

X-ray Investigation of Glyoxime Derivatives. V. Two Isomers of 2-(Thienyl)glyoxime. A Database Study of the Geometry and Hydrogen Bonding of the Oxime Group

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(Received 27 November 1993; accepted 19 April 1994)

Abstract

The crystal structures of two isomers of 2-(thienyl)glyoxime, 2-thienylethanedial dioxime, $C_6H_6N_2O_2S$, *E,E* [orthorhombic, *Pbca*, $a = 11.074$ (5), $b = 9.152$ (3), $c = 14.660$ (4) Å, $V = 1185.84$ Å³, $D_x = 1.522$ g cm⁻³, $Z = 8$, $R = 0.058$ for 1276 reflections with $I > 3\sigma(I)$] and *E,Z* [monoclinic, *P2/c*, $a = 12.189$ (3), $b = 3.865$ (3), $c = 16.022$ (5) Å, $\beta = 90.79$ (2)°, $V = 754.8$ Å³, $D_x = 1.498$ g cm⁻³, $Z = 4$, $R = 0.032$ for 1154 reflections with $I > 3\sigma(I)$] have been determined. An analysis, based on the structures of the title compounds and on other glyoxime derivatives showed that the *E,E*-configuration is the preferred form. A statistical study on the geometry of the oxime group and on hydrogen bonding in the oximes was performed using the Cambridge Structural Database.

1. Introduction

Glyoxime derivatives (dioximes), $HO-N=C(R^1)-C(R^2)=N-OH$, can exist as a number of configurational and/or conformational isomers. Since conformations about the N—O and C—C bonds have to be considered as well as *E* and *Z* configurations about the C=N bonds, there are 32 planar geometrical isomers and an infinite number in space for disubstituted glyoxime. X-ray analysis is the only method able to establish their structure unambiguously. The detailed study by neutron diffraction and *ab initio* molecular-orbital calculations of glyoxime (Jeffrey, Ruble & Pople, 1982) and X-ray studies of some glyoxime derivatives have been reported. In general, measurements have been carried out on a single isomer (presumably the more stable). As part of a systematic study on the structure of glyoxime derivatives (Chertanova *et al.*, 1989 and previous papers of this series), we have undertaken the X-ray analysis of 2-(thienyl)glyoxime. We have been fortunate to be able to grow suitable single crystals of both the *E,E*-

and *Z,E*-isomers of 2-(thienyl)glyoxime and thus have a unique opportunity to investigate a pair of isomers in the solid state.

Geometrical isomerization is a primary feature of these compounds, although the presence of at least two double bonds favours conjugative interactions. Hydrogen bonding is also an important factor. All these factors led us to examine all reported structures of molecules, that contain one, two or more oxime groups. A first survey of crystal structures containing the oxime group was conducted by Bertolasi, Gilli & Veronese (1982). They analysed the hydrogen-bond systems in the crystals of oximes and suggested a correlation between a pattern of hydrogen bonding and N—O bond lengths. In the last 10 years, the data for oxime structures have increased, but to the best of our knowledge, no further systematic survey of the crystallographic data has been carried out. We have therefore conducted such a survey using the Cambridge Structural Database (CSD, Version 5.04: Allen, Kennard & Taylor, 1983; Allen *et al.*, 1991). Thus, our paper is divided into three sections. First we report the structures of the two isomers of 2-(thienyl)glyoxime. Secondly, we consider the conformational properties and geometry of the glyoximes, and finally we present an empirical study of the link between glyoxime geometry and the packing environment of the oxime group.

2. The crystal structure of two isomers of 2-(thienyl)glyoxime

2.1. Experimental

The *E,E*- and *E,Z*-isomers of 2-(thienyl)glyoxime were prepared by recrystallization from dichloromethane and methanol, respectively. Crystal data for the two isomers of 2-(thienyl)glyoxime and details of the data collection and refinement procedures are summarized in Table 1. The lattice parameters were obtained from angular settings of 25 well-centred,

Table 1. Summary of crystal data and data collection parameters

	C ₆ H ₆ N ₂ O ₂ S	C ₆ H ₆ N ₂ O ₂ S
Chemical formula	C ₆ H ₆ N ₂ O ₂ S	C ₆ H ₆ N ₂ O ₂ S
<i>M_r</i>	170.19	170.19
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁c</i>
<i>a</i> (Å)	11.074 (5)	12.189 (3)
<i>b</i> (Å)	9.152 (3)	3.865 (3)
<i>c</i> (Å)	14.660 (4)	16.022 (5)
α (°)	90	90
β (°)	90	90.79 (2)
γ (°)	90	90
<i>V</i> (Å ³)	1485.8 (9)	754.8 (8)
<i>D_c</i> (Mg m ⁻³)	1.522	1.498
<i>Z</i>	8	4
θ -range for lattice parameters (°)	11–12	11–12
Absorption coefficient (mm ⁻¹)	0.365	0.365
No. of reflections measured	2163	2282
No. of reflections observed	1281	1232
Criterion for observed	3 σ	3 σ
<i>h</i> range	0–15	–17–17
<i>k</i> range	0–12	0–5
<i>l</i> range	0–20	0–22
θ_{\max} (°)	30	30
<i>F</i> (000)	704	352
<i>R</i>	0.058	0.032
<i>wR</i>	0.062	0.031
<i>S</i>	1.273	0.512
(Δ / σ) _{max}	0.2	0.27
No. of parameters refined	120	120
No. of reflections used in refinement	1276	1154
Final difference ($\Delta\rho$) _{max} (e Å ⁻³)	0.570	0.292

 Table 2. Atomic coordinates and equivalent isotropic thermal parameters of *E,E*-isomer with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$		
	<i>x</i>	<i>y</i>	<i>z</i>
S	0.6446 (1)	0.4718 (1)	0.68689 (9)
O1	0.5908 (2)	0.2173 (3)	0.6078 (2)
O2	0.1430 (2)	0.4987 (3)	0.5194 (2)
N1	0.4759 (2)	0.2456 (4)	0.5746 (2)
N2	0.2537 (3)	0.5095 (2)	0.5646 (2)
C1	0.4394 (3)	0.3780 (4)	0.5905 (2)
C2	0.3165 (3)	0.3971 (4)	0.5530 (3)
C3	0.5059 (3)	0.4962 (4)	0.6339 (2)
C4	0.4677 (3)	0.6483 (4)	0.6378 (3)
C5	0.5629 (4)	0.7284 (5)	0.6814 (3)
C6	0.6553 (4)	0.6507 (5)	0.7111 (3)
H1	0.599 (3)	0.162 (4)	0.589 (2)
H2	0.113 (4)	0.560 (5)	0.532 (3)
H3	0.289 (3)	0.323 (4)	0.520 (3)
H4	0.416 (4)	0.693 (3)	0.625 (3)
H5	0.550 (4)	0.809 (5)	0.686 (3)
H6	0.717 (4)	0.677 (4)	0.745 (3)

* Refined isotropically.

Friedel-related reflections, $22 < 2\theta < 24^\circ$ (*E,E*) and $18 < 2\theta < 24^\circ$ (*Z,E*). A total of 2163 (*E,E*) and 2282 (*Z,E*) reflections were collected on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo *K* α radiation ($\lambda = 0.71073$ Å) at room temperature. The intensity data were corrected for Lorentz–polarization effects but not for absorption. Structures of both isomers were solved using *MULTAN*11/82 (Main *et al.*, 1982). All H atoms

 Table 3. Atomic coordinates and equivalent isotropic thermal parameters of *Z,E*-isomer with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$		
	<i>x</i>	<i>y</i>	<i>z</i>
S	0.87444 (4)	0.0528 (2)	0.17996 (4)
O1	0.8991 (1)	0.4680 (6)	–0.06869 (9)
O2	0.5349 (1)	0.2219 (5)	–0.08281 (9)
N1	0.8864 (1)	0.3905 (5)	0.0155 (1)
N2	0.6080 (1)	0.1746 (5)	–0.0161 (1)
C1	0.7870 (1)	0.3144 (6)	0.0343 (1)
C2	0.6985 (1)	0.3303 (6)	–0.0283 (1)
C3	0.7680 (1)	0.2154 (6)	0.1208 (1)
C4	0.6743 (2)	0.2452 (6)	0.1684 (1)
C5	0.6921 (2)	0.1352 (7)	0.2513 (1)
C6	0.7954 (2)	0.0278 (7)	0.2662 (1)
H1	0.948 (2)	0.508 (7)	–0.073 (1)
H2	0.476 (2)	0.113 (8)	–0.067 (2)
H3	0.712 (2)	0.460 (6)	–0.079 (1)
H4	0.635 (1)	0.316 (5)	0.157 (1)
H5	0.632 (2)	0.136 (7)	0.289 (2)
H6	0.820 (2)	–0.059 (7)	0.312 (2)

* Refined isotropically.

Table 4. Bond angles (°)

	<i>E,E</i> -isomer	<i>Z,E</i> -isomer
C3—S—C6	91.8 (2)	92.1 (2)
O1—N1—C1	113.4 (3)	113.1 (2)
O2—N2—C2	111.4 (3)	111.5 (2)
N1—C1—C2	109.3 (3)	121.2 (3)
N1—C1—C3	127.9 (3)	116.3 (2)
C2—C1—C3	122.8 (3)	122.4 (2)
N2—C2—C1	123.9 (3)	120.4 (3)
S—C3—C1	123.3 (3)	119.5 (2)
S—C3—C4	111.3 (2)	110.4 (2)
C1—C3—C4	125.5 (3)	130.0 (3)
C3—C4—C5	107.0 (3)	112.1 (3)
C4—C5—C6	116.2 (4)	113.1 (3)
S—C6—C5	113.7 (3)	112.3 (3)
N1—O1—H1	98 (4)	107 (4)
N2—O2—H2	104 (4)	103 (3)
N2—C2—H3	121 (2)	122 (2)
C1—C2—H3	115 (2)	118 (2)
C3—C4—H4	139 (2)	124 (3)
C5—C4—H4	114 (4)	123 (3)
C4—C5—H5	114 (4)	119 (2)
C6—C5—H5	130 (4)	128 (2)
S—C6—H6	116 (3)	122 (3)
C5—C6—H6	130 (3)	126 (3)

were located on electron-density difference maps. Anisotropic thermal refinement was carried out for all non-H atoms and the isotropic mode for H atoms. All calculations were carried out using the Structure Determination Package (B. A. Frenz & Associates Inc., 1982). Final atomic parameters are reported in Tables 2 and 3, respectively. Bond distances, bond angles and the hydrogen-bond geometry are given in Tables 4, 5 and 6.*

* Due to exceptional circumstances beyond the control of the authors, tables of structure factors and atomic displacement parameters are not available for these structures. The Editorial Board feels that, in this unique situation, publication of the results should go ahead.

Table 5. Bond distances (Å)

	<i>E,E</i> -isomer	<i>Z,E</i> -isomer
S—C3	1.736 (3)	1.715 (3)
S—C6	1.680 (5)	1.698 (4)
O1—N1	1.387 (4)	1.393 (3)
O2—N2	1.397 (4)	1.394 (3)
N1—C1	1.298 (4)	1.286 (3)
N2—C2	1.253 (4)	1.273 (4)
C1—C2	1.477 (4)	1.464 (4)
C1—C3	1.456 (4)	1.460 (4)
C3—C4	1.456 (5)	1.386 (4)
C4—C5	1.434 (5)	1.410 (5)
C5—C6	1.320 (6)	1.343 (5)
O1—H1	0.58 (4)	0.62 (3)
O2—H2	0.68 (4)	0.87 (5)
C2—H3	0.89 (4)	0.97 (4)
C4—H4	0.73 (4)	0.58 (3)
C5—H6	0.76 (4)	0.95 (4)
C6—H6	0.88 (4)	0.86 (4)

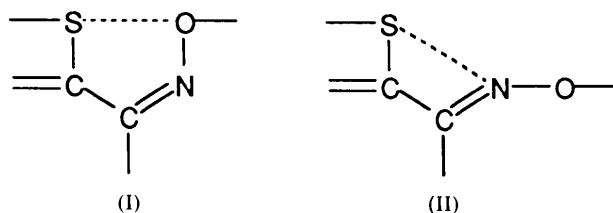
Table 6. Hydrogen-bond lengths and angles (Å, °)

Donor-acceptor	<i>D</i> ... <i>A</i>	H... <i>A</i>	<i>D</i> —H... <i>A</i>
	<i>E,E</i> -isomer		
O1—H1...O2 ⁱ	2.778 (4)	2.22 (4)	161 (5)
O2—H2...N1 ⁱⁱ	2.737 (4)	2.06 (5)	178 (1)
	<i>Z,E</i> -isomer		
O1—H1...N1 ⁱⁱⁱ	2.792 (3)	2.25 (3)	148 (4)
O2—H2...N2 ^{iv}	2.824 (3)	2.02 (5)	153 (4)

Symmetry codes: (i) $x + \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iii) $2 - x, 1 - y, -z$; (iv) $1 - x, -y, -z$.

2.2. Results and discussion

Fig. 1 shows *ORTEP* (Johnson, 1965) views of the molecules, together with the atom-labelling scheme. In both isomers, the orientation of the chain is the same, with the double bonds C1=N1 and C3=C4 *trans* with respect to the ring-chain link bond C1—C3. There is competition between the conjugated system N1=C1—C3=C4 and the steric hindrance between S and O (*E,E*) and N (*Z,E*). In the *E,E*-isomer (I), O1 is situated 2.669 (3) Å from the S atom (sum of van der Waals' radii = 3.25 Å). The chain is tilted slightly (11° rotation around C1—C3) so that O1 is only 0.38 Å from the thiophene mean plane. In the *Z,E*-isomer (II), it is the nitrogen atom N1 which comes closest to the S atom: S...N1 is 2.945 (3) Å (sum of van der Waals' radii = 3.35 Å). Here, the chain is more tilted (29° rotation about C1—C3 for the whole chain) and N1 is -0.59 Å from the thiophene plane. A large number of organosulfur compounds are known in which the



conformation is controlled by intramolecular sulfur-oxygen interactions (Angyan, Poirier, Kucsman & Csizmadia, 1987).

In the *E,E*-isomer, the thiophene ring is not precisely planar, but has a slight envelope conformation with C4 *exo*. The ring is perfectly planar in the *E,Z*-isomer, the planar conformation being allowed by strain relief due to the larger tilt of the chain. The glyoxime chain in the *E,E*-isomer is fully extended, with a slight torsion (6°) around C1—C2. The rotation of the C2—N2—O2 fragment is more accentuated in the *Z,E*-isomer with a value of 18° for the same torsion angle. Thus, in the latter compound, the thiophene ring makes an angle of 39° with the C1—C2—N2—O2 chain fragment. This rotation reduces the strain between O1 and the hydrogen that is bonded to C2.

Comparison of the bond lengths for *E,E*- and *Z,E*-isomers (Table 5) shows that bond-distance differences do not exceed 5σ in the glyoxime chain. They are in good agreement with the values obtained previously by neutron diffraction for the parent glyoxime (Jeffrey, Ruble & Pople, 1982). However, valence angles at C1 differ appreciably. The distortion arises from the sulfur-oxygen proximity: C3—C1—N1 = 116.3 (2)° in *Z,E* widens to 127.9 (3)° in *E,E* to accommodate the bulky O1 atom close to sulfur. Conversely, N1—C1—C2 = 121.2 (3)° in *Z,E* contracts to 109.3 (3)° in *E,E* (Table 4). If we compare the double-bond systems in both molecules, we see that in *Z,E*, with a larger tilt of the chain, the double-bond character is more localized: C3=C4

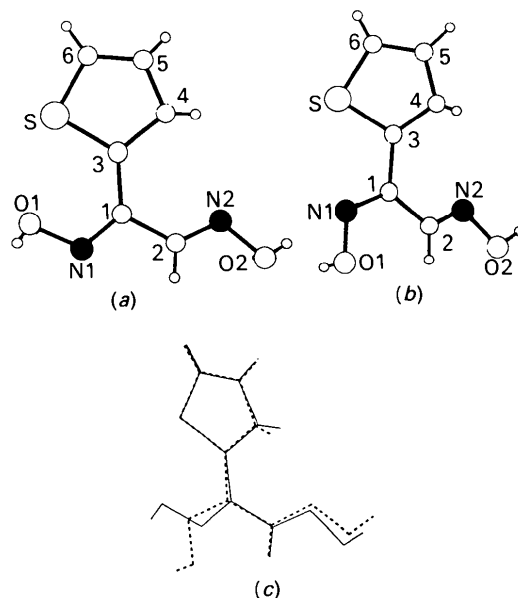


Fig. 1. Structures and numbering scheme of the *E,E*- and *Z,E*-isomers. Superposition of two isomers of the 2-(thienyl)glyoxime.

1.386 (4), N1=C1 1.286 (3) Å. In *E,E* the chain is more closely coplanar with thiophene, and the double-bond system is more delocalized: C3—C4 = 1.456 (5) and N1—C1 = 1.298 (4) Å. This is consistent with the larger values of N1—C1—C3 and C1—C3—C4 angles in the *E,E*-isomer.

2.2.1. *Molecular packing and hydrogen bonding.* In the *E,E*-isomer, one oxime group, C1=N1—O1—H1, participates as a donor in an O1—H1...O2 bond and as an acceptor in an N1...H2—O2 bond and the other oxime group, C2=N2—O2—H2, binds by O2—H2...N1 and O2...H1—O1 hydrogen bonds (Fig. 2); as a result, the hydrogen-bond system O1—H1...O2—H2...N1 forms layers orthogonal to the *c*-axis. The interlayer separation corresponds to van der Waals contacts. In the *Z,E*-isomer, every oxime is linked centrosymmetrically to its homologue (Fig. 2) to form infinite chains parallel to the *a*-axis. The hydrogen bonds lead to the formation of ten-membered (in *E,E*) and six-membered (in *E,Z*) hydrogen-bonded rings. The O...O and O...N separations are typical of such systems and indicate moderately strong hydrogen bonding (Table 6).

3. Database study of the functional groups of interest

As mentioned above, the conformational features as well as the presence of an O-donor—O-acceptor—N-acceptor system led us to perform a detailed database study of all reported structures of dioxime and oxime compounds.

3.1. Methods

Two subfiles of data, one containing 13 glyoxime derivatives (20 dioxime fragments) and the other containing 232 oxime groups were selected and subjected to statistical analysis. In both sets, the criteria for accepting an entry from the CSD were: (1) only organic compounds should be considered; (2) no

disorder should be present; (3) the *R*-factor for the crystal structure determination should be less than 0.080. In our work, we take $D-H\cdots A$ (D , A = oxygen, nitrogen) arrangements with the contact distances $D\cdots A$ in the range 2.0–3.2 Å, $H\cdots A$ in the range 1.4–2.2 Å and $D-H\cdots A$ in the range 90–180° as possible hydrogen bonds.

The two-dimensional substructure search and three-dimensional geometric search were carried out using the program *QUEST3D*. Multiple occurrences of a functional group within any entry were considered since they display independent information. If a particular crystal structure had more than one entry in the database, only the best and/or most recent analysis was accepted. Symmetry-equivalent fragments were removed after using the *GSTAT* routine, as the *NOD* (no duplicate) keyword of the *GSTAT* routine was found to be too discriminating in some cases and not selective enough in others. All the X-ray hydrogen positions were normalized (Jeffrey & Lewis, 1978). Statistical descriptors are defined by Snedecor & Cochran (1989). All the programs used are part of the *CSD* package. The results are represented as histograms and scatterplots using KaleidaGraph (1990).

3.1.1. Conformation of the glyoxime derivatives.

The following analysis was based on the dioxime structures. This fragment contains two vicinal oxime groups. With the information gathered from the CSD and our present data (22 examples), the dioxime fragment has been observed, in the solid phase, to adopt either *E,E*-, *E,Z*- or *Z,Z*-configurations.

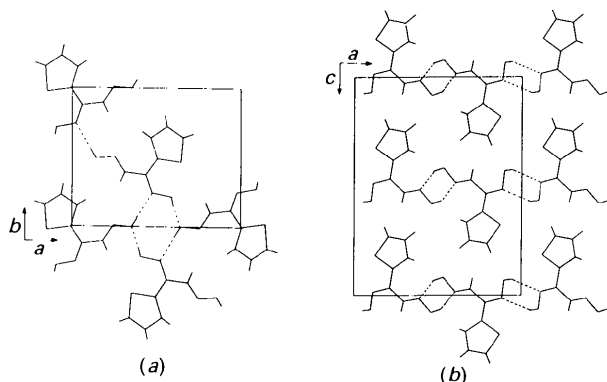
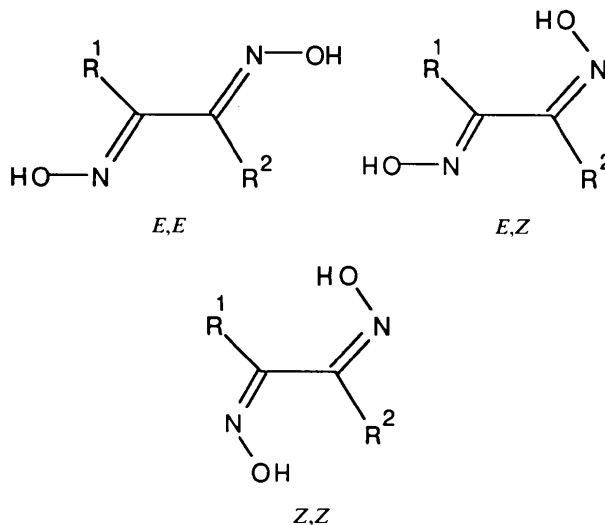


Fig. 2. Formation of the ten-membered (*E,E*) and the six-membered (*E,Z*) hydrogen-bonded rings.



According to the theoretical results (Jeffrey, Ruble & Pople, 1982) the *E,E*-configuration is more stable and this is consistent with the observation of the *E,E*-configuration in 13 fragments, *Z,E* in six fragments and only one example of the *Z,Z*-configura-

tion. In molecules with three and four oxime groups both *E,E*- and *E,Z*- or *E,E*- and *Z,Z*-dioxime configurations are present. The distribution of the absolute values of the torsion angle $C-C=N-O$ is shown in Fig. 3 [histogram (a)]. The torsion angle $C-C=N-O$ close to 0° corresponds to the *Z*-configuration and 180° to the *E*-configuration.

Histogram (b) (Fig. 3) reports the distribution of torsion angles around the $C-C$ bond. As expected, oxime groups show a clear preference for a *trans*-planar conformation; only six structures have a torsion angle $N=C-C=N$ within the range $60-120^\circ$. A scatterplot of $C-C$ bond lengths against $N=C-C=N$ torsion angles is shown in Fig. 3(c). The correlation of $C-C$ with $N=C-C=N$ is obvious, with the correlation coefficient $r = -0.74$. Shorter $C-C$ bond lengths are related to the planar arrangement of the dioxime fragment.

The geometry is expected to vary with the conformation. However, because analyses with small numbers of data tend to statistical inconsistencies, we performed a search for all molecules containing an oxime group.

3.1.2. *Geometry of the oxime derivatives.* The total number of data was satisfactory. The 167 structures found in the initial search contain 232 crystallographically unique fragments. In order to study the factors causing the visible variance of the oxime geometry, we have applied univariate and bivariate analyses to the retrieved fragment.

3.1.2.1. *Univariate statistics.* Fig. 4(a) illustrates the relative frequency of the torsion angle $C=N-O-H$. The $O-H$ bond may be either synplanar or antiperiplanar to the $C=N$ bond. The present results show that the antiperiplanar conformation is more favourable than synplanar; only a few (eight) structures have a (synplanar) torsion angle $C=N-O-H$ close to 0° .

The distributions of geometrical parameters $C=N-O$, $C=N$ and $N-O$ are shown in Fig. 4(b-d). The $C=N$ and $N-O$ histograms correspond closely to normal distributions which are nearly symmetrical, as measured by skewness (asymmetry) and kurtosis ('peakedness') coefficients (0.052, 1.130; -0.189 , -0.383). The $C=N-O$ distribution is less symmetrical: skewness and kurtosis coefficients are

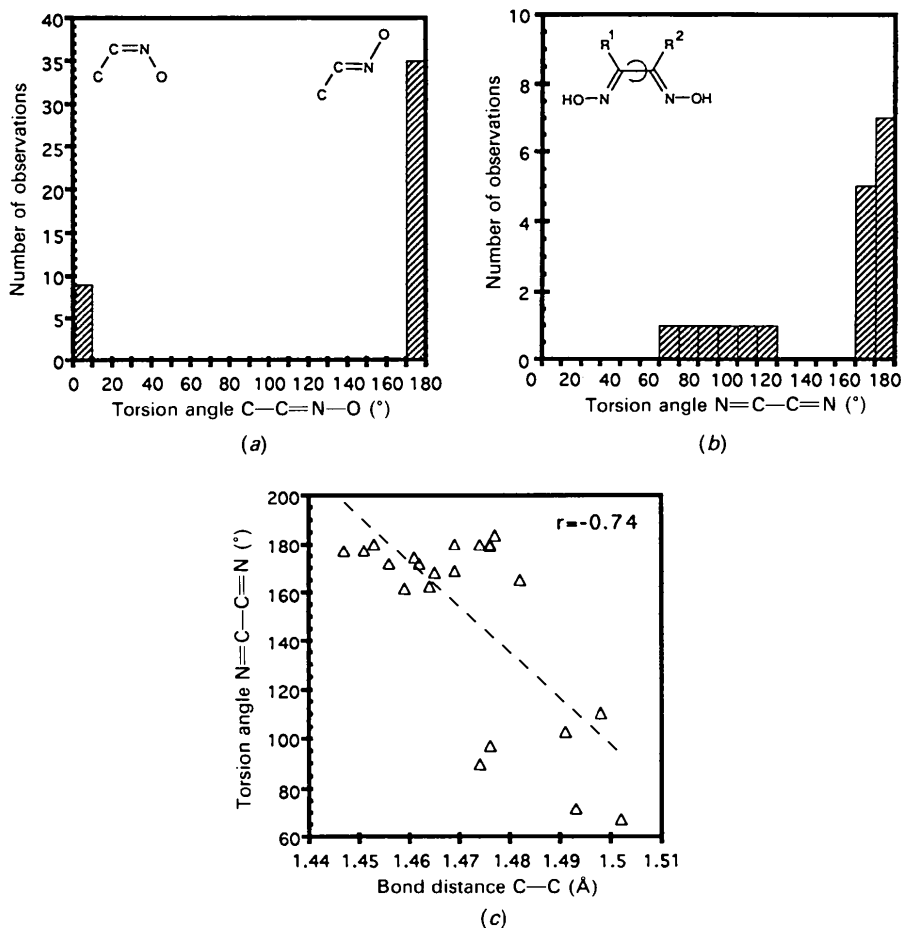


Fig. 3. Geometry of dioximes. Distribution of the absolute values of torsion angles (a) $C=N-O-H$ and (b) $N=C-C=N$; (c) scatterplot of the $C-C$ bond against the torsion angle $N=C-C=N$.

1.441 and 5.531. The oxime fragment shows very significant variation in parameters: the bond angle $C=N-O$ ranges from 108.0 to 121.2° with $\Delta(C=N-O) = 13.2^\circ$, the $N-O$ bond length ranges from 1.346 to 1.447 \AA with $\Delta(N-O) = 0.101 \text{ \AA}$ and $C=N$ bond distances are confined in a more narrow interval of 1.224 – 1.330 \AA with $\Delta(C=N) = 0.076 \text{ \AA}$.

3.1.2.2. Bivariate analysis. Bivariate correlations were calculated for all combinations of parameters. Surprisingly, the mutual correlation is very poor. The highest correlation ($r = -0.58$) is observed for the absolute value of the torsion angle $C=N-C-H$ with the bond angle $C=N-O$ (Fig. 5). It is clear that in all oximes with a synplanar orientation of the $O-H$ group, the value of the angle $C=N-O$ is larger than in examples with antiperiplanar orientations. Univariate statistics for the antiplanar oxime groups only show a small variation of $\Delta(C=N-O) = 8^\circ$ for this angle. Mean values for this parameter are 112° for the antiplanar fragment and 119° for synplanar. The calculated correlated coefficients are: for $C=N$ and $N-O$, $r = -0.06$, $C=N$ and $C=N-O$, $r = 0.00$, and for $N-O$ and $C=N-O$, $r = 0.33$.

It was assumed (Bertolasi, Gilli & Veronese, 1982) that most of the variance of $C=N$ is due to conjugation effects and the variance of $N-O$ is due to hydrogen bonding. In order to test more carefully the influence of the hydrogen bonding on the molecular geometry, a study of the hydrogen bonds was performed.

3.1.3. Modes of hydrogen-bonding in oxime groups. Statistical results are presented here in order to shed light on hydrogen-bond geometry and the structure of the oxime groups. It is known (Bertolasi, Gilli & Veronese, 1982) that oxime groups are able to form (see III) three kinds of hydrogen bonds:

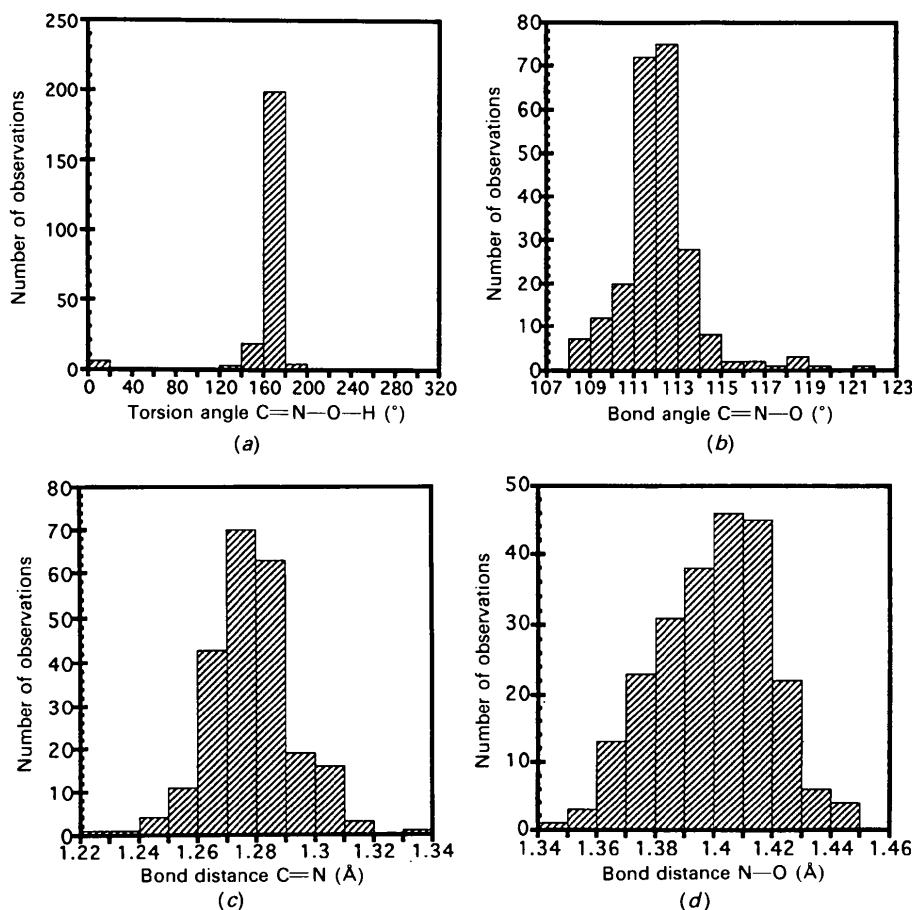
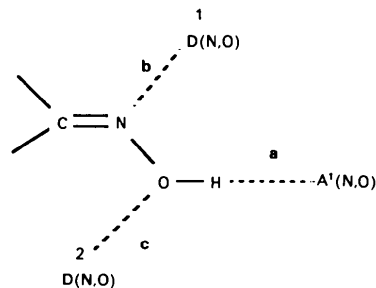


Fig. 4. Geometry of oximes. Distribution of geometrical parameters: absolute value of (a) the torsion angle $C=N-O-H$, (b) bond angle $C=N-O$, (c) bond distances $C=N$ and (d) $N-O$.

(a) $O-H\cdots A1$, (b) $N\cdots H-D1$, (c) $O\cdots H-D2$; the interactions forming separately or simultaneously. This raises a number of questions: which type of hydrogen bond is preferable? Are nitrogens better acceptors than oxygen? Is there a dependence between the configuration of the oxime group and the observed system of hydrogen bonds? In order to answer these and other questions, the hydrogen interactions have been characterized by the usual parameters ($D\cdots A$, $H\cdots A$ distances and the angle $D-H\cdots A$). Normalized hydrogen positions were computed using the mean $O-H$ and $N-H$ distances of 0.983 and 1.009 Å, respectively (Taylor & Kennard, 1984).

For the 232 crystallographically independent oxime groups hydrogen bonding of type (a) is observed in 207, type (b) in 127 and type (c) in 17 cases. In all cases, hydrogen bonding occurs only in antiplanar oxime groups, the synplanar conformation being unfavourable for hydrogen bonding. Fig. 6 shows the distributions of $D\cdots A$, $H\cdots A$ and $D-H\cdots A$ for each type of hydrogen bonding. In our case, the nature of the acceptor and donor partners is not taken into account. The selected hydrogen-bonding geometries are reported in Table 7. No significant differences were observed between parameters for hydrogen bonding of type (a) and (b), perhaps because oximes are packed as dimers through the bonded N and O atoms. Some differences were observed: the $D\cdots A$ and $H\cdots A$ distances are significantly longer in (c).

Within each type, the $H\cdots A$ distances and $D-H\cdots A$ angles were found to have rank correlation coefficients of -0.80 , -0.63 and -0.55 for (a), (b) and (c), respectively. These are significantly different from zero at the 99.9% confidence level, confirming the well known observation that shorter hydrogen bonds tend to be more linear than longer ones.

3.1.4. *Effect of hydrogen bonding on molecular geometry.* In order to evaluate the effect of hydrogen

Table 7. Selected hydrogen-bonding geometries (Å, °)

	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
Type (a)			
Mean	1.841	2.762	158.845
SD sample	0.116	0.075	13.734
SD mean	0.008	0.005	0.955
Minimum	1.540	2.514	115.263
Maximum	2.195	2.968	180.000
N_{obs}	207	207	207
Type (b)			
Mean	1.905	2.822	156.838
SD sample	0.108	0.090	12.031
SD mean	0.010	0.008	1.068
Minimum	1.689	2.659	117.775
Maximum	2.188	3.176	179.253
N_{obs}	127	127	127
Type (c)			
Mean	1.996	2.930	159.016
SD sample	0.142	0.129	14.069
SD mean	0.035	0.032	0.980
Minimum	1.750	2.724	122.806
Maximum	2.188	2.968	176.240
N_{obs}	17	17	17

bonding on molecular geometry, we calculated correlation coefficients for all related parameters. No significant correlations were observed: correlation coefficients of $C=N$ and $N-O$ with $D\cdots A$ are -0.14 and 0.34 for (a), -0.04 and -0.30 for (b), and 0.01 and -0.23 for (c). However, it is clear that non-zero factors correspond to real structural effects. The problem, then, is to define the cooperative contributions of the hydrogen bonds.

We can extend the former classification of oximes proposed by Bertolasi, Gilli & Veronese (1982) to seven classes by combining the various hydrogen-bond possibilities: $A = a$, $B = b$, $C = c$, $D = a + b$, $E = b + c$, $F = a + c$, $G = a + b + c$. We find that the number of observations in the CSD for A , B , C , D , E , F and G families are 81, 2, 5, 125, 0, 1 and 10, respectively. It seems that a single hydrogen bond occurs in 42% of structures; a pair in 54% and three hydrogen bonds in only 4%. As hydrogen bonding is observed mainly for A , D and G families, we performed a geometrical comparison for these families only. Within these groups of oximes, the mean values of $C=N$ bonds agree very well [mean value is 1.279 (1) Å] and the mean values of the $N-O$ bond are 1.391 (1), 1.408 (1) and 1.416 (5) Å for A , D and G , respectively. Fig. 7 illustrates the superposition of the distributions of the $N-O$ bonds for the oximes with one, two and three hydrogen bonds.

As mentioned above, the D family comprises hydrogen-bonded dimers (IV), containing only

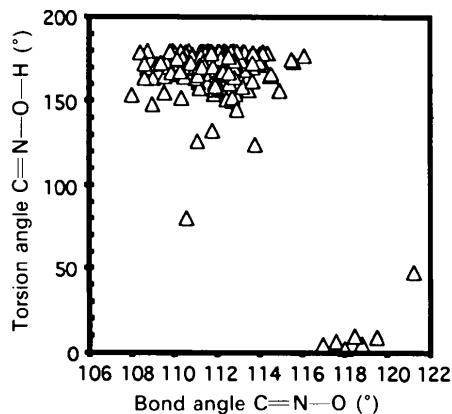
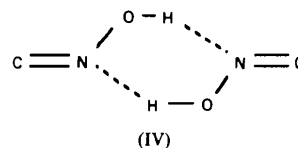


Fig. 5. Geometry of dioximes. Scatterplot of the $C=N-O$ bond angle against the torsion angle $C=N-O-H$.



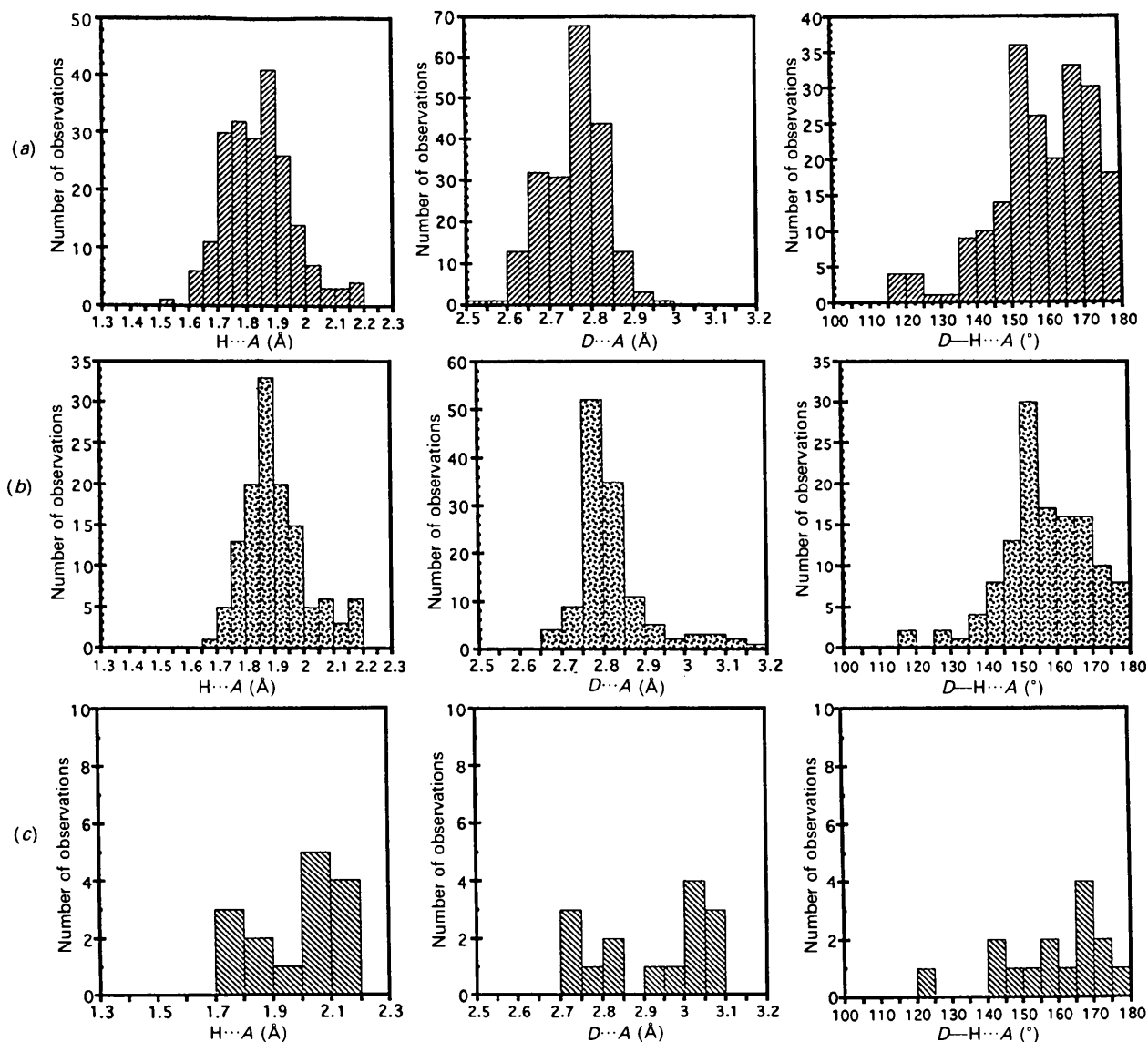


Fig. 6. Geometry of hydrogen-bonding in oximes. Distribution of $H\cdots A$, $D\cdots A$ and $D-H\cdots A$ observed in a survey of 232 oximes for each type of hydrogen bonding (see scheme for the parameter definitions).

O—H \cdots N hydrogen bonds, which have a mean value for the $H\cdots A$ distance of 1.905 Å, $D\cdots A$ of 2.822 Å and $D-H\cdots A$ angle of 157°. The corresponding parameters for the *A* family are significantly shorter (1.801, 2.729 Å) and the $D-H\cdots A$ angle is 161°. The evidence suggests that hydrogen bonds of type (a) are more linear. On the other hand, these values could be due to the participation of the O—H \cdots O bonds in hydrogen bonding. We see that the observed hydrogen-bonding arrangements are the results of a competition between two factors: a preference for including as many donors and acceptors as possible in the hydrogen-bonding scheme and a preference for stronger acceptors to form hydrogen bonds. Fig. 8 illustrates the super-

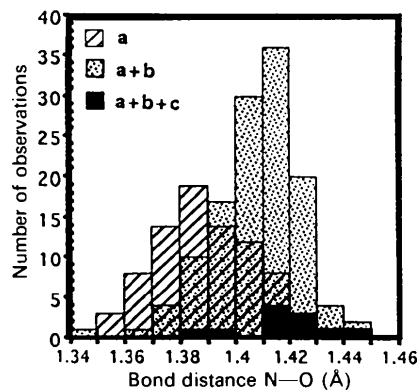


Fig. 7. Superposition of the distributions of N—O bond lengths for oxime groups involving in *A*, *D* and *G* families.

position of hydrogen-bonding related parameters for the *A* and *D* families.

4. Concluding remarks

The present study reports the first X-ray crystallographic analysis of a pair of isomers of a conforma-

tionally immobilized dioxime. In these crystal structures of two isomers of 2-(thienyl)glyoxime, the dioxime fragment adopts *E,E*- and *E,Z*-conformations, in which a pair of intermolecular hydrogen bonds are present in each case. However, in contrast to the *E,Z*-isomer, which forms a centrosymmetric motif, the *E,E*-isomer has a more extended conformation in the crystal and shows stronger and more linear hydrogen bonding.

The results of the survey of oximes in the CSD are summarized as follows: (i) in dioxime fragments the *E,E*-conformation occurs more often than for other conformations. The high flexibility of dioximes suggests that dioxime is capable of assuming a conformation close to optimal for maximum non-bonded interactions. (ii) In the oxime group, the antiperiplanar orientation of the O—H group is more favourable than synplanar. There is a correlation between the observed configuration of oxime groups and the hydrogen-bonding network in the crystal. Hydrogen bonding is not observed in oximes with a synplanar orientation of the O—H group. (iii) The N—O bond length is affected by the environment of the oxime fragment.

The authors thank the CNRS for financial support. We also are indebted to Dr J. Guilhem for fruitful discussions.

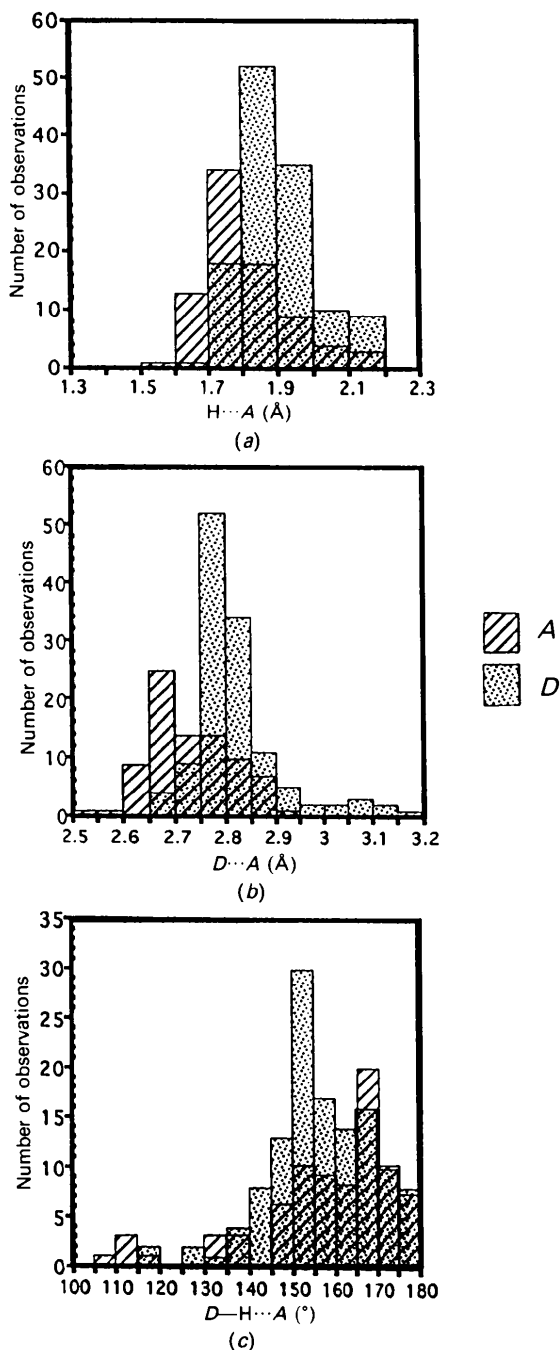


Fig. 8. Superposition of hydrogen-bonding related parameters [(a) $H\cdots A$, (b) $D\cdots A$ and (c) $D-H\cdots A$] for *A* and *D* families.

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