

## Structure of 2-Benzoylimino-3-methyl-1,3-thiazolidine: A Comparison of Intramolecular $X-S \cdots O=Y$ Interactions

BY ALAJOS KÁLMÁN AND LÁSZLÓ PÁRKÁNYI

Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest, POB 17, H-1525, Hungary

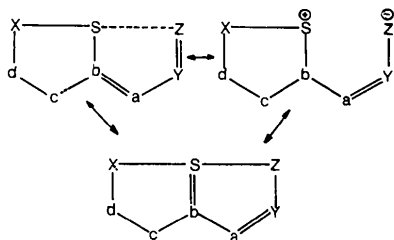
(Received 3 April 1980; accepted 13 May 1980)

### Abstract

$C_{11}H_{12}N_2OS$ ,  $M_r = 220.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.063$  (3),  $b = 12.461$  (4),  $c = 21.805$  (5) Å,  $Z = 8$  (two molecules in the asymmetric unit). Final  $R = 0.040$  for 1496 intensities. Both molecules in the asymmetric unit possess short intramolecular  $C=O \cdots S-C$  close contacts of 2.679 (5) and 2.655 (5) Å with  $C-S \cdots O$  angles of 164.1 (4) and 164.9 (4)°, respectively, suggesting a single-bond/no-bond resonance. These close contacts and their environments are discussed in a comparison with structures which exhibit  $C=O \cdots S-X$  ( $X = S, O, N$  and  $C$ ) distances in the range 2.0–3.0 Å.

### Introduction

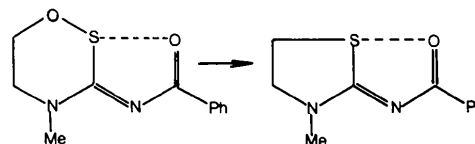
Since the solution of the structure of 2,5-dimethylthiathiophene (Bezzi, Mammi & Garbuglio, 1958) several dozen structures possessing appreciably shorter intramolecular  $X-S \cdots Z=Y$  approaches than the sum of the van der Waals radii of S and Z ( $Z = S, O, Se$  and  $N$ ) atoms have been determined by X-ray diffraction and discussed (Lozac'h, 1971). The characteristic feature of these bond systems is a bivalent S atom in a nearly coplanar environment and the presence of conjugation in a five-membered hetero ring closed by the  $S \cdots Z$  interaction.



Since most of the  $X-S \cdots Z=Y$  approaches revealed so far have  $Z = O$  atom in the electron-attracting  $Z=Y$  group, this type of interaction has been the focal point of some classifications (Lynch, Mellor & Nyburg,

1971; Kapecki, Baldwin & Paul, 1968; Johnson, Reid & Paul, 1971). Within the framework of these and other structural studies, there have also been numerous theoretical works on the nature of the attractive force between the S and Z atoms (Kapecki & Baldwin, 1969; De Barbeyrac, Gonbeau & Pfister-Guillouzo, 1973; Abrahamsson, Rehnberg, Liljefors & Sandström, 1974; Nyburg, Theodorakopoulos & Csizmadia, 1977).

A survey of the related literature has led to the conclusion that one of the strongest  $X-S \cdots O=Y$  interactions [ $S \cdots O = 2.255$  (6) Å] revealed by us in 3-benzoylimino-4-methylperhydro-1,2,4-oxathiazole (Sólyom, Sohár, Toldy, Kálmán & Párkányi, 1977) should be weakened by eliminating the ring O atom. Accordingly, an analysis of the title compound, which could also be obtained from the parent 3-benzoylimino-4-methylperhydro-1,2,4-oxathiazole *via* another reaction, has been performed.



### Experimental

Colourless needles of the title compound were provided by Dr S. Sólyom. Lattice parameters were determined from Weissenberg and precession photographs and refined by diffractometry.

### Crystal data

$C_{11}H_{12}N_2OS$ ,  $M_r = 220.3$ , orthorhombic,  $a = 8.063$  (3),  $b = 12.461$  (4),  $c = 21.805$  (5) Å,  $V = 2190.8$  (2.0) Å<sup>3</sup>,  $D_c = 1.335$ ,  $Z = 8$  (two molecules in the asymmetric unit),  $D_m = 1.34$  Mg m<sup>-3</sup>,  $F(000) = 928$ , space group  $P2_12_12_1$ .

The first set of intensities (1223 independent reflexions) were collected on a Stoe semi-automatic two-circle diffractometer with Ni-filtered  $Cu K\alpha$

Table 1. Fractional coordinates ( $\times 10^4$ ) and mean temperature factors for non-hydrogen atoms

E.s.d.'s are in parentheses.

	Molecule (a)				Molecule (b)			
	x	y	z	$B_{eq.} (\text{Å}^2)$	x	y	z	$B_{eq.} (\text{Å}^2)$
S(1)	3384 (2)	4323 (1)	3847 (1)	4.05 (1)	6910 (2)	6960 (1)	3532 (1)	5.32 (1)
O(1)	2147 (6)	4147 (3)	2711 (2)	5.23 (2)	8237 (7)	6521 (3)	4618 (2)	6.49 (2)
N(1)	2564 (6)	6262 (4)	4113 (2)	3.82 (2)	7080 (6)	5118 (4)	3008 (2)	4.33 (2)
N(2)	1711 (6)	5820 (3)	3144 (2)	3.39 (2)	8158 (6)	5049 (3)	3976 (2)	3.99 (2)
C(1)	2438 (6)	5559 (4)	3659 (2)	3.29 (2)	7463 (7)	5589 (4)	3538 (2)	4.09 (2)
C(2)	3599 (8)	5990 (5)	4633 (2)	4.36 (2)	6158 (8)	5735 (6)	2556 (3)	5.37 (2)
C(3)	3938 (8)	4806 (5)	4619 (3)	4.46 (2)	6066 (9)	6882 (6)	2759 (3)	6.62 (4)
C(4)	1950 (9)	7346 (5)	4049 (3)	5.32 (3)	7333 (9)	3989 (5)	2902 (3)	5.17 (3)
C(5)	1585 (7)	5065 (4)	2694 (2)	3.72 (3)	8531 (7)	5589 (5)	4510 (2)	4.26 (2)
C(6)	688 (6)	5446 (4)	2130 (2)	3.15 (2)	9367 (7)	4880 (5)	4983 (3)	4.07 (2)
C(7)	211 (8)	6521 (4)	2062 (2)	3.98 (2)	9592 (8)	3784 (5)	4908 (3)	4.93 (3)
C(8)	-609 (8)	6862 (5)	1547 (3)	4.65 (2)	10360 (10)	3185 (6)	5360 (3)	6.72 (4)
C(9)	-993 (8)	6135 (5)	1088 (3)	4.79 (3)	10912 (9)	3680 (7)	5883 (3)	7.09 (4)
C(10)	-521 (8)	5074 (5)	1151 (3)	4.59 (3)	10719 (8)	4749 (7)	5964 (3)	5.84 (4)
C(11)	320 (7)	4730 (4)	1663 (3)	3.98 (2)	9950 (8)	5370 (5)	5516 (3)	4.97 (3)

Table 2. Fractional coordinates ( $\times 10^3$ ) for H atoms

E.s.d.'s are in parentheses.

	Molecule (a)			Molecule (b)		
	x	y	z	x	y	z
H(21)	292 (6)	625 (4)	503 (2)	509 (7)	536 (3)	251 (2)
H(22)	466 (6)	643 (4)	466 (2)	682 (6)	568 (3)	216 (2)
H(31)	512 (6)	460 (3)	466 (2)	646 (6)	738 (3)	249 (2)
H(32)	340 (6)	442 (3)	491 (2)	514 (6)	712 (4)	283 (2)
H(41)	270 (6)	771 (3)	374 (2)	848 (6)	373 (3)	305 (2)
H(42)	92 (6)	732 (3)	393 (2)	660 (6)	351 (3)	307 (2)
H(43)	203 (6)	769 (3)	440 (2)	775 (6)	373 (4)	248 (2)
H(7)	39 (6)	696 (4)	234 (2)	925 (6)	342 (4)	457 (2)
H(8)	-90 (6)	754 (3)	149 (2)	1050 (6)	248 (4)	530 (2)
H(9)	-160 (6)	643 (3)	73 (2)	1141 (6)	326 (3)	618 (2)
H(10)	-80 (6)	464 (4)	82 (2)	1150 (6)	518 (3)	634 (2)
H(11)	68 (6)	396 (4)	170 (2)	969 (6)	618 (4)	559 (2)

radiation ( $\bar{\lambda} = 1.5418 \text{ Å}$ ) (Kálmán, Simon, Schwartz & Horváth, 1974). After data reduction 156 reflexions with  $|F| - 5\sigma(F) < 0$  were taken as unobserved. No absorption correction was made. The phase problem for 225 reflexions ( $E \geq 1.20$ ) was solved with *SHELX* (Sheldrick, 1976) giving  $R = 0.23$ . Block-diagonal least-squares refinement reduced  $R$  to 0.065 for 1059 reflexions. The H positions were generated from assumed geometries. The refinement was then continued with new data collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\bar{\lambda} = 0.71073 \text{ Å}$ ). 726 of 2222 independent reflexions with  $I - 3\sigma(I) < 0$  were regarded as unobserved. Full-matrix least-squares refinement of the positional parameters with anisotropic vibrational parameters for non-hydrogen atoms and with a mean  $B_{iso}$  ( $3.5 \text{ Å}^2$ ) for all H atoms resulted in a final  $R$  of 0.040. These calculations were performed with the Enraf-Nonius SDP system adapted

Table 3. Bond lengths (Å) for (a) and (b)

E.s.d.'s are in parentheses.

	(a)	(b)
S(1)···O(1)	2.679 (5)	2.655 (5)
S(1)-C(1)	1.767 (5)	1.766 (5)
S(1)-C(3)	1.843 (7)	1.821 (7)
C(1)-N(1)	1.326 (7)	1.332 (6)
C(1)-N(2)	1.308 (6)	1.296 (6)
N(1)-C(2)	1.448 (7)	1.454 (8)
N(1)-C(4)	1.445 (8)	1.440 (8)
C(2)-C(3)	1.501 (9)	1.498 (10)
N(2)-C(5)	1.363 (6)	1.378 (7)
C(5)-O(1)	1.231 (6)	1.208 (7)
C(5)-C(6)	1.504 (7)	1.516 (8)
C(6)-C(7)	1.402 (7)	1.387 (9)
C(7)-C(8)	1.371 (8)	1.383 (10)
C(8)-C(9)	1.385 (9)	1.371 (10)
C(9)-C(10)	1.383 (9)	1.353 (12)
C(10)-C(11)	1.375 (9)	1.392 (10)
C(11)-C(6)	1.386 (8)	1.394 (9)

Table 4. Bond angles ( $^{\circ}$ ) for (a) and (b)

E.s.d.'s are in parentheses.

	(a)	(b)
O(1)⋯S(1)–C(1)	72.3 (3)	72.1 (3)
O(1)⋯S(1)–C(3)	164.1 (4)	164.9 (4)
S(1)⋯O(1)–C(5)	95.1 (6)	95.9 (6)
C(1)–S(1)–C(3)	91.8 (5)	92.8 (5)
S(1)–C(1)–N(1)	111.7 (6)	111.2 (7)
S(1)–C(1)–N(2)	127.5 (7)	128.1 (7)
N(1)–C(1)–N(2)	120.7 (8)	120.7 (8)
C(1)–N(1)–C(2)	118.3 (8)	118.3 (8)
C(1)–N(1)–C(4)	121.3 (8)	122.5 (8)
C(2)–N(1)–C(4)	119.5 (8)	118.7 (9)
N(1)–C(2)–C(3)	108.6 (8)	109.2 (9)
C(2)–C(3)–S(1)	107.2 (7)	107.8 (8)
C(1)–N(2)–C(5)	118.7 (8)	117.6 (8)
N(2)–C(5)–O(1)	126.3 (8)	126.2 (9)
N(2)–C(5)–C(6)	114.0 (7)	112.8 (8)
O(1)–C(5)–C(6)	119.7 (8)	121.0 (9)
C(5)–C(6)–C(7)	121.4 (8)	123.5 (9)
C(5)–C(6)–C(11)	120.0 (8)	117.5 (9)
C(7)–C(6)–C(11)	118.6 (8)	119.0 (10)
C(6)–C(7)–C(8)	121.0 (9)	120.4 (11)
C(7)–C(8)–C(9)	119.8 (10)	119.7 (12)
C(8)–C(9)–C(10)	119.5 (10)	121.0 (12)
C(9)–C(10)–C(11)	121.0 (10)	120.5 (12)
C(10)–C(11)–C(6)	120.1 (9)	119.4 (10)

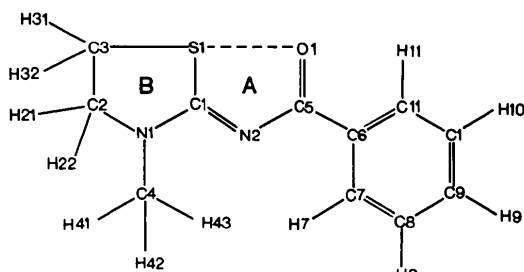


Fig. 1. Schematic drawing of the title compound with atom numbering for molecules (a) and (b).

to a PDP 11/60 minicomputer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final coordinates for non-hydrogen atoms are given in Table 1, the parameters for H atoms in Table 2, and the bond distances and angles in Tables 3 and 4. The atomic numbering is given in Fig. 1.\*

### Discussion

The corresponding bond lengths and angles in the symmetry-independent molecules (a) and (b) agree

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35428 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within experimental error. In each molecule the short exocyclic C=N bond and the valency angles at C(1) and N(1) are in accord with predicted values for the imino form of the 2-aminothiazoline moiety (Kálmán, Argay, Ribár & Toldy, 1977). The different hybridization of C(1) ( $sp^2$ ) and C(3) ( $sp^3$ ) accounts for the significantly different S<sup>II</sup>–C distances (Argay, Kálmán, Nahlovski & Ribár, 1975). As shown by the puckering parameters (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976)

	$Q$	$\varphi$	$\Delta C_s[C(2)]$
(a)	0.149 Å	121.7°	1.4°
(b)	0.075	286.4	2.0

the five-membered thiazoline ring in (b), though retaining an envelope conformation, is considerably more flattened than in (a). The opposite signs of the relevant torsion angles (Table 5) reveal a distorted mirror symmetry between (a) and (b). In each molecule the phenyl group lies approximately in the plane (Table 6) of the fairly planar hetero ring (A) formed by S(1), C(1), N(2), C(4) and O(1) and closed by the S⋯O approach of 2.679 (5) and 2.655 (5) Å, respectively. As was expected these S⋯O close contacts [the mean is 2.667 (5) Å] are significantly (by 0.4 Å) longer than in the related 3-benzoylimino-4-methylperhydro-1,2,4-oxathiazine [2.255 (3) Å] but still shorter than the sum of van der Waals radii for S and O (3.5 Å). According to Abrahamsson & Zacharis (1976) the interaction between the negatively polarized carbonyl O atom with the positively charged S is strong enough even at a distance of 2.8 Å to compensate the repulsion forces between S and O. Contrary to this Beer, McMonagle, Siddiqui, Hordvik & Jynge (1979), in accord with the conclusion of Adman, Jensen & Warrenner (1975), claim that in the range 2.6–2.8 Å there is very little or no bonding between S and O atoms. Beer and

Table 5. Endocyclic (for rings A and B) and other relevant torsion angles ( $^{\circ}$ ) for (a) and (b)

E.s.d.'s are in parentheses.

	(a)	(b)
S(1)–C(1)–N(1)–C(2)	8.2 (6)	–6.2 (6)
C(1)–N(1)–C(2)–C(3)	–16.0 (8)	9.2 (8)
N(1)–C(2)–C(3)–S(1)	15.4 (5)	–7.5 (6)
C(2)–C(3)–S(1)–C(1)	–10.0 (6)	3.9 (7)
C(3)–S(1)–C(1)–N(1)	1.7 (6)	1.0 (6)
S(1)–C(1)–N(1)–C(4)	176.9 (11)	–177.1 (11)
S(1)–C(1)–N(2)–C(5)	2.6 (5)	–0.1 (6)
C(1)–N(2)–C(5)–O(1)	–2.7 (8)	1.9 (9)
N(2)–C(5)–O(1)–S(1)	1.5 (5)	–1.9 (5)
C(5)–O(1)–S(1)–C(1)	–0.1 (6)	1.3 (6)
O(1)–S(1)–C(1)–N(2)	–1.3 (6)	–0.6 (6)
O(1)–C(5)–C(6)–C(11)	7.8 (9)	–7.1 (10)
N(1)–C(1)–S(1)–O(1)	–179.9 (9)	179.7 (10)

Table 6. Equations of planes in the form  $AX + BY + CZ = D$  where  $X$ ,  $Y$  and  $Z$  are orthogonal coordinates ( $\text{Å}$ ) related to  $a$ ,  $b$  and  $c$

Deviations ( $\text{Å} \times 10^3$ ) of relevant atoms from the planes are given in square brackets in the same order as the equations for molecules (a) and (b).

Plane (1) for ring (B): S(1), C(1), N(1), C(2) and C(3)

$$(a) 0.8647X + 0.2909Y - 0.4096Z = 0.4454$$

$$(b) 0.8874X + 0.2288Y - 0.4003Z = 3.8589$$

[S(1) 45 (2), -13 (2); C(1) 2 (5), -14 (5); N(1) -61 (5), 41 (5); C(2) 97 (6), -49 (7); C(3) -83 (6), 35 (7); O(1) 133 (5), -137 (5); N(2) 49 (5), -53 (5)]

Plane (2) for ring (A): S(1), C(1), N(2), C(5) and O(1)

$$(a) 0.8680X + 0.3219Y - 0.3781Z = 0.9285$$

$$(b) 0.9023X + 0.2388Y - 0.3588Z = 4.3300$$

[S(1) 3 (2), 5 (2); C(1) -9 (5), -5 (5); N(2) 12 (5), -3 (5); C(5) -8 (5), 12 (6); O(1) 3 (5), -9 (5); C(3) -53 (6), -27 (7); C(2) 174 (6), -143 (7)]

Plane (3) for phenyl ring C(6)–C(11)

$$(a) 0.8727X + 0.2036Y - 0.4438Z = -0.1910$$

$$(b) 0.8851X + 0.1631Y - 0.4359Z = 2.9458$$

[C(6) -5 (5), -5 (6); C(7) -2 (6), 4 (6); C(8) 6 (6), 0 (7); C(9) -4 (6), -2 (7); C(10) -2 (6), 0 (8); C(11) 7 (6), 4 (6); C(5) -16 (5), -8 (5); O(1) 130 (5), -131 (5); N(2) -171 (5), 123 (5)]

Angles between planes (e.s.d.'s  $0.5\text{--}1.1^\circ$ )

Planes (1) and (2):  $2.5$  and  $2.6^\circ$

Planes (2) and (3):  $7.8$  and  $6.3^\circ$

Planes (3a) and (3b):  $2.5^\circ$

co-workers, following an earlier suggestion of Sletten & Velsvik (1973), regard the Huggins constant energy distance of  $2.58 \text{ Å}$  as a margin between the real (*i.e.* strong) and fairly weak  $S \cdots O$  interactions. This margin seems, however, to be rather accidental. Since, as Huggins (1953) made clear, the value of  $E_{\text{rep}}^*$  (repulsion energy) is entirely arbitrary in equation (10)<sup>†</sup> the constant energy distances hardly have the physical meaning attributed to them. This is in accord with the opinion of Kapecki & Baldwin (1969) who, on the basis of extended Hückel calculations, queried the covalent character of  $S \cdots O$  contacts already from  $2.4 \text{ Å}$  onwards.

According to our semi-empirical (CNDO/2) calculation performed for simplified models, the two-centre energy terms for these close contacts rapidly decrease with increase of the  $S \cdots O$  distances. For  $S \cdots O$  close contacts in the range in which the title compound falls the static two-centre energy term is about 15–20% of that calculated for the range  $2.2\text{--}2.3 \text{ Å}$ . The strength of the van der Waals repulsion if it were not compensated in such compounds has been manifested by force-field calculations (White & Bovill,

<sup>†</sup> Huggins (1953) assumed it to have a value such that  $(a/a' - 1)E_{\text{rep}}^* = 4.2 \text{ kJ mol}^{-1}$ .

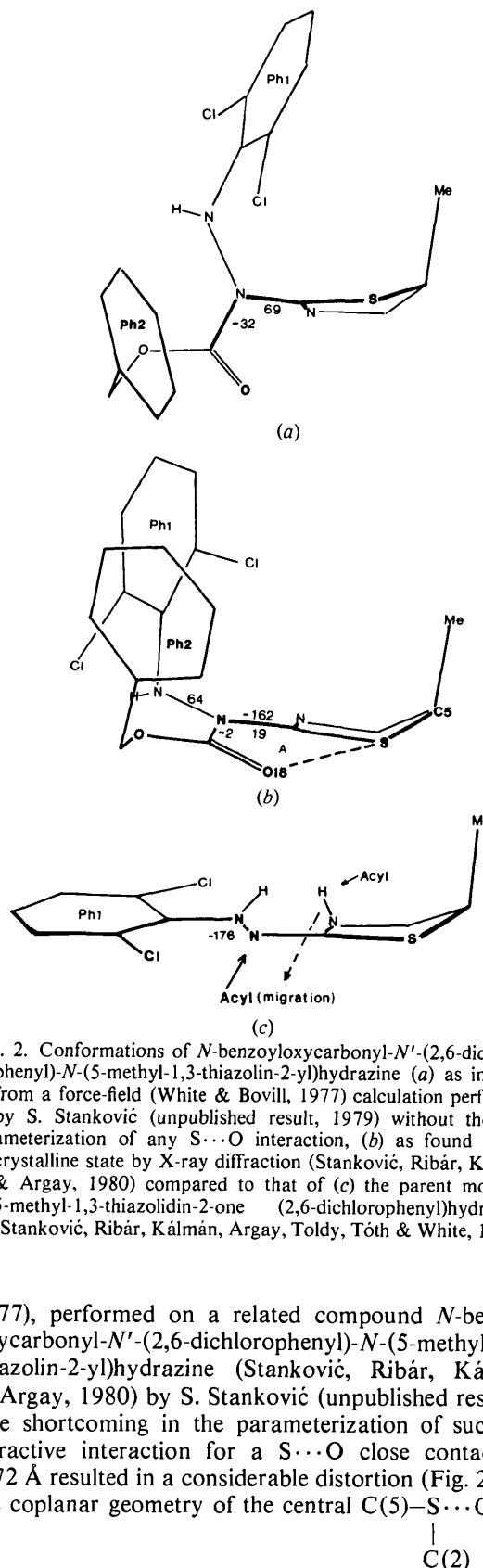


Fig. 2. Conformations of *N*-benzoyloxycarbonyl-*N'*-(2,6-dichlorophenyl)-*N*-(5-methyl-1,3-thiazolin-2-yl)hydrazine (a) as inferred from a force-field (White & Bovill, 1977) calculation performed by S. Stanković (unpublished result, 1979) without the parameterization of any  $S \cdots O$  interaction, (b) as found in the crystalline state by X-ray diffraction (Stanković, Ribár, Kálmán & Argay, 1980) compared to that of (c) the parent molecule 5-methyl-1,3-thiazolidin-2-one (2,6-dichlorophenyl)hydrazone (Stanković, Ribár, Kálmán, Argay, Toldy, Tóth & White, 1980).

1977), performed on a related compound *N*-benzoyloxycarbonyl-*N'*-(2,6-dichlorophenyl)-*N*-(5-methyl-1,3-thiazolin-2-yl)hydrazine (Stanković, Ribár, Kálmán & Argay, 1980) by S. Stanković (unpublished results). The shortcoming in the parameterization of such an attractive interaction for a  $S \cdots O$  close contact of  $2.72 \text{ Å}$  resulted in a considerable distortion (Fig. 2a) of the coplanar geometry of the central C(5)–S...O(18)

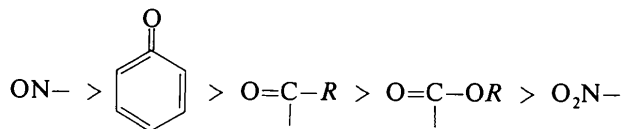
C(2)

moiety with respect to that found in the crystalline state (Fig. 2*b*). The existence of this single-bond/no-bond resonance energy which compensates the van der Waals repulsion and maintains the optimal *cis*-coplanar conformation becomes even more apparent from the geometry (Fig. 2*c*) of its parent molecule (Stanković, Ribár, Kálmán, Argay, Toldy, Tóth & White, 1980). As shown by Fig. 2(*b*) and (*c*) the entering acyl group alters the conformation of the parent molecule enabling the C=O group to occupy the optimal position in forming the S...O close contact characterized by the angle C(5)–S...O(18) = 161° and the torsion angle  $\epsilon = 177^\circ$  formed by the planes C(5)–S–C(2) and C(2)–S...O(18).

The fact that there is insufficient repulsion between S and O atoms 'to prevent these molecules being planar and hence achieving optimal  $\pi$ -orbital overlap (Mellor

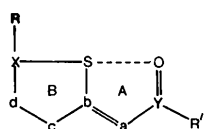
& Nyburg, 1971*b*)' is shown by the relevant parameters summarized for 26 structures in Table 7. It follows from them that the S...O distances in the range 2.0–3.0 Å are not accidental. They correspond to alterations in the environments of positively charged bi- or quadrivalent S atoms and the electron-attracting O=Y moieties closing five- or even four\*-membered hetero rings.

The relative ordering of the electron-attractive force of the O=Y–R' moieties is:



\* e.g. in *S,S*-dimethyl-*N*-trichloroacetylsulphilimine (Kálmán, Sasvári & Kucsman, 1973).

Table 7. A comparison of relevant bond parameters for 26 structures possessing S...O close contacts



No.	X	Y	a	b	c	d	R	R'	Coord.	S...O	X–S...O	X–O	X–S	s–b	b–a–Y	
1	S <sup>II</sup>	N	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	–	Y	2.03 Å	174°	1.31 Å	2.18 Å	1.72 Å	119°	
2	S <sup>II</sup>	C $\phi$	C $\phi$	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	C $\phi$	N	2.26	174	1.27	2.13	1.76	116	
3	O	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>3</sup>	–	Ph	Y	2.26	173	1.25	1.68	1.76	115	
4	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	OEt	N	2.29	164	1.25	1.74	1.78	113	
5	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	S <sup>IV</sup>	–	Ph	Y	2.31	172	1.22	1.66	1.79	114
6	S <sup>II</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	C $\phi$	–	Ph	Y	2.33	174	1.26	2.11	1.76	119	
7	S <sup>II</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	H	Y	2.38	174	1.26	2.11	1.76	116	
8	S <sup>II</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	Me	Y	2.42	174	1.26	2.10	1.76	119	
9	O	N	C $\phi$	C $\phi$	–	–	Me	O	N	2.44	177	1.24	1.65	1.77	115	
10	S <sup>II</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	S <sup>II</sup>	Csp <sup>2</sup>	–	iBu	Y	<2.51>	<175>	<1.21>	2.10	<1.74>	<119>	
11	S <sup>II</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Me	Me	Y	<2.55>	<172>	<1.21>	2.08	<1.74>	<123>	
12	Csp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>3</sup>	Nsp <sup>3</sup>	Ph	N	2.55	?	1.24	1.72	1.84	119	
13	C $\phi$	C $\phi$	C $\phi$	Nsp <sup>2</sup>	–	–	–	C $\phi$	N	2.60	178	1.23	1.77	1.64	?	
14	Csp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>3</sup>	–	Ph	N	2.63	?	1.23	1.81	1.76	118	
15	Csp <sup>3</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	S <sup>II</sup>	Csp <sup>2</sup> , Csp <sup>3</sup>	Me	Y	2.64	156	1.27	1.72	1.79	116	
16	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	–	S <sup>II</sup>	Csp <sup>2</sup>	Ph	Y	2.64	154	1.22	1.77	1.76	118	
17	Csp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>3</sup>	O	Ph	Y	2.67	163	1.19	1.79	1.78	114	
18	Csp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>3</sup>	–	Ph	Y	<2.67>	<164>	<1.23>	<1.83>	<1.77>	<118>	
19	Csp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>3</sup>	–	Ph	Y	2.69	163	1.23	1.83	1.76	118	
20	Csp <sup>3</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	S <sup>II</sup>	Csp <sup>3</sup>	–	Ph	N	2.70	?	1.25	1.83	1.72	119	
21	Csp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>3</sup>	–	Ph	Y	2.70	161	1.21	1.82	1.76	123	
22	Csp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>3</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Csp <sup>3</sup>	Me	O–	Y	2.72	161	1.21	1.83	1.77	123	
23	Csp <sup>3</sup>	Csp <sup>3</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	S <sup>II</sup>	–	–	CH <sub>2</sub>	Y	2.73	174	1.25	1.84	1.75	123	
24	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Nsp <sup>3</sup>	OH	Y	<2.79>	<165>	<1.21>	<1.78>	<1.74>	<121>	
25	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Nsp <sup>3</sup>	OMe	Y	2.89	161	1.21	1.78	1.72	121	
26	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Csp <sup>2</sup>	Nsp <sup>2</sup>	Nsp <sup>3</sup>	OMe	Y	2.96	157	1.26	1.72	1.86	110	

References: (1) Johnson, Reid & Paul (1971); (2) Pinel, Mollier, Llaguno & Paul (1971); (3) Sólyom, Sohár, Toldy, Kálmán & Párkányi (1977); (4) Leban (1976); (5) Gieren & Dederer (1978); (6) Sletten & Velsvik (1973); (7) Hordvik, Sletten & Sletten (1969); (8) Bardí, Piazzesi & Busetti (1979); (9) Hamilton & LaPlaca (1964); (10) Mellor & Nyburg (1971*b*); (11) Hordvik & Kjøge (1966); (12) Schmid *et al.* (1975); (13) Atkinson *et al.* (1977); (14) Cohen-Addad (personal communications, 1979); (15) Kapecki, Baldwin & Paul (1968); (16) Lynch, Mellor & Nyburg (1971); (17) Steple (1961); (18) present work; (19) Cohen-Addad & Viallet (1978); (20) Schmidt & Tulinsky (1967); (21) Cohen-Addad, Viallet & Boucherle (1979); (22) Stanković, Ribár, Kálmán & Argay (1980); (23) Mellor & Nyburg (1971*a*); (24) Adman, Jensen & Warrenner (1975); (25) Cameron & Hair (1971); (26) Amirthalingam & Muralidharan (1972).

The symbols Me, Et, iBu, Ph and C $\phi$  stand for methyl, ethyl, isobutyl, phenyl groups and phenyl-carbon, respectively. In column 'Coord.' Y and N mean published or non-published atomic coordinates. Mean values are given in angle brackets.

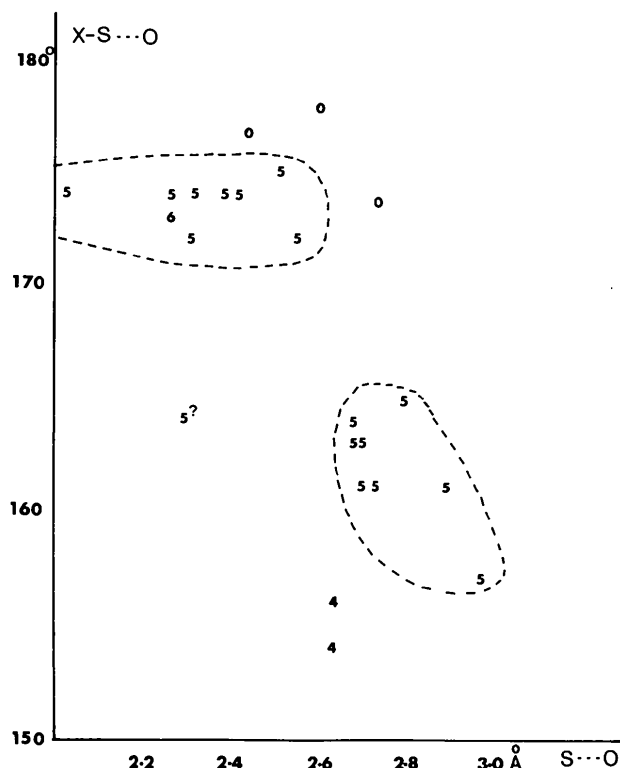


Fig. 3. Observed  $X-S\cdots O$  angles plotted against the  $S\cdots O$  distances listed in Table 7. Symbols 4, 5 and 6 stand for four-, five- or six-membered  $B$  rings (Table 7), while 0 represents structures in which there is no ring  $B$ .

while those of the  $X = S, O$  and  $N$  atoms, due to the limited number of solved structures for each type, cannot yet be determined. Neither can the relative ordering of groups  $a$  be established. The members of the upper range 2.55–2.96 Å are formed almost exclusively by  $X = C$ .<sup>\*</sup> Comparing the bonding of the title compound with that of the analogous 2-benzoylimino-3-methyl-5-thiazolidone (Steeple, 1961) no significant difference can be attributed to the difference in the hybridization ( $sp^3$  or  $sp^2$ ) of  $X = C$  atoms.

As suggested by Hamilton & LaPlaca (1964) an almost linear  $X-S\cdots O$  configuration which lies in the coplanar environment of a  $S$  atom seems to provide a favourable situation for  $S p$ - and  $d$ -orbital participation in the partial  $S\cdots O$  bonding. In fact the stronger (shorter) close contacts are accompanied by greater (nearer to  $180^\circ$ )  $X-S\cdots O$  angles. Nevertheless, as shown in Fig. 3, there is no strong correlation between the  $X-S\cdots O$  angles and the  $S\cdots O$  distances. Somewhat better correlation can be found, however, if the angles are plotted against the  $S\cdots O$  approaches of the  $S$  atoms which participate in five-membered rings.

<sup>\*</sup> In special circumstances  $S-S\cdots O=C$  approaches can also assume unusually long values [2.680 (2) and 2.689 (2) Å]. They will be discussed elsewhere (Párkányi, Kálmán, Kapovits & Kucsman, 1980).

The coplanar environment of a  $S$  atom may also be expressed by the angle formed by the planes  $X-S-b$  and  $b-S\cdots O$ . For example in the lattice of the title compound there is a more ( $a$ ) and a less ( $b$ ) puckered thiazoline ring (Table 5) but the dihedral angles ( $\epsilon$ ) are equally near to  $180^\circ$  [ $178.4$  (5) and  $178.7$  (5) $^\circ$ ] while the  $X-S\cdots O$  angles are  $164.1$  (4) and  $164.9$  (4) $^\circ$ , respectively.

To summarize, the  $C-S\cdots O$  close contacts observed in the symmetry-independent molecules of the title compound are governed by an energetically weakened interaction which is still strong enough to maintain a characteristic *cis*-coplanar conformation around  $S$  atoms.

The authors thank Dr S. Sólyom for the crystals, Mr Cs. Kertész for measuring data on a Stoe two-circle diffractometer, Dr F. van Meurs for providing data collected on a CAD-/SDP-34 system, Dr K. Fleischmann (Manager) for the invitation to one of us (AK) to work in their Application Laboratory (Enraf-Nonius Co. Ltd, Delft, Holland), and Professor I. C. Paul (Urbana, Illinois) and Mrs S. Stanković (Novi Sad, Yugoslavia) for valuable discussions.

#### References

- ABRAHAMSSON, S., REHNBERG, G., LILJEFORS, T. & SANDSTRÖM, J. (1974). *Acta Chem. Scand. Ser. B*, **28**, 1109–1120.
- ABRAHAMSSON, S. & ZACHARIS, H. M. (1976). *Acta Chem. Scand. Ser. A*, **30**, 375–380.
- ADMAN, E., JENSEN, L. H. & WARRENER, R. N. (1975). *Acta Cryst.* **B31**, 1915–1921.
- AMIRTHALINGAM, V. & MURALIDHARAN, K. V. (1972). *Acta Cryst.* **B28**, 2417–2421.
- ARGAY, GY., KÁLMÁN, A., NAHLOVSKI, Á. & RIBÁR, B. (1975). *Acta Cryst.* **B31**, 1956–1961.
- ATKINSON, A., BREWSTER, A. G., LEY, S. V., OSBORN, R. S., ROGERS, D., VILLIAMS, D. J. & WOODE, K. A. (1977). *J. Chem. Soc. Chem. Commun.* pp. 325–326.
- BARDI, R., PIAZZESI, A. M. & BUSETTI, V. (1979). *Acta Cryst.* **B35**, 2821–2822.
- BEER, R. J., MCMONAGLE, D., SIDDIQUI, M. S. S., HORDVIK, A. & JYNGE, K. (1979). *Tetrahedron*, **35**, 1199–1203.
- BEZZI, S., MAMMI, M. & GARBUGLIO, C. (1958). *Nature (London)*, **182**, 247–248.
- CAMERON, A. F. & HAIR, N. J. (1971). *J. Chem. Soc. B*, pp. 1733–1736.
- COHEN-ADDAD, C. & VIALLET, M. P. (1978). *Cryst. Struct. Commun.* **7**, 341–345.
- COHEN-ADDAD, C., VIALLET, M. P. & BOUCHERLE, A. (1979). *Acta Cryst.* **B35**, 2109–2112.
- CREMER, D. & POPLI, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- DE BARBEYRAC, J. P., GONBEAU, D. & PFISTER-GUILLOUZO, G. J. (1973). *J. Mol. Struct.* **16**, 103–115, 117–123.

- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Top. Stereochem.* **9**, 271–383.
- GIEREN, A. & DEDERER, B. (1978). *Acta Cryst.* **B34**, 2046–2049.
- HAMILTON, W. C. & LAPLACA, S. J. (1964). *J. Am. Chem. Soc.* **86**, 2289–2290.
- HORDVIK, A. & KJØGE, H. M. (1966). *Acta Chem. Scand.* **20**, 1923–1937.
- HORDVIK, A., SLETTEN, E. & SLETTEN, J. (1969). *Acta Chem. Scand.* **23**, 1377–1388.
- HUGGINS, M. L. (1953). *J. Am. Chem. Soc.* **75**, 4126–4133. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, P. L., REID, K. I. G. & PAUL, I. C. (1971). *J. Chem. Soc. B*, pp. 946–952.
- KÁLMÁN, A., ARGAY, GY., RIBÁR, B. & TOLDY, L. (1977). *Tetrahedron Lett.* pp. 4241–4244.
- KÁLMÁN, A., SASVÁRI, K. & KUCSMAN, Á. (1973). *Acta Cryst.* **B29**, 1241–1244.
- KÁLMÁN, A., SIMON, K., SCHAWARTZ, J. & HORVÁTH, G. (1974). *J. Chem. Soc. Perkin Trans. 2*, pp. 1849–1852.
- KAPECKI, J. A. & BALDWIN, J. E. (1969). *J. Am. Chem. Soc.* **91**, 1120–1123.
- KAPECKI, J. A., BALDWIN, J. E. & PAUL, I. C. (1968). *J. Am. Chem. Soc.* **90**, 5800–5805.
- LEBAN, I. (1976). *Acta Cryst.* **B32**, 1601–1604.
- LOZAC'H, N. (1971). *Adv. Heterocycl. Chem.* **13**, 161–234.
- LYNCH, T. R., MELLOR, I. P. & NYBURG, S. C. (1971). *Acta Cryst.* **B27**, 1948–1954.
- MELLOR, I. P. & NYBURG, S. C. (1971a). *Acta Cryst.* **B27**, 1954–1958.
- MELLOR, I. P. & NYBURG, S. C. (1971b). *Acta Cryst.* **B27**, 1959–1963.
- NYBURG, S. C., THEODORAKOPOULOS, G. & CSIZMADIA, I. (1977). *Theor. Chim. Acta*, **45**, 21–32.
- PÁRKÁNYI, L., KÁLMÁN, A., KAPOVITS, I. & KUCSMAN, Á. (1980). *Acta Cryst.* To be published.
- PINEL, R., MOLLIER, Y., LLAGUNO, E. C. & PAUL, I. C. (1971). *J. Chem. Soc. Chem. Commun.* pp. 1352–1353.
- SCHMID, U., HEIMGARTNER, H., SCHMID, H., SCHÖNHOLZER, P., LINK, H. & BERNAUER, K. (1975). *Helv. Chim. Acta*, **58**, 2222–2227.
- SCHMIDT, W. H. & TULINSKY, A. (1967). *Tetrahedron Lett.* pp. 5311–5313.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SLETTEN, J. & VELSVIK, M. (1973). *Acta Chem. Scand.* **27**, 3881–3888.
- SÓLYOM, S., SOHÁR, P., TOLDY, L., KÁLMÁN, A. & PÁRKÁNYI, L. (1977). *Tetrahedron Lett.* pp. 4245–4248.
- STANKOVIĆ, S., RIBÁR, B., KÁLMÁN, A. & ARGAY, GY. (1980). *Acta Cryst.* **B36**, 1235–1238.
- STANKOVIĆ, S., RIBÁR, B., KÁLMÁN, A., ARGAY, GY., TOLDY, L., TÓTH, I. & WHITE, D. N. J. (1980). *Acta Cryst.* **B36**, 2282–2286.
- STEEPLE, H. (1961). *Acta Cryst.* **14**, 847–853.
- WHITE, D. N. J. & BOVILL, M. J. (1977). *J. Chem. Soc. Perkin Trans. 2*, pp. 1610–1623.

*Acta Cryst.* (1980). **B36**, 2378–2385

## Constrained Powder-Profile Refinement Based on Generalized Coordinates. Application to X-ray Data of Isotactic Polypropylene

By ATTILIO IMMIRZI

*Istituto di Chimica delle Macromolecole del CNR, Via A. Corti 12, 20133 Milano, Italy*

(Received 27 November 1979; accepted 28 May 1980)

### Abstract

A computer program combining Rietveld's procedure of powder-profile refinement with the use of constrained variables has been set up with the purpose of studying polymeric materials in the presence of amorphous fractions with their own diffraction patterns. The program, suitable for both X-ray and neutron radiation applications, lends itself to treating any kind of constraint. A flexible profile function, *viz* Pearson's VII, which generalizes the Gauss, Lorentz and Cauchy distribution functions, is considered. An X-ray application, namely the structure of isotactic polypropylene ( $\alpha$  form) in the unoriented state, is illustrated.

The three models already proposed, *Cc*, *C2/c* [Natta & Corradini (1960). *Nuovo Cimento Suppl.* **15**, 40–51] and *P2<sub>1</sub>/c* [Mencick (1972). *J. Macromol. Sci. Phys.* **6**, 101–115] are analysed. The third is found to be the most reliable, but with a helix disordering mode rather different from that suggested by Mencick.

### Introduction

The use of powder-profile-refinement techniques in crystal structure analysis by diffraction methods (Rietveld, 1967, 1969) has received growing attention in recent years. So far, however, application of the method has been confined to problems with a moderate