		9.71
11	9.26[b]		9.89[c]	
14	8.83[b]		9.70[c]	
6[a]		9.44		9.92
9[a]		8.84		9.68
12	9.26[b]		9.85[c]	
15	8.80[b]		9.59[c]	

[a] Mixture of (*E*) and (*Z*) isomers. − [b] π(C=N). − [c] n(N).

The first two IPs of formaldoxime are found at 10.59 and 11.12 eV[77] and are assigned to ionizations from the π(C=N) and the n(N) MO, respectively. In acetone oxime and acetone *O*-methyloxime, the corresponding ionization energies are 9.67, 10.46 eV,[75] and 9.16, 9.95 eV,[79] respectively.

The IP values of the monoximes **10−12** and the monomethoximes **13−15** (Table 3) are 0.3−0.6 eV smaller than those of the two acetone derivatives owing to their larger skeletons. The spectra of the dioxime **5** and the dimethoxime **8** display three ionization bands in the low energy section (< 11 eV) instead of two bands of the monoxime **11** and the monomethoxime **14**. In these difunctional compounds, the first two IPs are assigned to π^-(C=N) and π^+(C=N) that are split by about 0.4 eV. In the case of dimethoxime **8**, the splitting is almost exactly symmetric to the value of IP[π(C=N)] found for monomethoxime **14** indicating through-space interaction of the orbitals. For the pair of compounds **5** and **11**, the splitting is less symmetric but also here prevailing through-space interaction is active. For the other dioximes and dimethoximes, i.e. those with six- and ten-membered rings, no indication of two different π(C=N) ionizations can be found in the PE spectra. The IP values of the difunctional compounds with a six-membered ring (**4**, **7**) are about 0.3 eV higher than in the corresponding monofunctional compounds (**10**, **13**). In compounds **6** and **9** with ten-membered rings, this stabilization is smaller (0.04−0.18 eV) because of the greater separation of the functional groups.

In the spectra of all difunctional compounds there is no indication of splitted n(N) ionizations, which are, however, slightly higher (0.01−0.08 eV in eight- and ten-membered rings, 0.25 eV in six-membered rings) than in the monoximes because of inductive stabilization of the orbitals by the second electronegative oxime group.

The PE spectra of the dioximes and dimethoximes studied here, indicate sizeable OITS effects for the eight-membered ring compounds **5** and **8**. The BC conformation has a short transannular distance and allows for effective overlap of the π(C=N) orbitals which is not possible in the six-membered ring and the preferred BCB conformation of the ten-membered ring. The PE-spectroscopic findings confirm the results of the quantum chemical calculations outlined in the preceding section.

3.4 ^{13}C-NMR Spectra

Several investigations have demonstrated that intramolecular interactions, including transannular effects, can be studied by ^{13}C-NMR spectroscopy. Nakashima and Maciel[85] realized transannular interactions in heterocyclooctan-5-ones. In 11-methyl-11-azabicyclo[5.3.1]undecan-4-one, the signal of the carbonyl carbon atom is shifted high-field by 12 ppm relative to that of cyclooctanone, and this is attributed to transannular interaction of the two functional groups. Spanka et al.[4] have proved such interactions in cyclic amino ketones and aminoalkenes by ^{13}C NMR. Senda et al.[13] have investigated 3,7-disubstituted bicyclo[3.3.1]nonanes, and Bishop[8][36] has studied disubstituted bicyclo[3.3.3]decanes, 1,5-disubstituted cyclooctanes, and related compounds. Furthermore, homoconjugation has been investigated by this method in cyclic and bicyclic diketones including **1−3**.[10][11]

In Table 4, the ^{13}C-NMR δ values of the oxime carbon atoms of dimethoximes **7−9** and methoximes **13−15** are summarized. Again, the six-membered ring compounds (**7**, **13**) are included for comparison. In addition, Δδ values are given for the investigated systems which are obtained as the differences of δ of the mono- and the difunctional compounds, Δδ = δ(monofunctional) − δ(difunctional), and transannular distances *d*. In all cases, there is a high-field shift in the difunctional compounds as compared to the monofunctional, and the size of Δδ is dependant on the distance *d* of the chromophores indicating strong transannular interactions in compound **8** and much smaller in **9**.

Table 4. ^{13}C-NMR δ values of the oxime carbon atoms of dimethoximes **7−9** and methoximes **13−15** (in $CDCl_3$) and transannular distances *d* [pm]

	δ(C=N)	*d*[a]		δ(C=N)	Δδ
7[b]	157.64	292.6	**13**	160.11	2.47
8[b]	160.32	287.1	**14**	163.65	3.33
9[b]	160.80	347.0	**15**	161.10	0.30

[a] MMX results (from Table 1). − [b] Mixture of (*E*) and (*Z*) isomers.

4. Discussion

It was the main purpose of this investigation to study the conformational properties of cyclic dioximes and dimethoximes in which the two functional groups are in opposite positions in a six-, eight-, or ten-membered ring and to find out how the conformations are related with the electronic structures. Depending on their relative geometric orientation, transannular orbital interactions between the π and n MOs are possible. This has been studied by quantum chemical calculations and by PE spectroscopy. In addition, ^{13}C-NMR spectroscopy was used.

The conformational properties have been analysed extensively by molecular mechanics (MMX) and by semiempirical quantum chemical AM1 calculations. For the most important conformers also ab initio HF and B3LYP calculations were performed. In most cases, the HF results are in better accordance with those of the MMX than those of the AM1 method. It was, however, unimportant to include electron correlation, i.e. the B3LYP results were rather the same as the HF.

The electronic structures were analysed by semiempirical, ab initio (HF and B3LYP) calculations as well as by PE spectroscopy. The natural sequence of the highest occupied MOs, $\pi^-(C{=}N) > \pi^+(C{=}N)$, was found for the cyclooctane derivatives **5** and **8** and for the cyclodecane derivatives **6** and **9**. However, the calculated splitting of the orbitals is much smaller for the latter than for the former pair of compounds. Only for **5** and **8** significant transannular interactions could be established unequivocally by PE spectroscopy. The spectra of the difunctional compounds comprise an additional π(C=N) ionization band as compared to the corresponding monofunctional compounds **11** and **14**. The observed effects are ascribed to through-space orbital interactions (OITS) caused by favourable geometric orientations of the functional groups in BC-3,7 or CC-3,7 conformations. On the other hand, no indications for such interactions were found in the PE spectra of compounds **4**, **6**, **7**, and **9** that have the functional groups in 1,4- or 1,6-positions of a six- or a ten-membered ring. Calculations indicated splittings of the π(C=N) orbitals resulting in an inverted sequence, $\pi^+(C{=}N) > \pi^-(C{=}N)$, for **4** and **7**. All these findings are in accord with the results of the quantum chemical calculations that indicate unfavourable conformations for the latter molecules **6** and **9**. Their prevailing conformer is the BCB-3,8 form in which the functional groups are far separated. Saturated ten-membered rings allow for conformers puckered in such a way that OITS might be effective, and such effects have been observed for other ten-membered rings.[1]

In the quantum chemical calculations, splittings of the n(N) orbitals of up to 0.4 eV were obtained for all difunctional compounds (**4−9**) (Table 2), but in no case could this be confirmed by PE spectroscopy. The natural sequence, $n^-(N) > n^+(N)$, was calculated only for compound ***8E***, whereas for all other compounds, ***4E***, ***5Z***, ***6E***, ***7E***, and ***9E***, the inverted sequence, $n^+(N) > n^-(N)$, was found.

Finally, it can be mentioned that for the interpretation of the PE spectra the MO energies calculated by the AM1 and the B3LYP method are superior to those of the HF method, indicating that inclusion of electron correlation is advantageous.

The results of our ^{13}C-NMR-spectroscopic analyses confirm the findings of the other methods. The ^{13}C-NMR δ values of the oxime carbon atoms (Table 4) give evidence for transannular interactions in the dimethoxime **8** with an eight-membered ring and no such or much smaller effects in the ten-membered homologue **9**. However, one has to be rather careful in the interpretation of the Δδ values since also inductive through-bond interactions as in the case of the cyclohexane derivative **7** contribute to it.

Experimental Section

General: Melting points (uncorrected) were determined with a Büchi 510 apparatus. − The ^{1}H-, and ^{13}C-NMR spectra were recorded with a Varian XL-200 or a Bruker AMX 300 spectrometer. The following frequencies were used: 200 or 300 MHz (^{1}H), and 50.3 or 75.5 MHz (^{13}C). The spectra were measured as solutions in a 5-mm tube at room temperature with the solvents $CDCl_3$ or $[D_6]$DMSO. The chemical shifts are reported in units of parts per million (δ) relative to tetramethylsilane (^{1}H, ^{13}C) as internal standard. Coupling constants *J* are given in Hz. − Infrared (IR) spectra were recorded with a Perkin−Elmer 1600 instrument. Only the most significant absorptions are given. − Electron impact mass spectra (MS) were obtained with a Hewlett Packard HP 5971A MSD instrument (70 eV). For GC/MS analyses this instrument was coupled with a Hewlett-Packard HP 5890 Ser.II gas chromatograph. The intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. For high resolution measurements the instrument Fisons VG Prospec 3000 (70 eV) was used. − Elemental analyses were performed with a Carlo Erba 1106 instrument. − PE spectra were recorded with a UPG200 spectrometer of Leybold-Heraeus equipped with an He(I) radiation source (21.21 eV). The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ± 0.03 eV for ionization energies, for broad and overlapping signals it was only ± 0.1 eV. − Semiempirical AM1[65] calculations were performed with the MOPAC93[86] program package, ab initio HF[66] and Becke3LYP[67−70] calculations with the program GAUSSIAN 94.[87] Geometries were fully optimized at the respective levels of theory. MOs were plotted by using the program PERVAL.[88]

Cyclohexane-1,4-dione Dioxime (4): To a solution of 1,4-cyclohexanedione (4.00 g, 35.7 mmol) in methanol (80 mL) a solution of hydroxylamine hydrochloride (8.00 g, 0.12 mol) and sodium acetate (10.00 g, 0.12 mol) in water (48 mL) was added. After the addition was completed, the mixture was heated to reflux for 13 h and then cooled to room temperature. Evaporation of the solvent afforded a colourless precipitate. The solid was filtered off and washed with water. Recrystallization from ethanol gave colourless crystals of ***4E***. Yield 3.69 g (73%), m.p. 196 °C (ref.[34] 191 °C). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.42 (m, 8 H, CH_2), 10.36 (s, 2 H, =NOH). − ^{13}C NMR ([D$_6$]DMSO): δ = 23.37 (CH_2), 26.43 (CH_2), 156.14 (C=N). − IR (KBr): $\tilde{\nu}$ = 3200 (ν_{O-H}), 2862 (ν_{C-H}), 1658 ($\nu_{C=N}$), 1487, 1433,1420 (δ_{CH2}), 1324, 1276 (δ_{O-H}), 1175, 1001, 953 cm^{-1}. − MS (70 eV, EI); *m*/*z* (%): 142 (44) [M$^+$], 125 (9) [M$^+$ − OH], 124 (33), 94 (100), 67 (88).

Cyclooctane-1,5-dione Dioxime (5): Compound ***5Z*** was synthesized from dione **2** (5.00 g, 35.7 mmol) and hydroxylamine hydrochloride (7.44 g, 0.11 mol) according to the literature procedure.[35] Yield 4.31 g (71%), m.p. 178 °C (ref.[35] 176−179 °C). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.90 (m, 4 H, CH_2), 2.15−2.28 (m, 8 H, CH_2C=N), 10.09 (s, 2 H, =NOH). − ^{13}C NMR ([D$_6$]DMSO): δ = 20.67 (CH_2), 21.36 (CH_2), 26.23 (CH_2C=N), 33.66 (CH_2C=N), 158.10 (C=N). − IR (KBr): $\tilde{\nu}$ = 3183 (ν_{O-H}), 2893 (ν_{C-H}), 1662 ($\nu_{C=N}$), 1490, 1464, 1433 (δ_{CH2}), 1334, 1219 (δ_{O-H}), 1079, 975 cm^{-1}. − MS (70 eV, EI); *m*/*z* (%):170 (20) [M$^+$], 153 (17) [M$^+$ − OH], 122 (66), 95 (64), 79 (100), 67 (60), 41 (95) [$C_2H_3N^+$]. − $C_8H_{14}N_2O_2$ (170.2): calcd. C 56.45, H 8.29, N 16.46; found C 56.33, H 8.19, N 16.40.

Cyclodecane-1,6-dione Dioxime (6): The same procedure as for dioxime **4** was applied to dione **3** (8.00 g, 47.6 mmol) and hydroxylamine hydrochloride (16.00 g, 0.23 mol). Yield 6.90 g (73%), m.p. 231 °C (ref.[89] 231 °C). − ^{1}H NMR ([D$_6$]DMSO) (mixture of ***6E*** and ***6Z***): δ = 1.64 (m, 8 H, CH_2), 2.13−2.36 (m, 8 H, CH_2C=N), 10.29 (s, 1 H, =NOH), 10.39 (s, 1 H, =NOH). − ^{13}C NMR ([D$_6$]DMSO) (two isomers): δ = 21.82 (CH_2), 23.28 (CH_2), 23.83 (CH_2), 24.89 (CH_2), 26.74 (CH_2C=N), 26.89 (CH_2C=N), 30.24 (CH_2C=N), 33.11 (CH_2C=N), 158.17 (C=N), 158.45 (C=N). − IR (KBr): $\tilde{\nu}$ = 3222 (ν_{O-H}), 2959, 2916 (ν_{C-H}), 1648 ($\nu_{C=N}$), 1483, 1424 (δ_{CH2}), 1329, 1279 (δ_{O-H}), 962, 908 cm^{-1}.

Cyclohexane-1,4-dione Bis(*O*-methyloxime) (7): In a flask fitted with stirrer and reflux condenser 1,4-cyclohexanedione (2.00 g, 17.8 mmol), *O*-methylhydroxylamine hydrochloride (3.34 g, 40.0 mmol) and sodium acetate (10.00 g, 0.12 mol) were dissolved in a mixture of water (12 mL) and methanol (6 mL). The reaction mixture was stirred at 60−70 °C for 14 h. Then the resulting solution was neutralized with a solution of sodium hydrogen carbonate in water and extracted with diethyl ether (3 × 100 mL). The extracts were dried with sodium sulfate, concentrated and then distilled to yield the product as colourless, wax-like crystals. Yield 1.68 g (56%), m.p. 54 °C, b.p. 61 °C/0.20 hPa (ref.[37]: 75−85 °C/0.3 Torr). − GC/MS analysis indicates a mixture of (*E*)/(*Z*) isomers, ***7E*/*7Z*** ≈ 3:1. − ^{1}H NMR ($CDCl_3$): δ = 2.53 (d/t, *J* = 6.2/19.4 Hz, 8 H, CH_2), 3.84 (s, 6 H, =$NOCH_3$). − ^{13}C NMR ($CDCl_3$) (***7E***, major isomer): δ = 24.01 (CH_2), 26.94 (CH_2), 61.36 (=$NOCH_3$), 157.64 (C=N). − IR (KBr): $\tilde{\nu}$ = 2937, 2817 (ν_{C-H}), 1637 ($\nu_{C=N}$), 1439 (δ_{CH2}), 1048 (ν_{C-O}), 980 cm^{-1}. − HR MS: $C_8H_{14}N_2O_2$, M$^+$: calcd. 170.1055; found 170.1042. − The same procedure was used for the synthesis of methoximes **8**, **9**, **14**, and **15**.

Cyclooctane-1,5-dione Bis(*O*-methyloxime) (8): Dione **2** (3.00 g, 21.4 mmol) and *O*-methylhydroxylamine hydrochloride (4.18 g, 50.0 mmol) afforded 3.16 g of **8** (75%), b.p. 70 °C/0.20 hPa. − GC/MS analysis indicates a mixture of (*E*)/(*Z*) isomers, ***8E*/*8Z*** ≈ 1.5:1. − ^{1}H NMR ($CDCl_3$): δ = 1.86−2.08 (m, 4 H, CH_2), 2.21−2.44 (m, 8 H, CH_2C=N), 3.80 (s, 6 H, =$NOCH_3$). − ^{13}C NMR ($CDCl_3$) (two isomers): δ = 20.81 (CH_2), 21.18 (CH_2), 23.40 (CH_2), 27.37 (CH_2C=N), 27.57 (CH_2C=N), 33.04 (CH_2C=N), 34.32 (CH_2C=N), 61.16 (=$NOCH_3$), 160.32 (C=N), 160.57 (C=N). − IR (liquid film): $\tilde{\nu}$ = 2938, 2813 (ν_{C-H}), 1624 ($\nu_{C=N}$), 1458, 1438 (δ_{CH2}), 1052 (ν_{C-O}), 908 cm^{-1}. − HR MS: $C_{10}H_{18}N_2O_2$, M$^+$: calcd. 198.1368; found 198.1390.

Cyclodecane-1,6-dione Bis(O-methyloxime) (9): Dione **3** (1.18 g, 7.0 mmol) and *O*-methylhydroxylamine hydrochloride (1.50 g, 18.0 mmol) afforded 1.12 g of **9** (71%), m.p. 57 °C, b.p. 97 °C/0.27 hPa. − GC/MS analysis indicates a mixture of (*E*)/(*Z*) isomers, ***9E*/*9Z*** ≈ 1.3:1. − ^{1}H NMR ($CDCl_3$) (two isomers): δ = 1.72 (m, 8 H, CH_2), 2.21−2.45 (m, 8 H, CH_2C=N), 3.82 (s, 3 H, =$NOCH_3$), 3.84 (s, 3 H, =$NOCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 22.49 (CH_2), 23.22 (CH_2), 24.46 (CH_2), 24.71 (CH_2), 27.84 (CH_2C=N), 27.93 (CH_2C=N), 31.64 (CH_2C=N), 33.81 (CH_2C=N), 61.17 (=$NOCH_3$), 160.80 (C=N), 161.06 (C=N). − IR (KBr): $\tilde{\nu}$ = 2942, 2816 (ν_{C-H}), 1618 ($\nu_{C=N}$), 1466, 1439 (δ_{CH2}), 104 (ν_{C-O}), 948 cm^{-1}. − HR MS: $C_{12}H_{22}N_2O_2$, M$^+$: calcd. 226.1681; found 226.1686. − $C_{12}H_{22}N_2O_2$ (226.2): calcd. C 63.69, H 9.80, N 12.38; found C 63.18, H 10.46, N 11.95.

Cyclooctanone *O*-Methyloxime (14): Cyclooctanone (2.00 g, 15.8 mmol) and *O*-methylhydroxylamine hydrochloride (1.67 g, 20.0 mmol) afforded 1.04 g of **14** (42%), b.p. 29−30 °C/ 0.05 hPa. − ^{1}H NMR ($CDCl_3$): δ = 1.48 (m, 6 H, CH_2), 1.72 (m, 4 H, CH_2), 2.28 (t, *J* = 6.4 Hz, 2 H, CH_2C=N), 2.38 (t, *J* = 6.4 Hz, 2 H, CH_2C=N), 3.82 (s, 3 H, =$NOCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 24.56 (CH_2), 24.87 (CH_2), 25.53 (CH_2), 26.51 (CH_2), 27.31 (CH_2C=N), 33.32 (CH_2C=N), 61.05 (=$NOCH_3$), 163.65 (C=N). − IR (liquid film): $\tilde{\nu}$ = 2911, 2800 (ν_{C-H}), 1622 ($\nu_{C=N}$), 1450 (δ_{C-H}), 1055 (ν_{C-O}), 883 cm^{-1}. − HR MS: $C_9H_{17}NO$, M$^+$: calcd. 155.1310; found 155.1322.

Cyclodecanone *O*-Methyloxime (15): Cyclodecanone (2.00 g, 13.0 mmol) and *O*-methylhydroxylamine hydrochloride (1.40 g, 16.8 mmol) afforded 1.27 g of **15** (53%), b.p. 85 °C/2 hPa. − ^{1}H NMR ($CDCl_3$): δ = 1.42 (m, 10 H, CH_2), 1.76 (m, 4 H, CH_2), 2.29−2.37 (m, 4 H, CH_2C=N), 3.82 (s, 3 H, =$NOCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 23.40 (CH_2), 23.98 (CH_2), 24.24 (CH_2), 24.54 (CH_2), 24.79 (CH_2), 25.53 (CH_2), 25.65 (CH_2), 28.72 (CH_2C=N), 33.85 (CH_2C=N), 61.10 (=$NOCH_3$), 161.10 (C=N). − IR (liquid film): $\tilde{\nu}$ = 2925, 2824 (ν_{C-H}), 1626 ($\nu_{C=N}$), 1458 (δ_{C-H}), 1052 (ν_{C-O}), 916, 879 cm^{-1}. − HR MS: $C_{11}H_{21}NO$, M$^+$: calcd. 183.1623; found 183.1618.

Acknowledgments

We thank the Fonds der Chemischen Industrie, Frankfurt am Main, for financial support.

---

[1] P. Rademacher, *Chem. Soc. Rev.* **1995**, *24*, 143−150.
[2] G. Spanka, P. Rademacher, *J. Org. Chem.* **1986**, *51*, 592−596.
[3] G. Spanka, R. Boese, P. Rademacher, *J. Org. Chem.* **1987**, *52*, 3362−3367.
[4] G. Spanka, H. Duddeck, P. Rademacher, *J. Chem. Soc., Perkin Trans. 2* **1988**, 2119−2121.
[5] R. F. Wiesmann, P. Rademacher, *Chem. Ber.* **1994**, *127*, 1517−1522.
[6] P. Rademacher, R. F. Wiesmann, *Chem. Ber.* **1994**, *127*, 509−518.
[7] R. F. Wiesmann, P. Rademacher, *Chem. Ber.* **1994**, *127*, 1105−1110.
[8] R. Bishop, *Aust. J. Chem.* **1984**, *37*, 319−325.
[9] B. Albert, D. Elsässer, D. Heckel, S. Kopmeier, H.-D. Martin, B. Mayer, T. J. Chow, T.-K. Wu, S.-K. Yeh, *Chem. Ber.* **1991**, *124*, 803−813.
[10] T. Doerner, R. Gleiter, T. A. Robbins, P. Chayangkoon, D. A. Lightner, *J. Am. Chem. Soc.* **1992**, *114*, 3235−3241.
[11] J. E. Gurst, E. M. Schubert, S. E. Boiadjiev, D. A. Lightner, *Tetrahedron* **1993**, *49*, 9191−9196.

[12] K. Shen, N. A. Kuebler, *Tetrahedron Lett.* **1973**, *24*, 2145−2148.
[13] Y. Senda, J. Ishiyama, S. Imaizumi, *J. Chem. Soc., Perkin Trans. 2* **1981**, 90−93.
[14] R. W. Alder, R. J. Arrowsmith, A. Casson, R. B. Sessions, E. Heilbronner, B. Kovac, H. Huber, M. Taagepera, *J. Am. Chem. Soc.* **1981**, *103*, 6137−6142.
[15] R. W. Alder, R. B. Sessions, *The chemistry of functional groups*, suppl. 7 ("The chemistry of amino, nitroso and nitro compounds and their derivatives") (Ed.: S. Patai), Wiley, Chichester, **1982**, vol. 2, chapter 18, p. 763.
[16] N. H. Werstiuk, D. N. Butler, S. Datta, *Can. J. Chem.* **1986**, *64*, 760−763.
[17] M. Braga, S. Larsson, *J. Phys. Chem.* **1992**, *96*, 9218−9224.
[18] P. Rademacher, *The chemistry of amino, nitroso, nitro and related groups* (Ed.: S. Patai), Wiley, Chichester, **1996**, vol. suppl. F2, p. 159.
[19] A. Strenge, P. Rademacher, *Eur. J. Org. Chem.* **1999**, 1611−1617, following paper.
[20] *The Chemistry of the Carbon-Nitrogen Double Bond* (Ed.: S. Patai), Wiley & Sons, New York, **1970**.
[21] *The Chemistry of Double-Bonded Functional Groups* (Ed.: S. Patai), Wiley, Chichester, **1997**, vol. suppl. A3.
[22] W. Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd ed., Cambridge University Press, Cambridge, **1992**.
[23] H. Krauch, W. Kunz, *Reaktionen der organischen Chemie*, 6th ed., Hüthig Verlag, Heidelberg, **1997**.
[24] P. Hlavica, M. Lehnerer, *The Chemistry of the Carbon-Nitrogen Double Bond* (Ed.: S. Patai), Wiley, Chichester, **1997**, chapter 26, p. 1625.
[25] J. Dale, *Stereochemie und Konformationsanalyse*, Verlag Chemie, Weinheim, **1978**.
[26] *Conformational Analysis of Medium-Sized Heterocycles* (Ed.: R. S. Glass), VCH, New York, **1988**.
[27] G. Haufe, G. Mann, *Chemistry of Alicyclic Compounds*, Elsevier, Amsterdam, **1989**.
[28] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley & Sons, New York, **1994**.
[29] R. Griffith, J. B. Bremner, S. J. Titmuss, *J. Comput. Chem.* **1997**, *18,* 1211−1221.
[30] H. C. Brown, *Organic Synthesis via Boranes*, Wiley & Sons, New York, **1975**.
[31] S. U. Kulkari, C. G. Rao, V. D. Patil, *Heterocycles* **1982**, *18*, 321−326.
[32] H. O. House, J. H. C. Lee, D. VanDerveer, J. E. Wissinger, *J. Org. Chem.* **1983**, *48*, 5285−5288.
[33] A. Baeyer, W. Noyes, *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 2168−2178.
[34] K. Hosino, *Bull. Chem. Soc. Jpn.* **1944**, *19*, 153−158.
[35] G. I. Glover, R. B. Smith, H. Rapoport, *J. Am. Chem. Soc.* **1965**, *87*, 2003−2011.
[36] R. Bishop, G.-H. Lee, *Aust. J. Chem.* **1987**, *40*, 249−255.
[37] S. Shatzmiller, R. Lidor, *Synthesis* **1983**, 590−593.
[38] L. Ruzicka, M. Kobelt, O. Häflinger, V. Prelog, *Helv. Chim. Acta* **1949**, *32*, 544−552.
[39] L. G. Donaruma, *J. Org. Chem.* **1957**, *22*, 1024−1029.
[40] A. Klesing, D. H. Sutter, *Z. Naturforsch A* **1990**, *45*, 817−826.
[41] O. Ohashi, H. Hara, K. Noji, T. Sakaizumi, M. Onda, I. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 834−836.
[42] O. Ohashi, R. Ishihara, K. Murakami, T. Sakaizumi, M. Onda, I. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 891−893.
[43] P. G. Kolandaivel, N. Kuze, T. Sakaizumi, O. Ohashi, K. Iijima, *J. Phys. Chem. A* **1997**, *101*, 2873−2878.
[44] K. Iijima, O. Ohashi, *J. Mol. Struct.* **1993**, *291*, 159−165.
[45] K. Yoshida, T. Sakaizumi, O. Ohashi, I. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1620−1622.
[46] M. Katayama, T. Sakaizumi, I. Yamaguchi, O. Ohashi, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2911−2912.
[47] K. Iijima, M. Suzuki, T. Sakaizumi, O. Ohashi, *J. Mol. Struct.* **1997**, *413 Special Issue SI,* 327−331 .
[48] T. Sakaizumi, I. Sasane, T. Kouno, S. Takeda, N. Kuze, O. Ohashi, K. Iijima, *J. Mol. Struct.* **1997**, *413 Special Issue SI,* 107−119 .
[49] K. Iijima, T. Miwa, T. Matsuyoshi, T. Sakaizumi, O. Ohashi, *J. Mol. Struct.* **1995**, *352/353*, 161−166.
[50] K. Iijima, T. Hanamori, T. Sakaizumi, O. Ohashi, *J. Mol. Struct.* **1993**, *299*, 149−153.
[51] M. Terashima, O. Ohashi, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3647−3648.
[52] U. Burkert, N. L. Allinger, *Molecular Mechanics*, Am. Chem. Soc., Washington, D.C., **1982**.
[53] P. Groth, O. Hassel, *Acta Chem. Scand.* **1964**, *18*, 923−931.
[54] T. Alvik, G. Borgen, J. Dale, *Acta Chem. Scand.* **1972**, *26*, 1805−1816.
[55] P. Dowd, T. Dyke, W. Klemperer, *J. Am. Chem. Soc.* **1970**, *92*, 6327.
[56] N. L. Allinger, M. T. Tribble, M. A. Miller, *Tetrahedron* **1972**, *28*, 1173−1190.
[57] D. M. Ferguson, D. J. Raber, *J. Am. Chem. Soc.* **1989**, *111*, 4371−4378.
[58] F. A. L. Anet, V. J. Basus, *J. Am. Chem. Soc.* **1973**, *95*, 4424−4426.
[59] J. Dunitz, *Pure Appl. Chem.* **1971**, *25*, 495−508.
[60] J. D. Dunitz, *Perspectives in Structural Chemistry* (Eds.: J. D. Dunitz, J. A. Ibers), Wiley & Sons, New York, **1968**, vol. 2, p. 1.
[61] F. A. L. Anet, M. S. Jacques, P. M. Henrichs, A. K. Cheng, J. Krane, L. Wong, *Tetrahedron* **1974**, *30*, 1629−1637.
[62] R. L. Hilderbrandt, J. D. Wieser, L. K. Montgomery, *J. Am. Chem. Soc.* **1973**, *95*, 8598−8605.
[63] F. A. L. Anet, M. S. Jacques, P. M. Henrichs, A. K. Cheng, J. Krane, L. Wong, *Tetrahedron* **1974**, *30*, 1629−1637.
[64] J. J. Gajewski, K. E. Gilbert, J. McKelvey, *Adv. Mol. Model.* **1990**, *2*, 65−92.
[65] M. J. S. Dewar, E. G. Zoebisch, H. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.
[66] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley & Sons, New York, **1986**.
[67] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5642.
[68] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372−1377.
[69] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.
[70] A. D. Becke, *J. Comput. Chem.* **1999**, *20,* 63−69.
[71] A. Strenge, Dissertation, University of Essen, **1997**.
[72] R. D. Bach, G. J. Wolber, *J. Org. Chem.* **1982**, *47*, 245−248.
[73] T.-K. Ha, *Chem. Phys. Lett.* **1982**, *86*, 477−481.
[74] D. R. Armstrong, G. T. Walker, *J. Mol. Struct. (Theochem)* **1987**, *149*, 369−389.
[75] A. Dargelos, C. Sandorfy, *J. Chem. Phys.* **1977**, *67*, 3011−3013.
[76] P. Dupuis, R. Roberge, C. Sandorfy, D. Vocelle, *J. Chem. Phys.* **1981**, *74*, 256−259.
[77] D. C. Frost, W. M. Lau, C. A. M. McDowell, N. P. C. Westwood, *J. Phys. Chem.* **1982**, *86*, 3577−3581.
[78] J. P. Dognon, C. Pouchan, A. Dargelos, J. P. Flament, *Chem. Phys. Lett.* **1984**, *109*, 492−499.
[79] F. Stunnenberg, H. Cerfontain, *J. Phys. Chem.* **1987**, *91*, 6490−6496.
[80] F. Stunnenberg, H. Cerfontain, A. Terpstra, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 1−4.
[81] F. Stunnenberg, H. Cerfontain, R. B. Rexwinkel, *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 438−447.
[82] T. Pasinszki, N. P. C. Westwood, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 43−51.
[83] M. DalColle, G. Distefano, A. Modelli, D. Jones, M. Guerra, P. R. Olivato, D. D. Ribeiro, *J. Phys. Chem. A* **1998**, *102,* 8037−8043.
[84] T. Koopmans, *Physica* **1934**, *1*, 104−113.
[85] T. T. Nakashima, G. E. Maciel, *Org. Magn. Reson.* **1972**, *4*, 321−326.
[86] J. J. P. Stewart, *MOPAC93.00 Manual*, Fujitsu Limited, Tokyo, Japan, **1993**.
[87] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision E.2*, Gaussian, Inc., Pittsburgh, PA, **1995**.
[88] R. Sustmann, W. Sicking, *Chem. Ber.* **1987**, *120*, 1323−1330.
[89] W. Hückel, A. Gercke, A. Gross, *Ber. Dtsch. Chem. Ges.* **1933**, *66B*, 563−567.

Received December 12, 1998
[O98588]