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UV spectroscopy and structures of α-bis(methoxyimino)alkanes

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Abstract. The UV spectra of the geometric isomers of the α-bis(methoxyimino)alkanes **1–8** and the structurally related conjugated (methoxyimino)isoxazolines **11** and **13** all exhibit a $\pi\pi^*$ absorption band, of which the maxima with cyclohexane as solvent are between 216 and 268 nm, and 258 and 282 nm, respectively. The differences in λ_{max} are discussed in terms of variations in the degree of inter-iminyl conjugation, as a result of (*i*) variations in the inter-iminyl dihedral angle due to steric hindrance and (*ii*) variations in the ring strain and/or the dipolar repulsion of the two methoxyimino moieties, as with the three geometric isomers of the four-membered ring compound **1**. The lower λ_{max} of (*E,E*)-**8** compared to (*E,E*)-**4** is ascribed to a lower degree of cross-conjugation of the phenyl group with the planar α-bis(methoxyimino) chromophore in the former compound; the absorption band of (*E,E*)-**8** is, in fact, similar to that of the aliphatic (*E,E*)-**5**. The energy of the $\pi\pi^*$ absorption maximum of the (*E,E*)-α-bis(methoxyimino)alkanes appears to be linearly related to that of the corresponding (*E*)-α-oxo oxime ethers with a slope close to unity, illustrating that the sensitivity for structural variations is very similar for the two types of compounds.
X-ray structure analysis showed the O–N=C–C=N–O chromophore of (*E,E*)-**5**, (*E,E*)-**8** and the (hydroxyimino)isoxazoline (*E*)-**10** in the crystalline state to be all planar within the limits of detection.

Introduction

The spectroscopy of α-diketones has been studied at great length and depth[1-5]. As an extension of our own spectroscopic studies on this class of compounds[3-5] and on the related α-oxo oxime *O*-alkyl ethers[6,7], we now report on the UV spectroscopy of the corresponding α-bis(methoxyimino)alkanes **1–8** and the related isoxazolines **10**, **11** and **13**. The (methoxyimino)isoxazolines **11** and **13** were included in the underlying study, since (*E*)- and (*Z*)-**11** may serve as model compounds for acyclic (*E,Z*)- and (*Z,Z*)-α-bis(methoxyimino)alkanes, respectively, and (*E*)- and (*Z*)-**13** likewise as models for acyclic (*E,E*)- and (*Z,E*)-α-bis(methoxyimino)alkanes, just as 3,5,5-trimethyl-4(5*H*)-isoxazolone (**9**) was found to be a model compound for the (*Z*)-isomers of simple α-oxo oxime ethers[7]. Very recently, we have reported on the effect of the geometric isomeric structure on the ground-state electron configuration of the rigid cyclic α-bis(methoxyimino)alkanes **1** and **2**[8,9].
With the acyclic α-bis(methoxyimino)alkanes, due to (*i*) the occurrence of stable (*E*) and (*Z*) orientation of the two methoxyimino groups and (*ii*) the relatively free rotation around the inter-iminyl C–C bond, we are confronted, in theory, with eight conformational geometric isomers (Figure 1). This number reduces to six if the α-bis(methoxyimino)alkane is symmetrical: the structures in column 3 then become equal to those in column 2 of Figure 1.
Experimental evidence[10,11] has shown that the C=N–O–H moiety of oximes is planar with the O–H and C=N in antiplanar orientation. A similar orientation has been proposed for the corresponding *O*-alkyl ethers[12]. The two methoxyimino moieties of an α-bis(methoxyimino)alkane will, due to their strong dipolar repulsion, preferentially adopt a trans(oid) orientation. In practice, we are thus confronted with only four isomers in case of an asymmetrical α-bis(methoxyimino)alkane and of only three isomers in case of a symmetrical one. With the (methoxyimino)isoxazolines **11** and **13**, the number of geometric isomers is limited to two, since one of the two alkoxyiminyl moieties is constrained in the five-membered ring, *viz.*, with **11** in the (*Z*)-orientation, but with **13** in the (*E*)-orientation.
The ground-state energy is very much lower for the (*E,E*)-isomer of **5** than the two other geometric isomers, since the thermal isomerization of a mixture of the three isomers of **5** [(*E,E*)-, (*E,Z*)- and (*Z,Z*)-**5**] in benzene as solvent using iodine as catalyst[13] yielded eventually only the (*E,E*)-isomer. Considering the limits of detection of the other isomers by GLC, this result infers that (*E,E*)-**5** is at least 16 kJ/mol more stable than the two other isomers.

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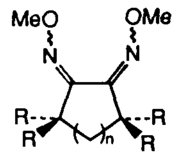
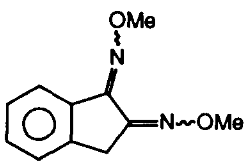


1 n = 0, R = Me
2 n = 1, R = Me
3 n = 2, R = H



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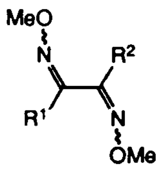
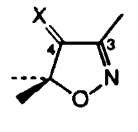
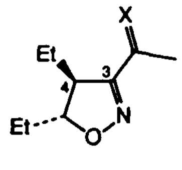


5 $R^1 = R^2 = Me$
6 $R^1 = Me, R^2 = Et$
7 $R^1 = Me, R^2 = Pr$
8 $R^1 = Me, R^2 = Ph$



9 X = O
10 X = NOH
11 X = NOMe



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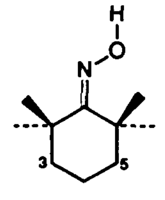
13 X = NOMe



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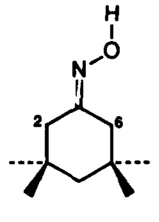

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With the objective of achieving a better understanding of the spectroscopic results to be discussed in the present paper and of the photochemistry to be reported in a subsequent paper, the molecular structures of the (*E*,*E*)-**5**, (*E*,*E*)-**8** and (*E*)-**10** have been determined using X-ray diffraction.

Results and discussion

Spectroscopy

The ground-state electronic structure of α-bis(methoxyimino)alkanes has two HOMOs of π character and two lone-pair orbitals of lower energy[8,9]. The only apparent band in the UV spectrum is, therefore, of ππ* character; the high molar extinction coefficients of the absorption bands are in line with this assignment. The forbidden *n*π* absorption is, even in the gas-phase, apparently hidden under the much intense ππ* band, as noted previously for non-conjugated oximes and derived oxime ethers[14-16].

The studied α-bis(methoxyimino)alkanes have an absorption maximum between 215 and 285 nm for the aliphatics and in between 230 and 315 nm for the aromatics (Table I). Typical spectra are shown in Figures 2 and 3.

We shall first examine the α-bis(methoxyimino)cycloalkanes **1**–**3**. In the absence of any steric constraint, the O–N=C–C=N–O chromophore of the (*E*,*E*)- and (*E*,*Z*)-isomers of both **1** and **2**, and probably also (*Z*,*Z*)-**1**, will be planar, whereas (*Z*,*Z*)-**2**[8] and (*E*,*E*)-, (*E*,*Z*)- and (*Z*,*Z*)-**3**[17] will not be planar. The observed λ_{max} follows the same order (*E*,*E*)-**2** = (*E*,*Z*)-**2** > (*E*,*E*)-**3** > (*Z*,*Z*)-**2** > (*E*,*Z*)-**3** = (*Z*,*Z*)-**3**. The λ_{max} values of the planar (*E*,*E*)- and (*E*,*Z*)-isomers of **1** are greater than those of the corresponding isomers of **2**, as observed previously for the absorption band of the corresponding 1,2-diketones at about 285 nm[3]. The difference may be ascribed to the enhanced ring strain and the reduced dipolar repulsion between the two methoxyimino groups in the (*E*,*E*)- and (*E*,*Z*)-isomers of **1**. The difference between the UV absorption of the aromatic compounds (*E*,*E*)-**4** and (*E*,*E*)-**8** (Figure 3) is worth noting. This can be explained in terms of the difference in conjugation between the phenyl(ene) group and the α-bis(methoxy-

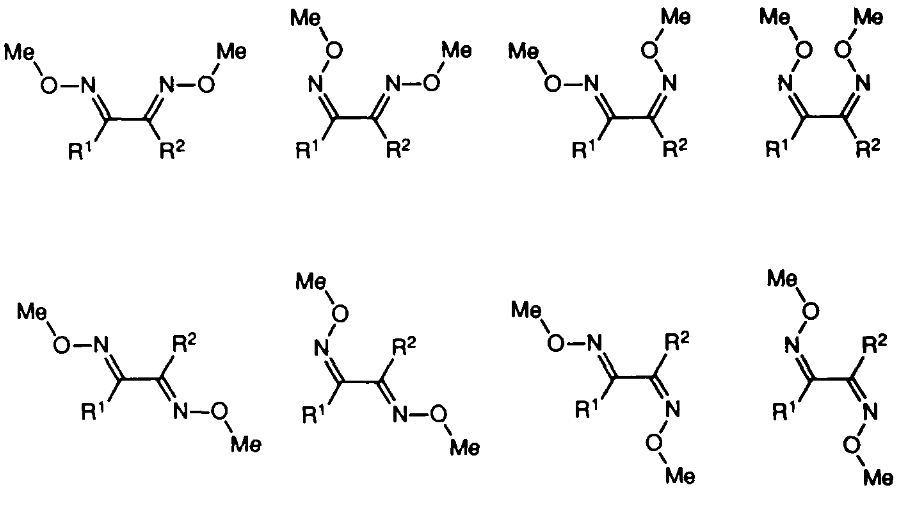

Figure 1. The eight geometric structures of an α-bis(methoxyimino)alkane.

iminyl) moiety. From studies with space-filling Catalin–Stuart molecular models, it appears that (*E,E*)-**4** is planar and, accordingly, the cross-conjugation will be optimal. X-ray analysis of (*E,E*)-**8** revealed that the phenyl group of this molecule intercepts, at an angle of 70°, the planar α-bis(methoxyiminyl)moiety (see section on X-ray structures)[18]. The UV absorption of (*E,E*)-**8** should thus be quite similar to that of the aliphatic (*E,E*)-**5**, and this is, in fact, observed.

As shown in Figure 4, a linear relationship appears to exist between the energy of the ππ* absorption maxima of the aliphatic (*E,E*)-α-bis(methoxyimino)alkanes **1**, **2** and **4**, and the corresponding (*E*)-α-oxime ethers[6] (slope 1.06, correlation coefficient 1.00, three data points). In the absence of (*E*)-2-(methoxyimino)cyclohexanone, (*E,E*)-**3** was correlated with (*E*)-6-(methoxyimino)-2,2-dimethylcyclohexanone[6] (A) and (*E*)-6-(methoxyimino)-2,2,5,5-tetramethylcyclohexanone[6] (B). Inclusion of these two additional points leads to a slope of 1.00 and a correlation coefficient of 0.96. The slope of Figure 4 is very close to unity, illustrating that structural variations have a very similar effect on the energy of the ππ* absorption maxima of the two types of compounds. For both the (*E,Z*)- and (*Z,Z*)-α-bis(methoxyimino)alkanes, there is an insufficient number of data points to allow a conclusion to be drawn.

The (*Z*)-isomer of the 4-(methoxyimino)isoxazoline **11** absorbs at *longer* wavelength (282 nm) than the (*E*)-isomer (274 nm). This difference, which was also observed for α-oxo oxime ethers[6], may be attributed to differences in the C–C=N and C=N–O bond angles of the exocyclic C–C=N–OMe moiety of the (*E*)- and (*Z*)-isomers. X-ray structural data show the oxime (*E*)-**10**, except for the two geminal methyls, to be planar and, hence, its methyl ether (*E*)-**11**, except for the two geminal methyls, is also likely to be planar. In view of its higher absorption wavelength and its very similar molar extinction coefficient, it follows that (*Z*)-**11** will also be planar. Accordingly, the (*Z,Z*)-isomers of **2**, **4** and **5**, which all absorb at wavelengths considerably shorter than the corresponding (*E,E*)-isomers, have a twisted inter-iminyl C–C bond and are thus not planar.

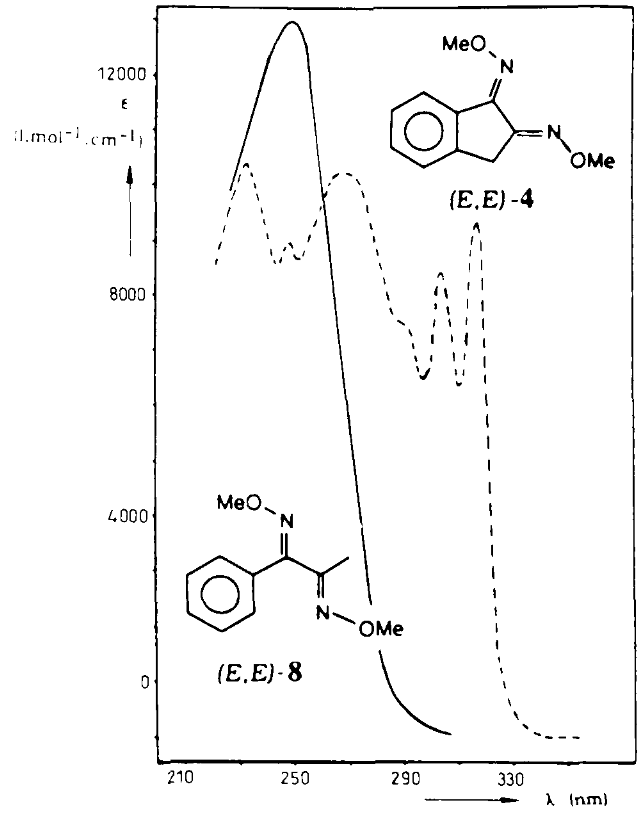

*Figure 3. UV spectra of (*E,E*)-**4** and (*E,E*)-**8** for cyclohexane as solvent.*

The situation for the various (*E,Z*)-isomers of the α-bis(methoxyimino)alkanes is somewhat more complex. The wavelength and extinction coefficient of the absorption maximum are the same for (*E,Z*)-**2** and (*E,E*)-**2**. Hence, since (*E,E*)-**2** is planar (see before), (*E,Z*)-**2** will also be

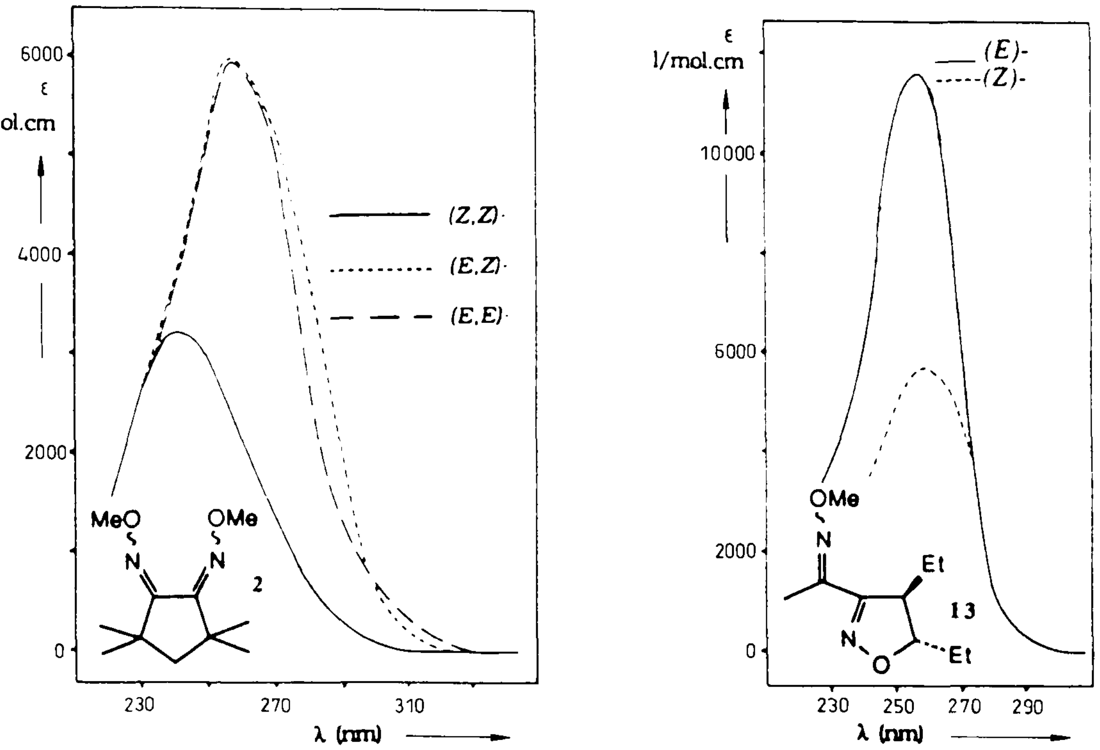

*Figure 2. UV spectra of the three geometric isomers of **2** and the two isomers of **13** for cyclohexane as solvent.*

Table I UV absorption data of α-bis(methoxyimino)alkanes[a].

Compound	Solvent[b]	λ_{max} (nm)	ε ($l \cdot mol^{-1} \cdot cm^{-1}$)
(*E,E*)-**1**	cH	262	9750
(*E,Z*)-**1**	cH	264	9100
(*Z,Z*)-**1**	cH	262	6700
(*E,E*)-**2**	cH	257	5970
(*E,Z*)-**2**	cH	257	5970
(*Z,Z*)-**2**	cH	240	3250
(*E,E*)-**3**	cH	246	6820
(*E,Z*)-**3**	cH	226	5700
(*Z,Z*)-**3**	cH	226	4460
(*E,E*)-**4**	cH	231	10500
		247	9050
		266	10400
		290 (sh)	7500
		302	8600
		315	9500
	M	232	19500
		269	10400
		290	1800
		305	8000
		316	7950
(*E,E*)-**5**	cH	242	14000
	gas phase	232	
(*E,Z*)-**5**	cH	236	8500
	gas phase	226	
(*Z,Z*)-**5**	cH	216	6600
	gas phase	219	
(*E,E*)-**6**	cH	242	13400
(*E,E*)-**7**	cH	244	13250
	M	244	13100
(*E,E*)-**8**	cH	250	13000
	M	247	13100
(*E*)-**11**	cH	274	7200
	gas phase	268	
	M	272	7650
(*Z*)-**11**	cH	282	7100
(*E*)-**13**	cH	258	11600
(*Z*)-**13**	cH	260	5650

[a] The data of the geometric isomers of **1** and **2** were taken from Refs. 2 and 1, respectively. [b] cH and M stand for cyclohexane and methanol respectively.

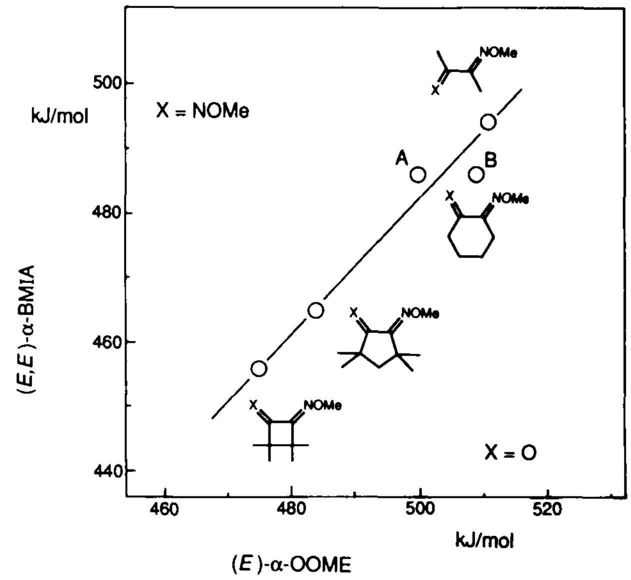

Figure 4. Relationship between the ππ absorption maximum energies of (*E,E*)-α-bis(methoxyimino)alkanes [(*E,E*)-α-**BMIA**] and the corresponding (*E*)-α-oxo oxime (m)ethyl ethers [(*E*)-α-OOME] for cyclohexane as solvent.*

planar. MNDO calculations confirm this conclusion[8]. The absorption maxima of the (*E,Z*)-isomers of both **4** and **5**, compared to those of the corresponding (*E,E*)-isomers, are shifted to shorter wavelength with a concomitant decrease in the molar extinction coefficients; these (*E,Z*)-isomers are, therefore, not planar. (*Z*)-**13** takes up an intermediate position. Its wavelength of maximum absorption (260 nm) is only slightly higher than that of the (*E*)-isomer (258 nm), but the corresponding extinction coefficient is very much smaller (5650 *versus* 11600 $l \cdot mol^{-1} \cdot cm^{-1}$). This leads us to suggest that the deviation from coplanarity may be somewhat larger for (*Z*)- than (*E*)-**13**. Apparently, steric hindrance between the methoxy group and the substituent at the adjacent iminoxy carbon is less for (*Z*)-**13** than for (*E,Z*)-**5**. This can be explained by the presence of the five-membered isoxazoline ring in (*Z*)-**13** for which the C(=NOMe)-C(=NOC)-CHEt angle will be larger than the C(=NOMe)-C(=NOC)-CH_3 angle of (*E,Z*)-**5**, rendering the degree of steric strain less with (*Z*)-**13** than with (*E,Z*)-**5**. A similar effect has been observed with the corresponding α-oxo oxime ethers[13].

X-ray structures

With the objective of obtaining geometric information on the configuration around the inter-iminyl C-C bond, in particular on the inter-iminyl dihedral angle, which determines

Table II Selected bond lengths, bond angles and dihedral angles.

Compound	Bond lengths (Å)				Bond angles (°)		Dihedral angle (°)
	C=N	N-O	NC-CN	H_2C-CN	C=N-O	N-O-R[a]	N=C-C=N
(*E,E*)-**5**	1.279	1.404	1.480		111.6	108.5	180
(*E,E*)-**8**	1.276	1.397	1.449		112.3	108.6	
	1.265	1.408			113.0	108.6	
(*E*)-**10**	1.283	1.403	1.459		110.9	91.0	179.6
	1.282	1.403			109.9		
14	1.278	1.416		1.529	115.4		180
				1.526			
15	1.258	1.415		1.515	114.4		
				1.485			

[a] For (*E,E*)-**5**, (*E,E*)-**8** and (*E*)-**10**, R stands for Me, Me and H, respectively.

the degree of conjugation between the two iminyl moieties, X-ray structures of (*E,E*)-**5**, (*E,E*)-**8** and (*E*)-**10** were determined. PLUTO[22] pictures of the three compounds are shown in Figures 5–7. Selected relevant bond lengths and angles of the O–N=C–C=N–O chromophore are collected in Table II. It appears that the inter-iminyl dihedral angles of the three compounds are all 180°. The acquired geometric information proved also to be useful for the assignment of the ^{1}H NMR absorptions to the various geometric isomers.

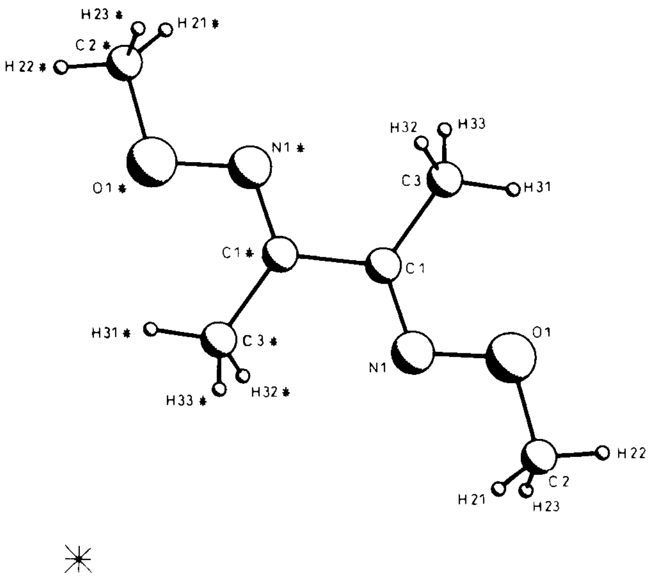

*Figure 5. X-ray structure of (*E,E*)-***5***.

The structures of the related and relevant (hydroxyimino)-tetramethylcyclohexanes **14** and **15** (X-ray structure determination of which are available[23,24]) will be first discussed. The positions of the four methyl groups essentially determine the geometry of the molecules. The cyclohexane ring of the 3,3,5,5-tetramethyl isomer **15** has the expected chair conformation, albeit slightly deformed due to repulsive interaction between the two axial methyl groups[24]. In contrast, the cyclohexane ring of the 2,2,6,6-tetramethyl isomer **14**, because of the added enhanced strain as a result of the close proximity of the hydroxy oxygen and the two adjacent methyl groups at C-6 has a somewhat twisted boat structure (Figure 8). The oxygen atom of **14** is positioned just between the two methyl groups attached to C-6, and the O, N, C-1, C-2, C-5 and C-6 atoms are located roughly in one plane. Although the ring structures of **14** and **15** are different, the structures of their C=N–O moieties are similar:

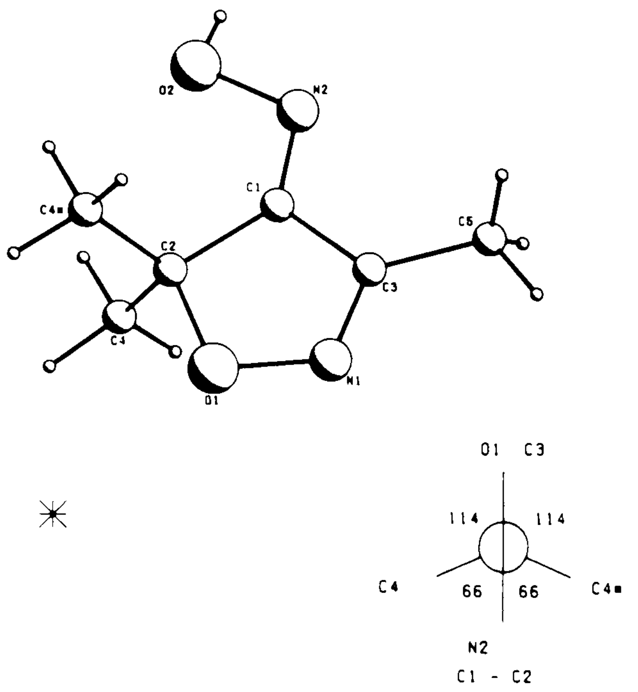

*Figure 7. X-ray structure of (*E*)-***10***.

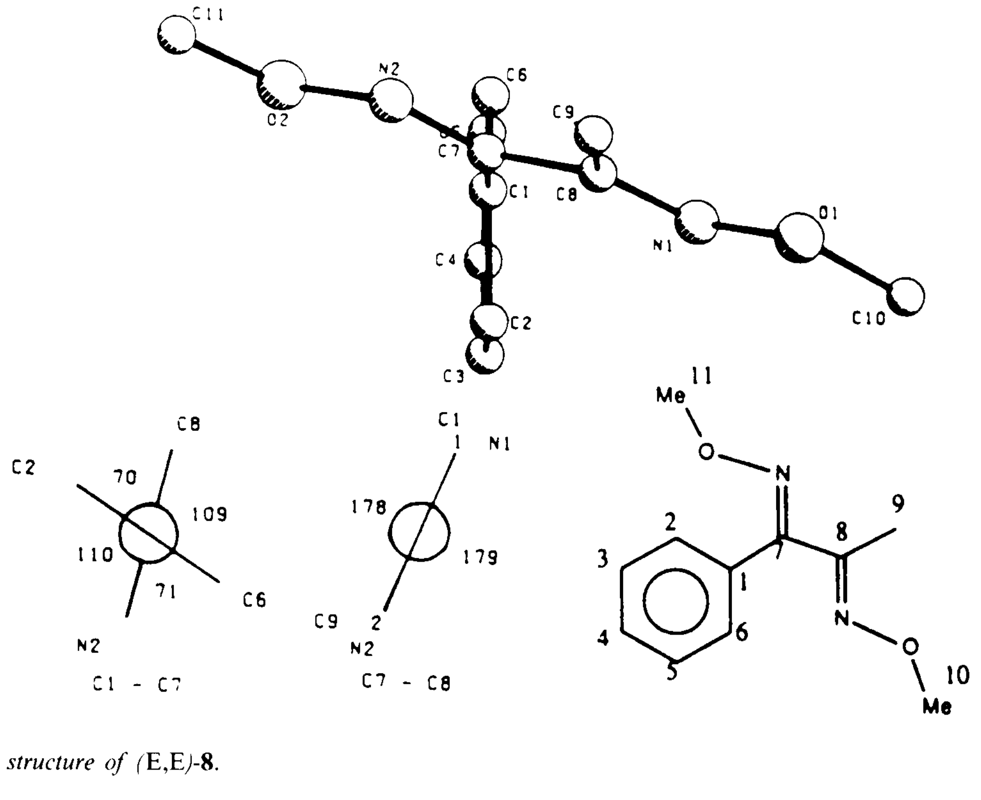

*Figure 6. X-ray structure of (*E,E*)-***8***.

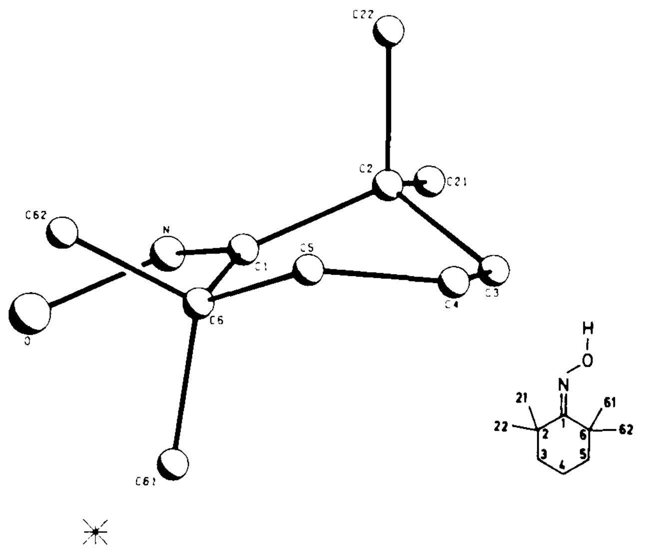

Figure 8. X-ray structure of **14**.

the C=N bond lengths are 1.258 and 1.278 Å, respectively, the N−O bond lengths are both 1.415 Å, and the C=N−O bond angles are 114.4 and 115.4°, respectively.

For the X-ray-analyzed α-bis(oxyimino) compounds, **5** and **8** both have the (*E*,*E*)-configuration, whereas the 4-(hydroxyimino)isoxazoline (*E*)-**10**, due to constraint of the C=N−O−C moiety in the five-membered ring, has the (*E*,*Z*)-configuration. In the crystalline state, the O−N=C−C=N−O chromophore of the three compounds is planar (Table II). This is also the case for (*E*)-**10** in methanol as solvent according to the UV data (λ_{max} 263 nm, ε 7350 $l \cdot mol^{-1} \cdot cm^{-1}$). For (*E*,*E*)-**3**, the UV data (Table I) suggest that its chromophore is somewhat twisted. A neutron-diffraction study and *ab-initio* calculations both showed (*E*,*E*)-1,2-bis(hydroxyimino)ethane to be planar[25]. The *ab-initio* calculations showed further that the predicted energy barriers between the various rotamers for the central inter-iminyl bond are sufficiently low for them all to be, in part, populated. For (*E*,*E*)-**5**, and probably (*E*,*E*)-**8**, the situation is apparently similar as for biacetyl, for which in solution various rotamers are populated at room temperature[26]. However, the very prodominant conformer will be the *s-trans* conformer.

For the 4-(hydroxyimino)isoxazoline (*E*)-**10**, the hydroxy oxygen is positioned just between the two methyl groups at C(2) (Figure 7) due to steric interaction between the geminal methyl groups and the hydroxy group, just as observed previously with **14**[23].

The established planarity of the O−N=C−C=N−O chromophores of the three compounds analyzed, even for (*E*,*E*)-**8**, of which the conjugation between the phenyl and the adjacent methoxyimino group is negligible, implies maximal conjugation within the bis(oxyimino) chromophore. These compounds, therefore, exhibit a large red shift of the UV absorption maximum when compared with simple monoximes and their *O*-alkyl ethers[14,27]. The MNDO π-orbital coefficients of the HOMO of any of the three α-bis(oxyimino) compounds under discussion are somewhat smaller than those of the HOMO of 2-(methoxyimino)propane[8]. In view of the bonding character of the HOMO between the C and N, the C=N bond will be slightly longer for the α-bis(oxyimino) compounds than the monoxyimino compound and, in view of its *anti*-bonding character between the N and O, the N−O bond will be somewhat shorter with the former compounds than the latter. The inter-iminyl bond, due to its additional π character, albeit anti-bonding, will thus be somewhat shorter than the C−C bonds adjacent to the C=N moiety in **14** and **15**, as is in fact observed (see Table II).

Experimental

The ^1H NMR spectra were recorded on Varian A-60D (using TMS as internal standard), Bruker AC-200 and Bruker WM-250 spectrometers. The latter two instruments were also used to obtain the ^{13}C NMR spectra. The IR spectra were obtained using Perkin-Elmer 254, 298 and 1310 spectrophotometers, while the UV absorption spectra were recorded on Cary 14 and Hewlett-Packard 8451-A diode array spectrophotometers, the latter having a resolution of 2 nm. The mass spectra and the accurate mass data were obtained using a Varian Mat-711 mass spectrometer at 70 eV.

Materials

The (*E*,*E*)-isomers of **2**, **3** and **5–7** were synthesized from the corresponding α-diketones, which were obtained commercially (as for the preparation of **3** and **5–7**) or prepared as described before (in the case of **2**)[28], by a modification of the method of *Karabatsos* and *Hsi*[29]. A solution of 2.2 equiv. of *O*-methylhydroxylamine and 1.0 equiv of potassium acetate dissolved in water was slowly added to a solution of a given α-diketone in ethanol. The resulting mixture was stirred until the yellow colour disappeared (2–5 h). When TLC or GLC did not show any remaining α-diketone, the mixture was worked-up as described previously[20]. The yields were: **2** (88%), **3** (65%), **5** (64%), **6** (55%) and **7** (90%).

(*E*,*E*)-1-Phenyl-1,2-bis(methoxyimino)propane [(*E*,*E*)-**8**] was synthesized from 1-phenyl-1,2-propanedione according to the method reported by *Eisterd* et al.[30], essentially identical to the procedure described above, but using pyridine as catalyst instead of potassium acetate. After recrystallization from ethanol, (*E*,*E*)-**8** was obtained as white crystals (m.p. 84°C) at a yield of 35%.

(*E*,*E*)-1,2-Bis(methoxyimino)indan [(*E*,*E*)-**4**] was prepared starting from 1-indanone, which was converted into (*E*)-2-(hydroxyimino)-1-indanone, as described for the preparation of (*E*)-4,7-dimethyl-2-(hydroxyimino)-1-indanone[31]. Methylation of the (*E*)-2-(hydroxyimino)-1-indanone according to the method of *Curtin* et al.[32] gave the crude corresponding methoxyimino compound in 75% yield, which was subsequently converted by the method of *Karabatsos* and *Hsi*[29] into (*E*,*E*)-**4** at a yield of 65%, after purification by column chromatography (silica + CH_2Cl_2).

(*E*)-3,4-Dihydro-4-(methoxyimino)-3,5,5-trimethylisoxazole [(*E*)-**11**]. (*E*)-**10**[7] (1.2 g, 8.5 mmol) was added to a solution of 0.25 g (10.9 mmol) of sodium in ethanol. The solution immediately turned yellow due to the formation of the oxime anion. Methyl iodide (1.5 equiv 1.0 ml) was then added and the mixture was stirred for 3 h at room temperature. The ethanol was removed by rotary evaporation, water was then added and the mixture extracted twice with ether. The combined ethereal solutions were washed twice with a 5% aqueous $NaHCO_3$ solution, once with brine and once with water.

The ethereal solution was dried over magnesium sulfate. Evaporation of the solvent gave 0.7 g (53%) of (*E*)-**11** as a colourless oil.

(*E*)-*trans*-4,5-Diethyl-3,4-dihydro-3-[(1-methoxyimino)ethyl]isoxazole [(*E*)-**13**]. This compound was prepared from the corresponding ketone **12**, which was synthesized according to the patent of *Duranleau*[33]. A solution made up of 20–25 mmol of nitroacetone[34], 10 ml of dry ethyl acetate, 30 ml of dry toluene, 40 equiv (70 ml) of (*E*)-3-hexene and a catalytic amount of 4-toluenesulfonic acid was refluxed for 19 h using a Dean–Stark trap for azeotropic removal of water. The excess 3-hexene was then distilled off (and collected for re-use) and, subsequently, under reduced pressure, toluene was also removed. The resulting crude mixture was purified by preparative GLC. The *trans*-3-acetyl-4,5-diethyl-4,5-dihydroisoxazole (**12**) obtained was converted into (*E*)-**13** according to the method of *Karabatsos* and *Hsi*[29] at a yield of 80%.

The geometric isomers of the various (*E*,*E*)-bis(methoxyimino)alkanes and of (*E*)-**11** and (*E*)-**13** were obtained[35] by photoisomerization of the synthetically obtained isomer in acetonitrile as solvent either by direct irradiation at 300 nm or by triplet photosensitization. Subsequent semi-preparative GLC separation then yielded the desired pure isomer(s).

Spectral data of α-bis(methoxyimino)alkanes and **12**

(*E*,*E*)-**2**. ^{1}H NMR (CDCl$_3$, δ): 1.337 (s, 12H), 1.638 (s, 2H), 3.939 (s, 6H). IR (CHCl$_3$, cm^{-1}): 2980, 2960, 2930, 2860, 2820, 1630, 1460, 1360, 1140, 1035, 910, 880, 860. MS (70 eV, *m/z*): 212 ($M^{+\cdot}$), 41 (base); accurate mass: obsd.: 212.1509, calcd. for $C_{11}H_{20}N_2O_2$: 212.1525; UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 257 (5970).
(*E*,*Z*)-**2**. ^{1}H NMR (CDCl$_3$, δ): 1.197 (s, 6H), 1.355 (s, 6H), 1.646 (s, 2H), 3.72 (s, 6H). IR (CHCl$_3$, cm^{-1}): 2960, 2930, 2850, 2820, 1590, 1460, 1360, 1140, 1075, 1030, 910, 890, 860. MS (70 eV, *m/z*): 212 ($M^{+\cdot}$), 41 (base); accurate mass obsd.: 212.1530, calcd. for $C_{11}H_{20}N_2O_2$: 212.1525. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 257 (5970).
(*Z*,*Z*)-**2**. ^{1}H NMR (CDCl$_3$, δ): 1.163 (s, 12H), 1.590 (s, 2H), 3.910 (s, 6H). IR (CHCl$_3$, cm^{-1}): 2960, 2930, 2900, 2850, 2820, 1620, 1465, 1455, 1385, 1375, 1080, 1050, 1020, 1005, 900, 840. MS (70 eV, *m/z*): 212 ($M^{+\cdot}$), 41 (base); accurate mass obsd.: 212.1513, calcd. for $C_{11}H_{20}N_2O_2$: 212.1525. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 240 (3250).

(*E*,*E*)-**3**. ^{1}H NMR (CDCl$_3$, δ): 1.61 (m, 4H), 2.58 (m, 4H), 3.98 (s, 6H). IR (CHCl$_3$, cm^{-1}): 2990, 2940, 2900, 2860, 2820, 1620, 1460, 1435, 1420, 1350, 1330, 1150, 1050, 980, 950, 910, 840, 660. MS (70 eV, *m/z*): 170 ($M^{+\cdot}$), 109 (base); accurate mass obsd.: 170.1046, calcd. for $C_8H_{14}N_2O_2$: 170.1055. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1})in cyclohexane], 246 (6820).
(*E*,*Z*)-**3**. ^{1}H NMR (CDCl$_3$, δ): 1.73 (br, 4H), 2.426 (t, *J* 6 Hz, 2H), 2.602 (t, *J* 6 Hz, 2H), 3.863 (s, 3H), 3.949 (s, 3H). IR (CHCl$_3$, cm^{-1}): 3000, 2940, 2900, 2860, 2820, 1610, 1460, 1435, 1420, 1260, 1155, 1040, 900, 875, 840. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 226 (5700).
(*Z*,*Z*)-**3**. ^{1}H NMR (CDCl$_3$,): 1.80 (br, 4H), 2.39 (br, 4H), 3.849 (s, 6H). IR (CHCl$_3$, cm^{-1}): 3000, 2940, 2900, 2860, 1660, 1625, 1460, 1445, 1320, 1160, 1035, 960, 950, 920, 875, 835. MS (70 eV, *m/z*): 170 ($M^{+\cdot}$), 109 (base). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 226 (4460).

(1*E*,2*E*)-**4**. ^{1}H NMR (CDCl$_3$, δ): 3.763 (s, 2H), 4.066 (s, 3H), 4.167 (s, 3H), 7.27–7.43 (m, 3H), 8.307 (d, *J* 7.7 Hz, 1H). ^{1}H NMR (C_6D_6, δ): 3.430 (s, 2H), 3.851 (s, 3H), 3.900 (s, 3H), 6.76–7.15 (m, 3H), 8.46 (d, 1H). MS (70 eV, *m/z*): 204 ($M^{+\cdot}$), 116 (base). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1})]: cyclohexane, 231 (10500), 247 (9050), 266 (10400), 290 (7500), 302 (8600), 315 (9500); methanol, 232 (9500), 269 (10400), 290 (8000), 305 (8000), 316 (7950).
(1*E*,2*Z*)-**4**. ^{1}H NMR (CDCl$_3$, δ): 3.753 (s, 2H), 4.106 (s, 3H), 4.164 (s, 3H), 7.28–7.38 (m, 3H), 7.69 (d, 1H). ^{1}H NMR (C_6D_6, δ): 3.44 (s, 2H), 3.89 (s, 3H), 4.00 (s, 3H), 6.7–7.0 (m, 3H), 7.85 (d, 1H). IR (CHCl$_3$, cm^{-1}): 3000, 2940, 2900, 2820, 1630, 1605, 1570, 1465, 1330, 1040, 1020, 1010, 900, 875, 830.
(1*Z*,2*E*)-**4**. ^{1}H NMR (CDCl$_3$, δ): 3.907 (s, 2H), 4.077 (s, 3H), 4.187 (s, 3H), 7.29–7.60 (m, 3H), 7.93 (d, 1H). ^{1}H NMR (C_6D_6, δ): 3.579 (s, 2H), 3.946 (s, 3H), 3.951 (s, 3H), 6.90–7.08 (m, 3H), 7.99 (d, 1H).
(1*Z*,2*Z*)-**4**. ^{1}H NMR (CDCl$_3$, δ): 3.707 (s, 2H), 4.020 (s, 3H), 4.097 (s, 3H), 7.28–7.32 (m, 3H), 7.66 (d, 1H). ^{1}H NMR (C_6D_6, δ): 3.339 (s, 2H), 3.902 (s, 3H), 3.986 (s, 3H), 6.74 (m, 1H), 6.94 (m, 2H), 7.79 (d, 1H).

(*E*,*E*)-**5**. ^{1}H NMR (CDCl$_3$, δ): 2.00 (s, 6H), 3.95 (s, 6H). ^{13}C NMR (CDCl$_3$, δ): 9.35 (Me), 61.75 (OMe), 153.40 (C=N). IR (CHCl$_3$, cm^{-1}): 3000, 2960, 2940, 2820, 1590, 1460, 1440, 1365, 1130, 1040, 975, 895. MS (70 eV, *m/z*): 144 ($M^{+\cdot}$), 18 (base). UV [λ_{max} *(nm)*, (*ε*) (l·mol^{-1}·cm^{-1}) in cyclohexane], 242 (14000).
(*E*,*Z*)-**5**. ^{1}H NMR (CDCl$_3$, δ): 1.99 (s, 3H), 2.02 (s, 3H), 3.82 (s, 3H), 3.89 (s, 3H). IR (CHCl$_3$, cm^{-1}): 3000, 2960, 2940, 2820, 1625, 1460, 1435, 1370, 1140, 1050, 1035, 900, 890. MS (70 eV, *m/z*): 144 ($M^{+\cdot}$), 18 (base). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 236 (8500).
(*Z*,*Z*)-**5**. ^{1}H NMR (CDCl$_3$, δ): 1.94 (s, 6H), 3.81 (s, 6H). IR (CHCl$_3$, cm^{-1}): 3000, 2960, 2940, 2820, 1620, 1460, 1440, 1370, 1150, 1070, 1035, 995, 890. MS (70 eV, *m/z*): 144 ($M^{+\cdot}$), 18 (base). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane, 216 (6600).

(*E*,*E*)-**6**. ^{1}H NMR (CDCl$_3$, δ): 1.01 (t, *J* 7.5 Hz, 3H), 1.97 (s, 3H), 2.56 (q, *J* 7.5 Hz, 2H), 3.91 (s, 3H), 3.93 (s, 3H). IR (CHCl$_3$, cm^{-1}): 2980, 2940, 2900, 2880, 2820, 1585, 1465, 1440, 1365, 1140, 1050, 960, 880. FI-MS *(m/z)*: 158 ($M^{+\cdot}$). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane] 242 (13400).

(*E*,*E*)-**7**. ^{1}H NMR (CDCl$_3$, δ): 0.89 (t, *J* 7.5 Hz, 3H), 1.50 (m, 2H), 1.97 (s, 3H), 2.53 (t, *J* 7.5 Hz, 2H), 3.90 (s, 3H), 3.92 (s, 3H). IR (CHCl$_3$, cm^{-1}): 2960, 2940, 2900, 2860, 2820, 1580, 1460, 1440, 1360, 1140, 1050, 980, 910, 895, 880. MS (70 eV, *m/z*): 172 ($M^{+\cdot}$), 141 (base); accurate mass obsd.: 172.1213, calcd. for $C_8\,H_{16}N_2O_2$: 172.1212. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}]: cyclohexane, 244 (13250); methanol, 244 (13100).

(*E*,*E*)-**8**. ^{1}H NMR (CDCl$_3$, δ): 2.13 (s, 3H), 3.82 (s, 3H), 3.92 (s, 3H), 7.23–7.38 (m, 5H). ^{13}C NMR (APT, CDCl$_3$, d): 10.72 (3-C), 62.19 + 62.63 (2 × OMe), 127.45–129.07 (Ph C-2, C-3, C-5, C-6), 128.33 (Ph C-4), 131.36 (Ph C-1), 154.14 + 154.83 (2 × C=N). IR (CHCl$_3$, cm^{-1}): 3080, 3060, 2990, 2960, 2940, 2900, 2820, 1600, 1460, 1440, 1370, 1060, 1030, 1015, 975, 870, 695. MS (70 eV, *m/z*): 206 ($M^{+\cdot}$), 103 (base): accurate mass obsd.: 206.1044, calcd. for $C_{11}H_{14}N_2O_2$: 206.1055. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}]: cyclohexane, 250 (13000); methanol, 247 (13100).

(*E*)-**11**. ^{1}H NMR (CDCl$_3$, δ): 1.561 (s, 6H), 2.024 (s, 3H), 3.911 (s, 3H). ^{1}H NMR (C_6D_6, δ): 1.483 (s, 6H), 1.852 (s, 3H), 3.544 (s, 3H). ^{13}C NMR (APT, CDCl$_3$, δ): 8.99 (5,5-Me$_2$), 21.91 (3-Me), 62.48 (OMe), 83.99 (5-C), 150.59 (3-C), 162.74 (4-C). IR (CHCl$_3$, cm^{-1}): 2990, 2980, 2930, 2900, 2820, 1630, 1580, 1460, 1440, 1400, 1380, 1360, 1260, 1180, 1150, 1080, 1040, 1010, 930, 920, 900. 845, 700. MS (70 eV, *m/z*): 156 ($M^{+\cdot}$), 43 (base); accurate mass obsd.: 156.0898: calcd. for $C_8H_{14}N_2O_2$: 156.0899. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1})]: cyclohexane, 274 (7200); methanol, 272 (7650).
(*Z*)-**11**. ^{1}H NMR (CDCl$_3$, δ): 1.415 (s, 6H), 2.316 (s, 3H), 3.893 (s, 3H). ^{1}H NMR (C_6D_6, δ): 1.286 (s, 6H), 2.194 (s, 3H), 3.565 (s, 3H). UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane]: 282 (7100).

12. ^{1}H NMR (CDCl$_3$, δ): 0.860 (t, *J* 7.4 Hz, 3H), 0.940 (t, *J* 7.4 Hz, 1.44–1.77 (m, 2 × 2H), 2.462 (s, 3H), 3.03–3.10 (m, 1H), 4.36–4.43 (m, 1H). ^{13}C NMR (APT, CDCl$_3$, δ): 8.9 + 10.6 (2 × Me), 23.8 (4-CH$_2$), 26.8 (acetyl Me), 27.9 (5-CH$_2$), 50.7 (4-C), 90.3 (5-C), 159.9 (C=N), 193.3 (C=O). IR (CHCl$_3$, cm^{-1}): 2960, 2930, 2880, 1680, 1565, 1460, 1375, 1350, 1310, 1280, 1080, 935, 840. MS (70 eV, *m/z*): 169 ($M^{+\cdot}$), 43 (base, MeC=O^{+}); accurate mass obsd.: 169.1103, calcd. for $C_9H_{15}NO_2$: 169.1103. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1})]: cyclohexane, 259 (6500), 320 (30); ethanol, 261 (6900), 320 (25).
(*E*)-**13**. ^{1}H NMR (CDCl$_3$, δ): 0.808 (t, *J* 7.5 Hz, 3H, ethyl Me), 0.866 (t, *J* 7.5 Hz, 3H, ethyl Me), 1.3–1.7 (m, 4H, 2 × CH$_2$), 2.010 (s, 3H, N=CCH$_3$), 3.03–3.10 (m, 1H), 3.878 (s, 3H, OMe), 4.24–4.33 (m, 1H). Accurate mass obsd.: 198.1358, calcd. for $C_{10}H_{18}N_2O_2$: 198.1368. UV [λ_{max} (nm), (ε) (l·mol^{-1}·cm^{-1}) in cyclohexane], 258 (11600).
The presumed *trans* orientation of the two ethyl groups in (*E*)-**13** is based on the observation that the reaction according to *Duranleau*[33] using an isomeric mixture of 2-pentene instead of (*E*)-3-hexene yields a mixture of *trans*-3-acetyl-4(5)-ethyl-4,5-dihydro-5(4)-methylisoxazoles. The *trans* orientation of the two alkyl groups was concluded from the 250-MHz ^{1}H-shift-correlated 2D NMR spectrum of the mixture of the two compounds.

X-ray structure determinations

All the crystallographic data have been published previously[36].

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[17] The O–N=N–N=N–O chromophores of the three geometric isomers of **3** are not planar, as result of their constraint with the cyclohexane ring. For the same reason the O=C–C=O chromophore of 3,3,5,5-tetramethyl-1,2-cyclohexanedione is not planar, its inter-carbonyl dihedral angle being in fact 42°[13].

[18] The situation with (*E*,*E*)-**8** differs strongly from that of the corresponding dioxo compound 1-phenyl-1,2-propanedione of which the phenyl group is strongly conjugated with the adjacent carbonyl group but the conjugation between the two carbonyl groups is only very limited, the inter-carbonyl phenyl and the inter-carbonyl dihedral angles being estimates as 0–10° and 70–110°, respectively[19]. It should be realized that differences in geometry between a ketone and the corresponding oxime ether were observed previously[20,21].

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