Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Self-association and stereochemistry study of 2-methylthio-, 2-dimethylaminocyclohexanone oximes and the parent cyclohexanone oxime

Paulo R. Olivato,[a]* Douglas S. Ribeiro,[a] J. Zukerman-Schpector[a,b] and Gabriella Bombieri[c]

[a]Instituto de Química, Universidade de São Paulo, CP 26077, CEP, 05513-970 São Paulo, SP, Brazil, [b]Laboratório de Cristalografia Estereodinâmica e Modelagem Molecular, DQ-UFSCar, CP 676, CEP, 13565-905 São Carlos, SP, Brazil, and [c]Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, I-20131 Milan, Italy

Correspondence e-mail: prolivat@quim.iq.usp.br

Received 5 April 2001
Accepted 1 June 2001

X-ray diffraction analyses of 2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ [X = SMe (1), NMe_2 (2)] and of the parent compound [X = H (3)] showed that their cyclohexyl rings are in a slightly distorted chair conformation. These compounds assume in the solid state the (*E*) configuration bearing the 2-substituents in the axial conformation. Compounds (1) and (2) exist as dimeric and polymeric hydrogen-bond associates, respectively. Low-temperature X-ray analysis of the cyclohexanone oxime (3) showed that the molecules are associated forming two independent trimers. The dimer in (1) and the trimer in (3) are built up *via* [$O-H\cdots N{=}C$] hydrogen bonds, while the polymer of (2) is *via* the [$OH\cdots NMe_2$] hydrogen bond. The comparative IR ν_{OH} and $\nu_{C=N}$ analysis of the title compounds, in the solid state and in CCl_4 solution, fully supports the nature of the associates for (1)–(3) obtained by X-ray diffraction. The IR azomethyne frequency shift analysis ($\Delta\nu_{C=N}$) also suggests the occurrence of the $\pi_{C=N}/\sigma^*_{C-X}$ orbital interaction which stabilizes the axial conformations of (1) and (2).

1. Introduction

A previous study (Olivato *et al.*, 1995) on some α-hetero-substituted acetone oximes by IR, ^{1}H and ^{13}C NMR spectroscopies, and X-ray crystal analysis (of the α-dimethylamino derivative) supported by molecular mechanics calculations indicated that these compounds in the gas phase and in solution exist predominantly in the (*E*)-diastereomeric form and in the *gauche* conformation which is stabilized by $\pi_{C=N}/\sigma^*_{C-X}$ orbital interactions. Moreover, ν_{OH} and $\nu_{C=N}$ bands in the IR spectra show the existence of only a monomeric form in chloroform solutions at concentrations below 10^{-2} *M*, while in carbon tetrachloride self-associated species are also present.

A ^{1}H NMR study (Denmark *et al.*, 1990) on a series of *trans*-3-alkyl-2-chloro(methoxy)cyclohexanone oximes indicated that the compounds exist in the diaxial chair conformation and suggests that the $\sigma^*_{C-X} \leftarrow \pi_{C=NOH}$ interaction is the main factor which stabilizes this conformation. Our recent study (Ribeiro *et al.*, 2000) on some α-hetero-substituted cyclohexanone oximes by ^{1}H and ^{13}C spectroscopy supports these findings, showing that the 2-substituents preferentially adopt the axial conformation with the (*E*) configuration in chloroform solution.

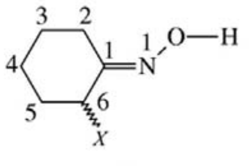
In order to further investigate the self-association and stereochemistry of the 2-substituted oximes, the present paper reports the X-ray crystal structure and IR spectra (in the solid state and in carbon tetrachloride solution) of 2-substituted cyclohexanone oximes: (I) with X = SMe (1), NMe_2 (2) and H (3). The atom labeling was chosen so that in all cases C2 in the

Table 1
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_7H_{13}NOS$	$C_8H_{16}N_2O$	$C_6H_{11}NO$
Chemical formula weight	159.24	156.23	113.16
Cell setting, space group	Monoclinic, $P2_1/c$	Orthorhombic, Pb_{ca}	Trigonal, $P3$
a, b, c (Å)	5.2634 (9), 23.222 (3), 7.3962 (8)	12.5662 (6), 10.1714 (6), 14.3863 (9)	20.9830 (3), 20.9830 (3), 7.6210 (3)
β (°)	107.66 (1)	90	90
V (Å^3)	861.4 (2)	1838.8 (2)	2905.9 (1)
Z	4	8	18
D_x (Mg m^{-3})	1.228	1.129	1.16
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	25	23	Cell parameters refined with all data
θ range (°)	9.14–18.02	9.81–18.27	–
μ (mm^{-1})	0.312	0.076	0.08
Temperature (K)	293 (2)	293 (2)	100
Crystal form, color	Irregular, colorless	Irregular, colorless	Prismatic, colorless
Crystal size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.25 × 0.10	0.38 × 0.30 × 0.24
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius KappaCCD
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
No. of measured, independent and observed parameters	1725, 1602, 979	1711, 1711, 1204	12 992, 4440, 3993
Criterion for observed reflections	$F^2 > 2\sigma F^2$	$F^2 > 2\sigma F^2$	$F^2 > 2\sigma F^2$
$R_{\rm int}$	0.0244	0	0.03
$\theta_{\rm max}$ (°)	25.49	25.47	27.46
Range of h, k, l	$-6 \rightarrow h \rightarrow 6$ $0 \rightarrow k \rightarrow 28$ $-8 \rightarrow l \rightarrow 0$	$0 \rightarrow h \rightarrow 15$ $-12 \rightarrow k \rightarrow 0$ $0 \rightarrow l \rightarrow 17$	$0 \rightarrow h \rightarrow 27$ $-26 \rightarrow k \rightarrow 23$ $-9 \rightarrow l \rightarrow 9$
No. and frequency of standard reflections	3 every 60 min	3 every 60 min	–
Intensity decay (%)	1.3	0.4	–
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0364, 0.1017, 1.003	0.039, 0.1146, 1.031	0.092, 0.270, 1.061
No. of reflections and parameters used in refinement	1602, 92	1711, 103	3393, 496
H-atom treatment	Mixed	Riding	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.2459P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.2888P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1771P)^2 + 2.9548P]$, where $P = (F_o^2 - 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.000	0.000	0.03
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.132, −0.204	0.129, −0.147	0.38, −1.14

Computer programs used: *CAD*-4 *Software* (Enraf–Nonius, 1989), *MolEN* (Fair, 1990), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*86 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *ORTEP*II (Johnson, 1976), *ZORTEP* (Zsolnay, 1995).

ring is that eclipsed with respect to the O atom.



(I)

2. Experimental

2.1. Materials

The spectrograde carbon tetrachloride for IR measurements was used without further purfication.

The preparation of the 2-methylthio- (1), 2-dimethylaminocyclohexanone oxime (2) and the parent cyclohexanone oxime (3) have already been described in the literature (Ribeiro *et al.*, 2000). Suitable crystals of (1)–(3) for the X-ray analyses were obtained by vapor diffusion from chloroform/*n*-hexane at 273 K.

2.2. IR measurements

The IR spectra were obtained in an FT-IR Nicolet Magna 550 spectrometer with 1.0 cm^{-1} resolution. For oximes (1)–(3) the $\nu_{\rm OH}$ (4000–3000 cm^{-1}) and $\nu_{\rm C{=}N}$ stretching (1800–1500 cm^{-1}) regions were recorded in 3.0–5.0 × 10^{-2} mol dm^{-3} carbon tetrachloride solution using a 0.519 mm sodium chloride cell, and in the solid phase using KBr pellets.

2.3. Crystal data

The measurements of (1) and (2) were performed on a CAD-4 Mach3 Enraf–Nonius diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at room

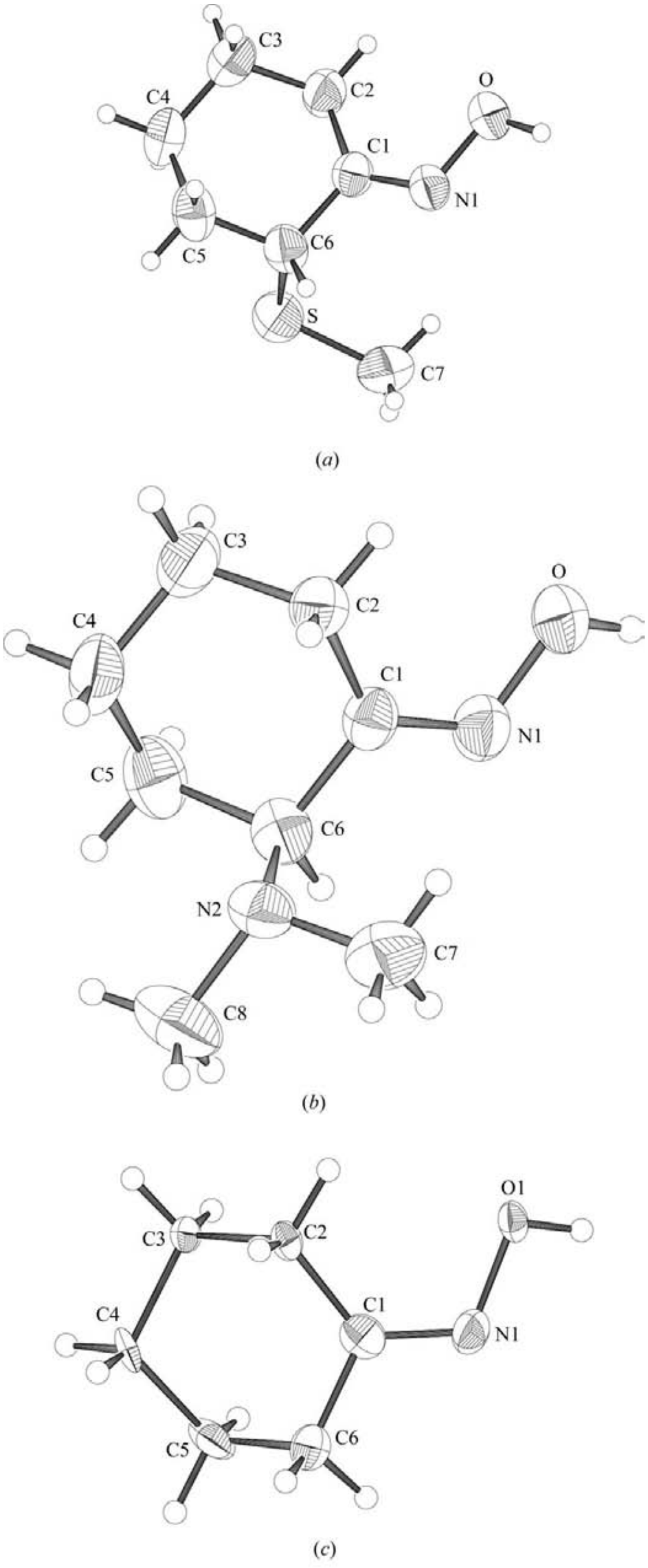


Figure 1
Crystal structures of (*a*) (1), (*b*) (2) and (*c*) (3), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

temperature ($T = 293$ K), using the $\theta/2\theta$ scan method. H atoms were located on stereochemical grounds, except those of the hydroxyl groups which were found in difference Fourier maps; all were refined riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they were attached. For (3) the data collection was first made on a Nonius CAD-4 diffractometer with cell parameters $a = b = 12.120\,(3)$, $c = 8.066\,(2)$ Å, $\gamma = 120°$, hexagonal system, space group $P6_3$ ($Z = 6$), in agreement with that previously obtained by Okaya *et al.* (1956). The structure showed problems of thermal diffuse scattering as already evidenced by Okaya *et al.* (1956) and it was impossible to refine the structure below 20%. A new data collection at 100 K was then performed on a Nonius CAD-4 CCD diffractometer and a supercell was discovered with cell parameters $a = b = 20.9830\,(3)$, $c = 7.6210\,(3)$ Å, $\gamma = 120°$, belonging to the trigonal system ($Z = 18$). φ scan with 2° steps followed by ω scan, graphite-monochromated Mo $K\alpha$ radiation. Among the possible space groups are $P3$ and $P\bar{3}$. The refinement converged by using the non-centrosymmetric space group $P3$ with six independent molecules in the asymmetric unit, but severe disordering problems were still present in the structure. A difference Fourier map calculated in the final cycles of refinement ($R = 0.12$) showed the presence of residuals of electron density of the order 1.6 e Å^{-3}. They have been interpreted as alternative orientations of the molecules 2, 3 and 6 (identified in Fig. 4 by the numbering of the respective N atoms). In particular, in molecule 2 C21*A*, C22*A* and C25*A* are the alternative positions of the corresponding unlabeled *A* atoms, in 3 O3*A*, N3*A*, C31*A*, C32*A*, C34*A* and C35*A*, in 6 O6*A*, C62*A*, C64*A* and C65*A*, and in 5 only O5*A*. They have been assigned, on average, an occupancy factor of 0.2. They have been refined using the *SHELXL*97 program (Sheldrick, 1997) with isotropic thermal parameters, while the other non-H atoms were refined anisotropically. The H atoms were treated as in the two previously mentioned derivatives. At this point the conventional R value lowered to 0.092, which was considered as final because no better agreement was possible nor apparent pseudosymmetries confirmed. In any case, the molecular conformations were judged reliable by comparison with the molecular conformations detected in the two comparable structures of (1) and (2). Specific details of the structure analyses are given in Table 1.[1]

2.4. Calculations

The geometric parameters of the (*E*)-2-methylthio- (1) and 2-dimethylaminocyclohexanone oximes (2) were computed at the HF/6-31G* *ab initio* level, using the *Gaussian*94 series of programs (Frisch *et al.*, 1995).

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0119). Services for accessing these data are described at the back of the journal.

3. Discussion

The single molecules are shown in Fig. 1 and the ways in which they are linked are presented in Figs. 2, 3 and 4. The selected X-ray geometrical data for the title compounds are collected in Table 2. In all compounds the cyclohexyl ring is in a slightly distorted chair conformation, as shown in Table 3, where Cremer & Pople's (1975) puckering parameters are given, as calculated by *PARST*95 (Nardelli, 1995).

In (2) the intermolecular interaction involves the hydrogen bond between the hydroxyl H atom, as a proton donor, and the sp^3 lone pair of the dimethylamino nitrogen atom N2 (Table 2). The angles around N2, which are all $\sim 110^\circ$, indicate an evident pyramidalization of the bonds supporting the sp^3 hybridization of the N2 lone pair.

In (1) the molecules form centrosymmetric dimers (Fig. 2) through hydrogen bonds between the hydroxyl H atom and the less basic sp^2 lone pair of the N1 atom of the azomethyne group (Table 2).

In the case of (2) the hydroxyl H atom is bonded to the more basic dimethylamino sp^3 nitrogen lone pair [IE[2] = 8.46 eV, for MeC(=NOH)CH$_2$NMe$_2$; Dal Colle *et al.*, 1998], instead of the less basic azomethyne sp^2 nitrogen lone pair [IE = 10.15 eV, for MeC(=NOH)CH$_2$NMe$_2$; Dal Colle *et al.*, 1998]. However, the H$\cdots$N2 distance (1.98 Å) in (2) is only marginally longer than the H$\cdots$N1 distance (1.94 Å) in the dimer of (1). This unexpected behavior for the H$\cdots$N2 contact of (2) is due to the existence of an intermolecular contact between the axial methylene H atom on C2 and the azomethyne nitrogen (H2$\cdots$N1 = 2.59 Å, C2—H2$\cdots$N1 = 154°), close to the sum of the van der Waals radii (2.7 Å; Bondi, 1964), precluding a closer H$\cdots$N2 approach between the more basic sp^3 nitrogen lone pair and the hydroxyl H atom. In spite of this, IR data show that the O—H$\cdots$N(2) hydrogen bond for (2) is stronger than the OH$\cdots$N(1) hydrogen bond for the dimer of (1) (see below).

It should be pointed out that in the solid state the N1—C1—C6—X torsion angle α (Table 2) for (1) and (2) is in the range 101–110°, while the O—N1—C1—C2 β angle is close to 0°, indicating that in both compounds the 2-substituents assume the axial conformation with the (*E*)-configuration in relation to the O atom of the hydroxyl azomethyne moiety.

This geometry allows the occurrence of the $\pi_{\rm C=N}/\sigma^*_{{\rm C}-X}$ orbital interaction (Denmark *et al.*, 1990), which should overcome the 1,3-diaxial steric repulsion between the axial substituent at C6 and the axial H atoms at C2 and C4. Additionally, the H—O—N1—C1 torsion γ angle for (1) and (2) is close to 180°, indicating, as in the case of acetone oximes (Olivato *et al.*, 1995), that the hydroxyl H atom lies on the same side of the 2-substituent.

Table 2 also shows that the cyclohexanone oxime molecules (3) are associated in the solid state by forming two independent trimers, each one held together *via* three O—H$\cdots$N hydrogen bonds.

A possible crystallographic threefold axis in the center of the trimers must be ruled out due to the presence of different conformations in the cyclohexyl rings, *i.e.* the relative position

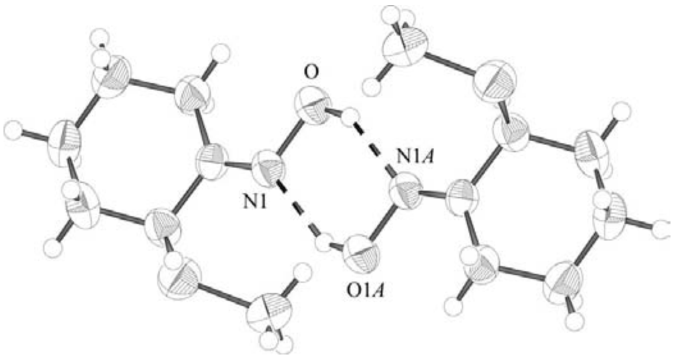

Figure 2
Dimer of (1) showing hydrogen bonding between the hydroxyl hydrogen and azomethyne N atoms.

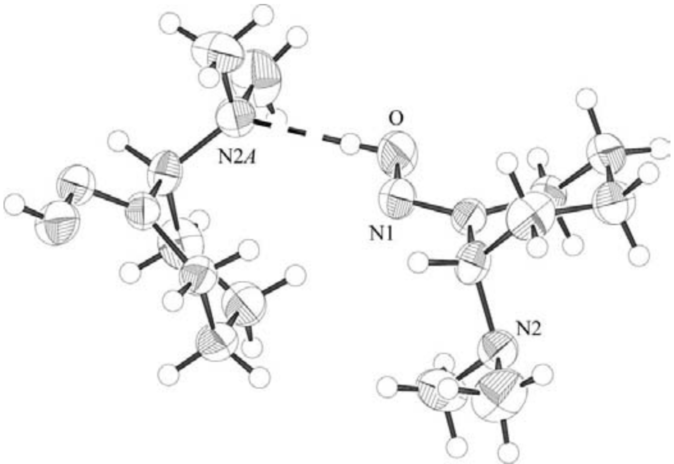

Figure 3
Two molecules of the polymer of (2) held together by the hydrogen bonding between the hydroxyl hydrogen and dimethylamino nitrogen atoms (symmetry operation: $A = -x, \frac{1}{2} + y, -\frac{1}{2} - z$).

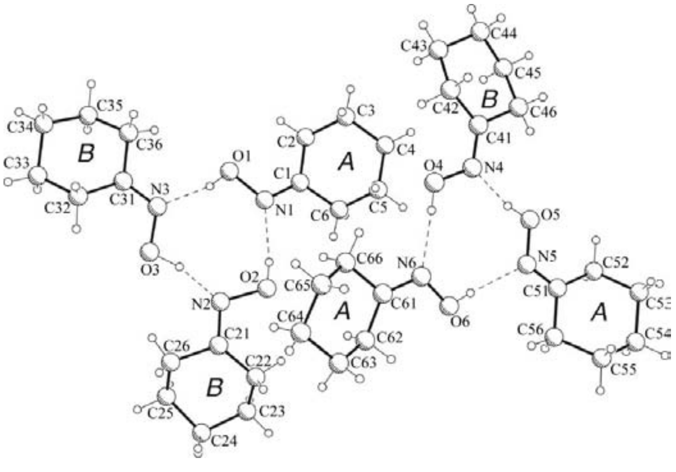

Figure 4
The two independent trimers of (3) with the atom numbering. Dotted lines indicate the hydrogen bonds. The letters *A* and *B* inside the rings indicate the two main inverted chairs conformations of the cyclohexyl rings. (Alternative conformations are omitted for sake of clarity.)

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[2] IE = ionization energy.

Table 2
Selected X-ray geometrical data of the 2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ [(1) and (2)] and of the parent compound (3).

Conf. refers to the axial (ax.) conformation. For the torsion angles, the labeling of the atoms are shown in Fig. 1; α = N1—C1—C6—X, β = O—N1—C1—C2, γ = H—O—N1—C1, δ = C1—C6—S—C7(Me) for (1) and C1—C6—N2—C7(Me) for (2); δ' = C1—C6—N2—C8(Me) for (2).

			Torsion angles (°)								
Compound	X	Conf.	α	β	γ	δ	δ'		$D\cdots A$ (Å)	$H\cdots A$ (Å)	$D—H\cdots A$ (°)
(1)	SMe	ax.	−101.2 (2)	−0.5 (3)	176	68.3 (2)	–	O—H···N1	2.803 (2)	1.94	150
(2)	NMe_2	ax.	109.6 (1)	1.6 (2)	180	57.4 (2)	−178.4 (1)	O—H···N2	2.797 (2)	1.98	177
(3)†	H^1	–	–	3.2 (9)	−172			O1—H1···N3	2.762 (8)	1.94	165
	H^2	–	–	−23 (1)	−180			O2—H2···N1	2.862 (9)	2.06	167
	H^3	–	–	−1.5 (9)	178			O3—H3···N2	2.755 (7)	1.72	166
	H^4	–	–	0.9 (7)	178			O4—H4···N6	2.799 (6)	1.98	176
	H^5	–	–	2.7 (8)	−173			O5—H5···N4	2.783 (6)	1.86	168
	H^6	–	–	−4 (1)	176			O6—H6···N5	2.737 (9)	1.96	175

† The superscripts in H identify the molecules shown in Fig. 4.

Table 3
Cremer & Pople's (1975) puckering parameters of cyclohexyl rings of some 2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ [(1) and (2)] and of the parent compound (3) (main conformations).

	X	q_2 (Å)	q_3 (Å)	φ_2 (°)	Q (Å)	θ_2 (°)
(1)	SMe	0.107 (3)	−0.504 (2)	−6 (1)	0.515 (2)	168.0 (3)
(2)	NMe_2	0.067 (2)	0.538 (2)	−151 (1)	0.543 (2)	7.1 (2)
(3)	H					
	C1···C6	0.116 (6)	0.517 (7)	179 (4)	0.530 (7)	12.6 (7)
	C21···C26	0.180 (13)	−0.442 (1)	10 (4)	0.477 (13)	158 (1)
	C31···C36	0.121 (8)	−0.525 (7)	−6 (3)	0.538 (8)	167.0 (8)
	C41···C46	0.067 (6)	−0.540 (7)	10 (6)	0.545 (7)	172.9 (6)
	C51···C56	0.092 (6)	0.553 (6)	−149 (4)	0.560 (6)	9.4 (7)
	C61···C66	0.128 (14)	0.492 (12)	−65 (5)	0.508 (10)	15 (2)

Table 4
Deviations (Å) of C1(*ipso*) and C4(*para*) atoms from the central mean plane for the cyclohexyl rings in the crystal of the cyclohexanone oxime (3) (main conformations).

The numbering of the atoms is illustrated in Fig. 4.

Ring	C(*ipso*)	C(*para*)
C1···C6	−0.508 (6)	0.698 (8)
C21···C26	0.387 (11)	−0.688 (15)
C31···C36	0.510 (6)	−0.711 (10)
C41···C46	0.564 (5)	−0.674 (7)
C51···C56	−0.571 (5)	0.700 (6)
C61···C66	−0.661 (9)	0.636 (11)

of the out-of-plane C atoms are different. However, the main conformations could be restricted mainly to the two inverted chairs labeled with the letters *A* and *B*, respectively, in Fig. 4. They are present in an approximate 1:2 ratio, in both trimers, as evidenced by the deviations of C1 and C4, the two out-of-plane C atoms, with respect to the mean plane calculated through the four central C atoms C2, C3, C5 and C6. This can be seen in Table 4, for each trimer C1 is on the same side in two rings and in the opposite side in the third ring, so that the deviation of C4 is reversed.

One 'trimer' is mainly formed by the combination *ABB* and the second by *BAA*. However, if we consider the alternative disordered positions of some atoms (see §2) we notice, to a minor extent, the presence of additional conformations. In molecule 2 the cyclohexyl ring can also assume the *A* conformation, in 3 the twist conformation and in 6 the *B* conformation (at least in the approximation of the analysis.) This explains the difficulties of the structure refinement. The molecular packing is shown in Fig. 5 (alternative positions are not shown for clarity).

Ab initio calculations at the 6-31G* level (Table 5) were performed on the (*E*)-diastereomers of (1) and (2), which is the more stable isomer with respect to (*Z*) in solution (Ribeiro *et al.*, 2000; Denmark *et al.*, 1990) and the only one present in the solid state. In fact, the *ab initio* computations show that the (*E*) configuration is more stable than (*Z*) by 9.82 kJ mol^{-1} for (1) and by 2.64 kJ mol^{-1} for (2) in the gas phase. It should be mentioned that the (*E*) diastereomers of (1) and (2) are stabilized, both in the gas and in the solid state, by an intramolecular electrostatic interaction between the negatively charged O atom ($q_O \simeq -0.61e$) and one or two H atoms ($q_H \simeq +0.20e$) of the *syn* CH_2 group, which are *ca* 2.3 Å away from O atom in the solid and gas phases, which is less than the sum of

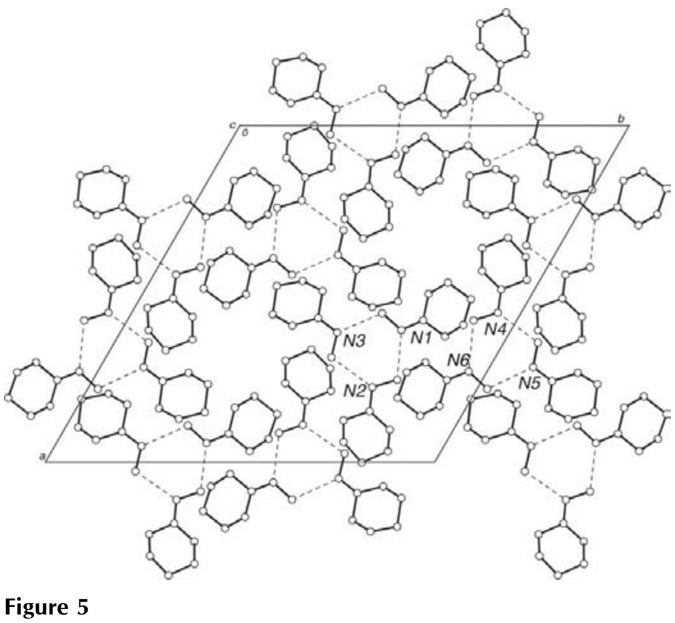

Figure 5
Molecular packing of (3) viewed down **c**. H atoms are omitted for clarity.

Table 5
Relative energy, dipole moment (dpm) and selected torsion angles optimized for the *equatorial* and *axial* conformers of some (*E*)-2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ (1) and (2) at the 6-31G* level.

Conf. refers to equatorial (eq.) or axial (ax.) conformation; *P*: molar fraction of each rotamer as a percentage; dihedral angles: the labeling of the atoms is shown in Fig. 1; α = N1—C1—C6—*X*; β = O—N1—C1—C2; γ = H—O—N1—C1; δ = C1—C6—S—C(Me) for (1) and C1—C6—N2—C[Me(*A*)] for (2); δ' = C1—C6—N2—C[Me(*B*)] for (2).

						Dihedral angles (°)				
Compound	*X*	Conf.	*E* (kJ mol^{-1})	*P* (%)	dpm (D)	α	β	γ	δ	δ'
(1)	SMe	eq.	6.65	1.3	1.84	0.8	0.3	177.7	68.0	–
		ax.	0.0	98.7	0.95	106.8	1.1	178.1	69.0	–
(2)	NMe_2	eq.	13.23	0.5	1.47	3.5	0.3	178.2	76.3	151.2
		ax	0.0	99.5	0.99	118.6	1.3	179.9	61.9	172.7

Table 6
O—H stretching bands (cm^{-1}) in the IR spectra of some 2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ [(1) and (2)] and of the parent compound (3).

Solid and CCl_4: see §2. $\nu_{OH(ass.)}$ and $\nu_{OH(free)}$ refer to the associate and free forms, respectively; $\bar{\nu}_{OH(ass.)}$ is the mean frequency value of the $\nu_{OH(ass.)}$ doublet; $\Delta\bar{\nu}_{OH(ass.)}$ refers to the difference $\bar{\nu}_{OH(ass.)}$ [$C_5H_9(X)C{=}NOH$] − $\bar{\nu}_{OH(ass.)}$ [$C_5H_9(SMe)C{=}NOH$]. The abbreviations s, ms, m and w refer to the relative intensity of each doublet component: strong, medium–strong, medium and weak, respectively.

		Solid				CCl_4		
Compound	*X*	$\nu_{OH\ (ass.)}$	$\bar{\nu}_{OH\ (ass.)}$	$\Delta\bar{\nu}_{OH\ (ass.)}$	Assignment	$\nu_{OH\ (free)}$	$\nu_{OH\ (ass.)}$	Assigment
(1)	SMe	3272(s) 3122(m)	3197	0	Dimer†	3601	3285 3100(sh)	Dimer
(2)	NMe_2	3182(ms) 3074(s)	3128	−69	Polimer†	3603	3278 3175(sh)	Dimer
(3)	H	3190(s) 3113(ms)	3151	−46	Trimer‡	3606	3288 3150(sh)	Dimer§

† See text. ‡ From Okaya *et al.* (1956). § From Behrens *et al.* (1978).

the corresponding van der Waals radii (2.72 Å; Bondi, 1964). In (3) the same type of intramolecular interaction is present. Moreover, the *ab initio* computations, on the (*E*) diastereomers of (1) and (2), showed that the axial conformation is the most stable (*ca* 99%), the equatorial conformation being almost nonexistent. The computed α torsion angles of 107 and 119° for (1) and (2), respectively (Table 5), present the same trend as the corresponding angles in the solid state (Table 2), the α angles of the isolated molecules being slightly larger than those in the crystal by *ca* 7°. The calculated torsion angles β, γ, δ and δ' for (1) and (2) are also close to the corresponding angles in the solid state (Table 5).

Table 6 shows that oximes (1)–(3) display free (*ca* 3600 cm^{-1}) and associated (*ca* 3280 cm^{-1}) ν_{OH} stretching bands in carbon tetrachloride solution, whose frequencies and relative intensities (*ca* 1:1) are almost the same for the whole series (Fig. 6). Thus, considering that the ν_{OH} associated band at 3288 cm^{-1} for (3), in CCl_4, has been ascribed to a dimer (Behrens *et al.*, 1978; Geiseler *et al.*, 1975), it seems reasonable to assume that the same attribution should also be valid for the ν_{OH} associated band for (1) and (2) in the same solvent, whose frequencies are very close to that of (3). Moreover, the frequency at 3272 cm^{-1} of the most intense component of the ν_{OH} associated band in the solid state of (1) is reasonably close to that observed in CCl_4 solution (3285 cm^{-1}). This suggests that (1) should also exist as a dimer in the solid state. Therefore, IR

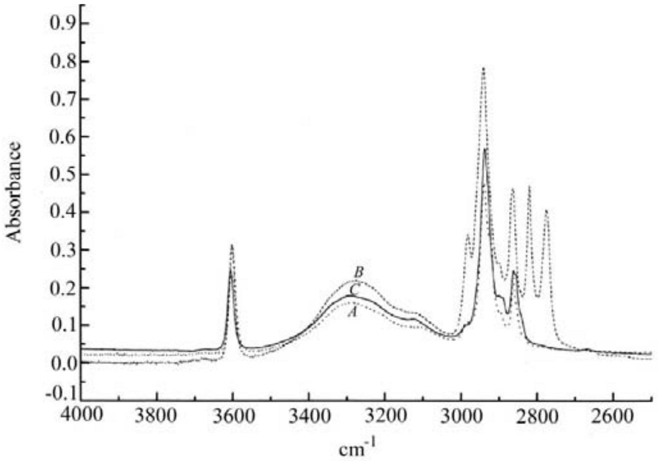

Figure 6
IR ν_{OH} stretching bands (free ~3600 cm^{-1} and associated ~3280 cm^{-1} forms) in a carbon tetrachloride solution of the 2-substituted cyclohexanone oximes (1)–(2) and the parent cyclohexanone oxime (3) corresponding to absorption curves *A*, *B* and *C*, respectively.

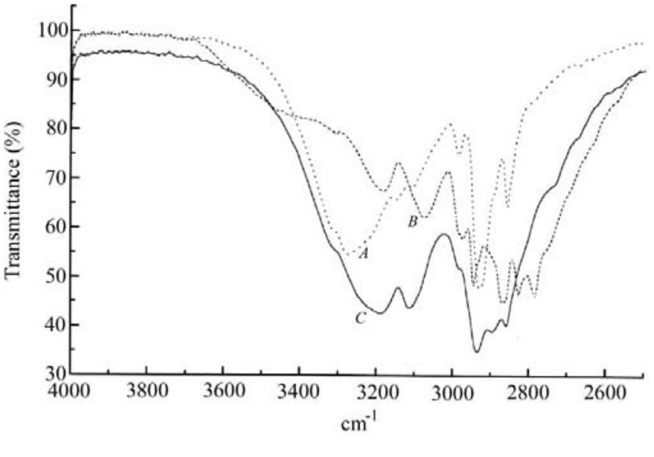

Figure 7
IR ν_{OH} associated stretching bands in the solid state of the 2-substituted cyclohexanone oximes (1), (2) and the parent cyclohexanone oxime (3), corresponding to absorption curves *A*, *B* and *C*, respectively, showing the progressive decrease of the doublet frequency components of the ν_{OH} associated band, on going from (1) to (3) to (2).

Table 7

Frequencies of C═N stretching bands (cm^{-1}) in the IR spectra of the 2-substituted cyclohexanone oximes $C_5H_9(X)C{=}NOH$ [(1) and (2)] and of the parent compound (3).

Solid and CCl_4: see §2. $\Delta\nu_{C=N}$ refers to the difference: $\nu_{C=N}$ [$C_5H_9(X)C{=}NOH$] − $\nu_{C=N}$ [$C_5H_{10}C{=}NOH$]; $\Delta\nu'_{C=N}$ refers to the difference $\nu_{C=N(solid)} - \nu_{C=N(CCl_4\ soln)}$.

		Solid		CCl_4		
Compound	X	$\nu_{C=N}$	$\Delta\nu_{C=N}$	$\nu_{C=N}$	$\Delta\nu_{C=N}$	$\Delta\nu'_{C=N}$
(1)	SMe	1660	−6	1646	−11	+14
(2)	NMe_2	1662	−4	1657	0	+5
(3)	H	1666	0	1657	0	+9

analysis is in agreement with the X-ray structure of (1), which shows that this compound exists in the solid state as a dimer (Fig. 2).

Fig. 7 illustrates the ν_{OH} associated stretching bands for (1), (2) and (3) in the solid state. It should be pointed out that the ν_{OH} associated bands in the solid state for (1)–(3) always display two absorption maxima, which is in agreement with the postulation of the occurrence of Fermi resonance (Kurkchi & Zimina, 1989, and references cited therein) between the fundamental transition of the stretching vibration ν_{OH} and the first overtone of the in-plane deformation mode δ_{OH}, both of the associated form.

For the sake of comparison it has been assumed in the present discussion that the mean frequency value of the ν_{OH} (associated) doublet corresponds approximately to the center of gravity of the ν_{OH} (associated) band in the solid. Moreover, its frequency ($\bar{\nu}_{OH}$) should be an indication of the strength of the hydrogen bond between the hydroxyl H atom and the lone pair of the acceptors.

In the solid state the $\bar{\nu}_{OH(assoc.)}$ frequency of the cyclohexanone oxime (3) is 46 cm^{-1} lower than the frequency of the 2-methylthio derivative (1), which is a dimer in the solid (Tables 2 and 6). This frequency shift for (3) is in agreement with the fact that this compound exists as a trimer in the solid, as shown by its X-ray structure. The basicity of the N atom of the azomethyne group, evaluated from the ν(OH) frequency shift in the oxime–methanol complex with respect to methanol, is almost the same for (1) and (3) (CCl_4, $\Delta\nu_{OH} \simeq 200$ cm^{-1}; Ribeiro, 1999). Moreover, these data are in line with practically the same IE value of 10.2 eV for the sp^2 nitrogen azomethyne lone pair of the Me(Me) C═NOH and EtS(Me)C═NOH molecules (Dal Colle *et al.*, 1998). Therefore, it seems reasonable that the trimer of (3) in the solid has a more suitable O—H···N angle (in the range 164–178°) for orbital overlapping than the dimer of (1) (150°), thus leading to a stronger hydrogen bond between the hydroxyl H atom and the sp^2 nitrogen lone pair of the azomethyne group in the trimer of (3) than in the dimer of (1).

Although in the crystals of (1) and (2) the OH···N(sp^2) and OH···N(sp^3) distances are almost the same (~1.96 Å; Table 2), the $\bar{\nu}_{OH(assoc.)}$ band for (2) is shifted to an even lower frequency with respect to that of (1), $\Delta\bar{\nu}_{OH(assoc.)} = -69$ cm^{-1}, in comparison to that of (3) [$\Delta\bar{\nu}_{OH(assoc.)} = -46$ cm^{-1}]. This behavior is in accordance with the fact that, in spite of the same OH···N distance for the dimer of (1) and the polymer of (2), the higher basicity of the sp^3 nitrogen lone pair relative to that of the sp^2 nitrogen gives rise to a stronger hydrogen bond

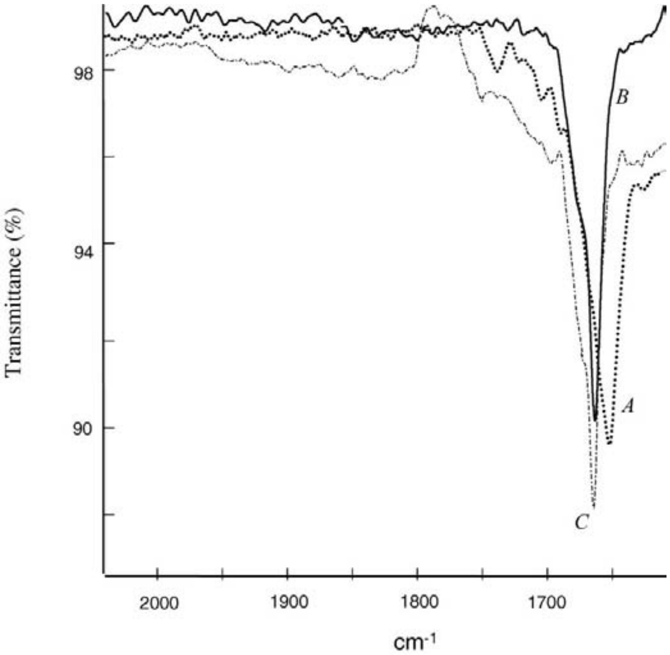

Figure 8

IR $\nu_{C=N}$ stretching bands in carbon tetrachloride solution of the 2-substituted cyclohexanone oximes (1) and (2), and the parent cyclohexanone oxime (3) corresponding to absorption curves *A*, *B* and *C*, respectively.

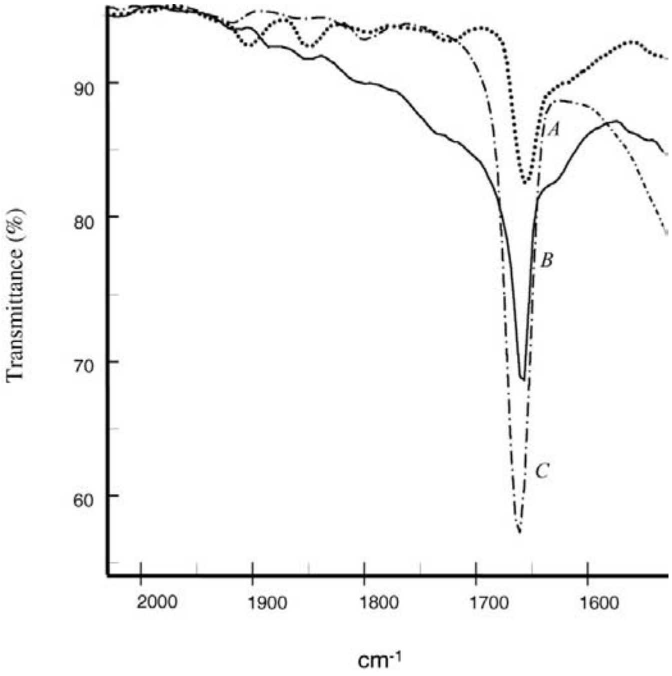

Figure 9

IR $\nu_{C=N}$ stretching bands in the solid state of the 2-substituted cyclohexanone oximes (1) and (2), and the parent cyclohexanone oxime (3) corresponding to absorption curves *A*, *B* and *C*, respectively.

in (2) having a more favorable geometry for orbital overlapping (O—H···N = 177°) than in (1) (O—H···N = 150°).

As previously reported (Olivato *et al.*, 1995) self-association in oximes through hydrogen bonding between the hydroxyl H atom and the nitrogen lone pair of the azomethyne group gives rise to an increase of the $\nu_{C{=}N}$ frequency compared with that of the monomer.

Table 7 shows that for (1) and (3), on going from a diluted carbon tetrachloride solution (which corresponds to the monomer; Fig. 8) to the solid state (which corresponds to the associated forms; Fig. 9) the $\nu_{C{=}N}$ bands are shifted to higher frequencies ($\Delta\nu'_{C{=}N}$) by *ca* +11 cm^{-1} for (1) and (3), while for (2) this frequency shift is only +5 cm^{-1}. Therefore, the larger positive frequency shifts ($\Delta\nu'_{C{=}N}$) for (1) and (3) with respect to that of (2) further support the fact that the intermolecular hydrogen bond for (1) and (3) occurs between the hydroxyl H atom and the azomethyne N atom, while the hydrogen bond in (2) is between the hydroxyl H atom and the nitrogen lone pair of the 2-dimethylamino group. The smaller positive frequency shift for (2) may be ascribed to the O—H···NMe$_2$ hydrogen bond which induces some increase in the normal −I effect of the NMe$_2$ group. This effect should decrease the $C^{\delta+}{=}N^{\delta-}$ polarization, which in turn increases the azomethyne force constant and its frequency.

Table 7 also shows that the C=N frequency shifts of 2-heterosubstituted oximes (1) and (2) in relation to the parent oxime (3) ($\Delta\nu_{C{=}N}$) are negative, both in carbon tetrachloride and in the solid state, and varies from 0 to −11 cm^{-1} (in CCl$_4$) and from 0 to −6 cm^{-1} (in the solid state).

This trend is similar to that previously observed for the α-heterosubstituted acetone oximes (Olivato *et al.*, 1995), for which the observed negative azomethyne frequency shifts have been ascribed to the $\pi_{C{=}N}/\sigma^*_{C-Y}$ orbital interaction which stabilizes their *gauche* conformers which are in the (*E*) configuration.

From *ab initio* calculations (Table 5) and from our NMR study (Ribeiro *et al.*, 2000), it seems quite reasonable that the 2-substituents in the cyclohexanone oximes (1) and (2) in carbon tetrachloride solution assume almost exclusively the axial conformation, for which the α torsion angles are suitable for the $\pi_{C{=}N}/\sigma^*_{C-X}$ orbital interaction.

The larger negative frequency shift for the methylthio derivative (1) in relation to the dimethylamino derivative (2) should be ascribed to the closer proximity of the empty σ^*_{C-S} orbital [AE[3] = 3.25 eV for MeSMe (Modelli *et al.*, 1991)] to the unperturbed $\pi_{C{=}N(OH)}$ orbital energy level [IE = 9.40 eV for C$_6$H$_{10}$C=NOH (Strenge & Rademacher, 1999)] rather than to the proximity between the empty σ^*_{C-N} orbital [AE = 4.80 eV for Me$_3$N (Giordan *et al.*, 1985)] to the unperturbed $\pi_{C{=}N(OH)}$ orbital. This effect originates stronger $\pi_{C{=}N}/\sigma^*_{C-X}$ orbital interactions for (1) than (2), which in turn leads to a larger decrease of the C=N bond order and thus in the $\nu_{C{=}N}$ frequency of (1) with respect to (2).

Moreover, the smaller α torsion angle of (1) compared with that of (2) of *ca* 10° (see Tables 2 and 5) allows a better $\pi_{C{=}N}/\sigma^*_{C-X}$ overlap in (1) than in (2), which also should contribute to the larger negative frequency shifts for (2) in relation to (1).

The Brazilian authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support, for a postdoctoral fellowship (to DSR) and for concession of the CAD-4 Mach 3 X-ray diffractometer, and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a scholarship (to DSR) and for a grant (to PRO and JZS). The Italian author thanks Professor V. Bertolasi, University of Ferrara, for the data collection on the Nonius CCD diffractometer, the Ministero della Ricerca Scientifica e Tecnologica and Consiglio Nazionale delle Ricerche (CNR) for financial support. The authors would also like to thank the referees for many enlightening comments.

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[3] AE = attachment energy.

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