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The Crystal Structures of the Two Isomers of Methyl(phenylsulphonyl)furoxan, $C_9H_8N_2O_4S$

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3-Methyl-4-(phenylsulphonyl)furoxan is the lower-melting isomer (83–85°) of the title compound. It is monoclinic, space group $P2_1/c$, with $a=14{\cdot}345$, $b=5{\cdot}508$, $c=13{\cdot}855$ Å, $\beta=108{\cdot}26°$, $Z=4$. 4-Methyl-3-(phenylsulphonyl)furoxan, the higher-melting isomer (97–98°), is orthorhombic, space group $P2_12_12_1$, with $a=16{\cdot}835$, $b=5{\cdot}044$, $c=12{\cdot}455$ Å, $Z=4$. Both structures were solved by Patterson and Fourier methods from diffractometer data (Cu $K\alpha$ radiation) and refined by full-matrix least squares to R 0·047 and 0·041 respectively. All H atoms were located on difference syntheses and isotropically refined. The phenyl ring and the plane through C–S–C are roughly orthogonal in both isomers, while the latter plane and the furoxan group are roughly coplanar in the lower-melting and roughly orthogonal in the higher-melting isomer. The furoxan moiety and the sulphone group do not seem to conjugate at all in the lower-melting isomer, while they show a small conjugation in the higher-melting compound. Some conjugation between the sulphone groups and the phenyl rings seems to be present in both isomers.

Introduction

The present article deals with two positional isomers, which were prepared by Gasco, Mortarini, Ruà & Serafino (1973) as part of a general study on the chemical and pharmacological properties of furoxan derivatives. These authors assigned structures on the basis of n.m.r. observations and classified the lower-melting isomer (LMI hereinafter) as 3-methyl-4-(phenylsulphonyl)furoxan and the higher-melting isomer (HMI) as 4-methyl-3-(phenylsulphonyl)furoxan, in compliance with the widely accepted convention of regarding the 'pentavalent' N atom as the 2-position of the furoxan ring. Gasco & Boulton (1973) studied the isomerization reactions and the equilibration rates for the title and several other pairs of furoxan isomers.

A concise report on the structure of LMI has been published (Chiari, Viterbo, Gaetani Manfredotti & Guastini, 1973); in this paper the complete description of the two structures is given and a comparison between the two isomers made.

Structure determination

Experimental results

LMI prepared by Gasco *et al.* (1973) was recrystallized from aqueous alcohol and gave colourless transparent prisms, with the pinacoidal forms well developed, usually elongated along *y*. For HMI the only crystals suitable for X-ray analysis were those recrystallized from methanol as slender prisms, markedly elongated along *y*.

The crystal classes and space groups were determined from Weissenberg photographs (Cu $K\alpha$); the cell constants and intensities were measured at room temperature on an automated Siemens AED single-crystal diffractometer (Cu $K\alpha$, Ni-filtered radiation) by the θ–2θ scanning technique.

Crystal data

LMI: $C_9H_8N_2O_4S$, $M=240{\cdot}24$, m.p. 83–85°C; monoclinic, $a=14{\cdot}345$ (4), $b=5{\cdot}508$ (2), $c=13{\cdot}855$ (3) Å, $\beta=108{\cdot}26$ (4)°, $U=1039{\cdot}6$ Å^3, space group: $P2_1/c$, $F(000)=496$, $D_c=1{\cdot}53$ g cm^{-3}, $Z=4$, $\mu(\text{Cu } K\alpha)=27{\cdot}5$ cm^{-1}.

HMI: $C_9H_8N_2O_4S$, $M=240{\cdot}24$, m.p. 97–98°C; orthorhombic, $a=16{\cdot}835$ (6), $b=5{\cdot}044$ (5), $c=12{\cdot}455$ (8) Å, $U=1057{\cdot}6$ Å^3, space group: $P2_12_12_1$, $F(000)=496$, $D_c=1{\cdot}51$ g cm^{-3}, $Z=4$, $\mu(\text{Cu } K\alpha)=27{\cdot}0$ cm^{-1}.

For LMI 1976 reflexions were explored ($6° \leq 2\theta \leq 140°$), 1832 of which, having $I>2\sigma(I)$, were included in the analysis. For HMI 1186 reflexions were explored ($6° \leq 2\theta \leq 140°$) and 1138 were used in the analysis.*

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* The final F_o, F_c tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31297 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The observations were corrected for Lorentz–polarization effects, but not for absorption ($\mu\bar{r} < 0{\cdot}5$). Scattering factors were from *International Tables for X-ray Crystallography* (1962), for neutral atoms.

Structure solution and refinement

Both structures were solved by Patterson and Fourier methods; LMI turned out to be 3-methyl-4-(phenylsulphonyl)furoxan and HMI to be 4-methyl-3-(phenylsulphonyl)furoxan, in agreement with the n.m.r. assignments. The refinement was started by block-diagonal least-squares methods and completed by anisotropic full-matrix cycles. All H atoms were located from difference syntheses and refined isotropically. At the end of the refinements the shifts were no more than one tenth of the standard deviations. The weighting scheme for both was: $1/w = A + B|F_o| + C|F_o|^2$: the values of the coefficients were deduced from the $\langle|\Delta F|\rangle vs. |F|$ distribution (Stout & Jensen, 1968). The coefficients so obtained were, for LMI: $A = 0{\cdot}0900$, $B = 0{\cdot}0175$, $C = 0{\cdot}0009$; for HMI: $A = 0{\cdot}1201$, $B = 0{\cdot}0389$, $C = 0{\cdot}0031$.

For LMI the final R was 0·047 ($R_w = 0{\cdot}068$; $R = 0{\cdot}048$ including 144 weak reflexions with zero weight in the refinement). For HMI the final R was 0·041 ($R_w = 0{\cdot}058$; $R = 0{\cdot}044$ including 48 zero-weight reflexions).

Table 1. *LMI: fractional coordinates* ($\times 10^4$ *for* S,O,N,C; $\times 10^3$ *for* H) *and vibrational parameters with the significant figures of e.s.d.'s in parentheses*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1880 (0)	1249 (1)	1143 (0)	2·30 (2)	2·63 (2)	3·11 (3)	−0·02 (3)	0·64 (3)	0·02 (4)
O(1)	2862 (1)	5935 (4)	−366 (1)	3·29 (10)	4·79 (9)	3·92 (10)	−1·15 (10)	1·06 (8)	0·24 (9)
O(2)	1636 (1)	6876 (4)	−1848 (1)	5·05 (14)	4·77 (12)	3·92 (11)	−0·22 (10)	1·25 (9)	1·16 (9)
O(3)	1812 (1)	−1148 (3)	727 (2)	4·81 (11)	2·92 (10)	4·38 (11)	−0·62 (10)	0·56 (10)	−0·66 (9)
O(4)	1058 (1)	2257 (4)	1368 (1)	2·98 (9)	5·32 (12)	4·82 (12)	0·66 (10)	1·65 (9)	1·00 (9)
N(1)	1871 (1)	5598 (4)	−1075 (2)	3·12 (11)	3·62 (13)	3·30 (13)	−0·18 (10)	0·92 (10)	−0·01 (11)
N(2)	2951 (1)	4423 (4)	445 (2)	2·78 (11)	4·53 (12)	3·72 (12)	−0·54 (11)	0·72 (10)	0·15 (10)
C(1)	1433 (2)	3920 (4)	−700 (2)	2·65 (11)	3·18 (14)	3·05 (13)	−0·06 (10)	0·73 (10)	−0·15 (11)
C(2)	2118 (2)	3260 (4)	246 (2)	2·39 (11)	3·17 (15)	3·11 (13)	−0·03 (11)	0·73 (11)	−0·21 (11)
C(3)	431 (2)	3035 (6)	−1245 (2)	2·79 (15)	5·21 (26)	4·48 (18)	−0·61 (13)	0·01 (12)	0·31 (15)
C(4)	2939 (2)	1538 (4)	2197 (2)	2·92 (11)	2·90 (14)	2·91 (13)	0·03 (12)	0·86 (10)	0·05 (12)
C(5)	3691 (2)	−163 (4)	2345 (2)	3·20 (14)	3·35 (15)	3·68 (14)	0·36 (12)	0·97 (11)	−0·05 (13)
C(6)	4523 (2)	99 (5)	3177 (2)	3·15 (15)	4·59 (19)	4·28 (17)	0·44 (13)	0·54 (12)	0·59 (15)
C(7)	4601 (2)	2025 (6)	3840 (2)	4·00 (17)	5·18 (20)	3·53 (16)	−0·80 (15)	0·31 (12)	0·28 (14)
C(8)	3851 (2)	3694 (5)	3682 (5)	5·52 (20)	4·12 (19)	3·63 (16)	−0·85 (16)	0·82 (14)	−0·95 (14)
C(9)	3010 (2)	3473 (5)	2857 (2)	4·21 (17)	3·28 (16)	3·93 (15)	0·10 (13)	1·22 (12)	−0·46 (13)

	x	y	z	B		x	y	z	B
H(5)	363 (3)	−162 (8)	183 (3)	5·4 (1·1)	H(9)	244 (3)	467 (9)	274 (3)	6·7 (1·3)
H(6)	508 (3)	−109 (8)	326 (3)	5·0 (1·1)	H(31)	−5 (3)	334 (9)	−82 (3)	8·5 (1·4)
H(7)	527 (3)	212 (9)	443 (3)	6·3 (1·2)	H(32)	40 (4)	127 (10)	−133 (4)	10·7 (1·6)
H(8)	394 (3)	503 (9)	415 (3)	6·8 (1·3)	H(33)	16 (3)	384 (9)	−178 (3)	7·8 (1·4)

Table 2. *HMI: fractional coordinates* ($\times 10^4$ *for* S,O,N,C; $\times 10^3$ *for* H) *and vibrational parameters with the significant figures of e.s.d.'s in parentheses*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	589 (0)	94 (1)	343 (0)	3·66 (3)	2·96 (3)	4·16 (3)	0·06 (2)	−0·10 (1)	−0·80 (2)
O(1)	2320 (1)	−4818 (6)	−297 (2)	4·20 (9)	6·63 (14)	5·91 (10)	1·54 (10)	0·50 (6)	−0·45 (12)
O(2)	1656 (2)	−2291 (7)	−1508 (2)	8·81 (14)	7·96 (16)	3·71 (8)	2·27 (14)	1·50 (8)	0·57 (10)
O(3)	789 (1)	2203 (4)	−383 (2)	5·79 (9)	3·23 (9)	6·65 (10)	−0·75 (8)	−0·36 (8)	0·25 (8)
O(4)	445 (1)	637 (5)	1454 (2)	5·48 (8)	5·71 (11)	5·00 (9)	0·41 (9)	0·18 (8)	−2·15 (8)
N(1)	2282 (1)	−5217 (7)	798 (2)	4·35 (9)	6·54 (14)	5·77 (11)	1·27 (12)	−1·18 (7)	−0·05 (15)
N(2)	1735 (1)	−2889 (6)	−562 (2)	4·24 (8)	4·92 (12)	4·25 (9)	0·48 (11)	0·50 (7)	−0·20 (10)
C(1)	1733 (1)	−3698 (7)	1173 (2)	3·76 (11)	4·95 (11)	4·16 (12)	−0·23 (12)	−0·75 (9)	−0·20 (12)
C(2)	1385 (1)	−2183 (6)	347 (2)	3·34 (10)	3·60 (13)	3·65 (10)	−0·07 (9)	0·01 (8)	−0·49 (11)
C(3)	1540 (3)	−3645 (12)	2356 (2)	7·89 (19)	9·25 (29)	3·88 (10)	1·30 (10)	−1·03 (11)	0·27 (17)
C(4)	−198 (1)	−1732 (5)	−195 (2)	3·39 (9)	3·12 (11)	3·92 (9)	0·23 (10)	0·14 (8)	−0·24 (11)
C(5)	−384 (2)	−1381 (7)	−1275 (2)	4·17 (11)	4·58 (14)	4·18 (10)	0·03 (11)	0·26 (8)	0·27 (11)
C(6)	−988 (2)	−2909 (7)	−1717 (2)	4·45 (11)	5·37 (16)	4·23 (10)	−0·26 (11)	−0·36 (10)	−0·22 (12)
C(7)	−1385 (2)	−4730 (8)	−1095 (2)	4·08 (11)	5·37 (18)	5·06 (13)	−0·36 (13)	−0·01 (9)	−0·70 (15)
C(8)	−1199 (2)	−5026 (8)	−18 (2)	4·17 (12)	5·23 (16)	5·24 (13)	−1·07 (14)	0·18 (9)	0·74 (14)
C(9)	−607 (1)	−3525 (7)	448 (2)	4·11 (11)	4·51 (20)	3·95 (11)	0·04 (11)	0·36 (9)	0·04 (10)

	x	y	z	B		x	y	z	B
H(5)	−10 (2)	−1 (9)	−171 (3)	5·4 (0·8)	H(9)	−47 (2)	−363 (8)	124 (3)	6·0 (0·9)
H(6)	−112 (2)	−232 (9)	−248 (3)	6·2 (0·9)	H(31)	179 (2)	−526 (10)	271 (3)	7·7 (1·0)
H(7)	−185 (2)	−594 (9)	−139 (3)	7·3 (1·0)	H(32)	100 (2)	−423 (8)	245 (3)	5·9 (0·9)
H(8)	−154 (2)	−619 (9)	50 (3)	6·6 (0·9)	H(33)	177 (3)	−150 (10)	250 (3)	9·9 (1·4)

The final atomic parameters are listed in Tables 1 and 2 for LMI* and HMI respectively. The thermal parameters B_{ij} are the coefficients of the function $\exp(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*)$.

Description and discussion of the structures

Figs. 1 and 2 show projections of LMI and HMI onto the least-squares planes through the five atoms of the furazan group; they also give the unconventional numbering scheme adopted in preceding papers for the furoxan isomer pairs (*cf.* Calleri, Chiari, Germain & Viterbo, 1973; Chiesi Villa, Guastini, Calleri & Chiari, 1974; Calleri, Viterbo, Gaetani Manfredotti & Guastini, 1974; Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975). The bond distances and angles are recorded in Tables 3 and 4. The equations of the least-squares planes through several molecular fragments are given in Table 5 with their mutual angles; from this table it appears that the furazan ring is not strictly planar in either isomer, even though the deviations of the atoms are rather small; the ring is more planar in HMI. On the other hand, the phenyl ring, which is rigorously planar in LMI, deviates slightly from planarity in HMI. It is possible that these small deviations have no real physical meaning, since uncorrected systematic and model errors may be present.

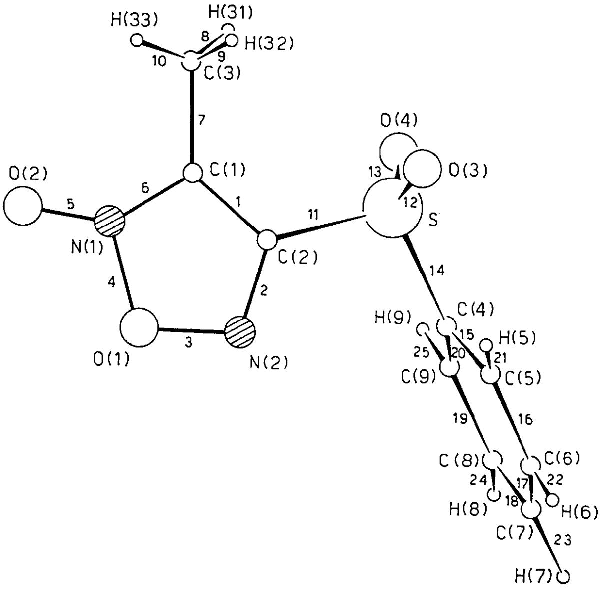

Fig. 1. LMI. Projection of the molecule onto the least-squares mean plane of the furoxan ring.

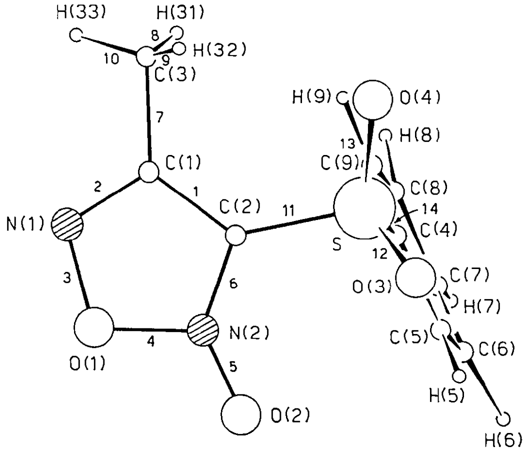

Fig. 2. HMI. Projection of the molecule onto the least-squares mean plane of the furoxan ring. For the numbering of the phenyl ring see Fig. 1.

Table 3. *LMI: bond distances and angles with e.s.d.'s in parentheses*

1	1·417 (3) Å	8	1·06 (5) Å	14	1·754 (2) Å	20	1·387 (4) Å
2	1·307 (3)	9	0·98 (5)	15	1·395 (3)	21	1·06 (4)
3	1·372 (3)	10	0·85 (5)	16	1·383 (3)	22	1·01 (4)
4	1·465 (3)	11	1·776 (3)	17	1·384 (5)	23	1·05 (5)
5	1·237 (3)	12	1·432 (2)	18	1·380 (4)	24	0·96 (5)
6	1·313 (4)	13	1·423 (4)	19	1·383 (4)	25	1·02 (4)
7	1·481 (4)						

⟨C–C⟩ in the phenyl ring: 1·3875 (2) Å

Table 3 (*cont.*)

1,2	113·1 (2)°	7,10	113 (3)°	12,14	110·5 (1)°	17,18	120·6 (2)°
2,3	106·3 (2)	8,9	102 (5)	13,14	110·0 (1)	17,22	122 (2)
3,4	107·2 (2)	8,10	101 (5)	14,15	119·3 (2)	17,23	115 (3)
4,5	117·0 (2)	9,10	115 (4)	14,20	119·0 (2)	18.19	120·5 (3)
4,6	107·9 (2)	11,1	125·3 (2)	15,16	118·6 (2)	18 23	125 (3)
5,6	135·1 (2)	11,2	121·4 (2)	15,20	121·7 (2)	18,24	118 (3)
6,1	105·5 (2)	11,12	107·2 (2)	15,21	121 (2)	19,20	118·6 (2)
6,7	122·6 (2)	11,13	105·4 (1)	16,17	120·2 (3)	19,24	122 (2)
7,1	131·9 (2)	11,14	102·7 (1)	16,21	121 (2)	19,25	121 (3)
7,8	111 (2)	12,13	119·5 (1)	16,22	119 (2)	20,25	120 (3)
7,9	113 (3)						

Mean tetrahedral angle at sulphur: 109·2 (1)°

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* The values reported in a preliminary paper (Chiari *et al.*, 1973) are slightly different, being obtained from block-diagonal least-squares refinement with unit weights.

The tetrahedral coordination around the S atoms (Tables 3 and 4) shows considerable distortions as in other phenylsulphones (*e.g.* Sime & Abrahams, 1960; O'Connell & Maslen, 1967; Pokrywiecki, Weeks & Duax, 1973). The O–S–O angle increases to 120° (av.) while the C–S–C angle narrows to 103° (av.). These large deviations from the ideal tetrahedral configuration probably result from the non-bonded interactions described by Bartell (1962). The distance O(3)···O(4) (2·48 Å, av.) is shorter than C(2)···C(4) (2·76 Å, av.), so that repulsion between the O atoms is greater than between the C atoms. The average value of the angles around S is close to the ideal value (Tables 3 and 4). The S–O bonds have comparable and high π-bond character, >60% according to Cruickshank (1961).

Table 4. *HMI*: *bond distances and angles with e.s.d.'s in parentheses*

1	1·409 (4) Å	8	1·02 (5) Å	14	1·747 (3) Å	20	1·390 (4) Å
2	1·288 (4)	9	0·96 (4)	15	1·393 (4)	21	1·00 (4)
3	1·380 (4)	10	1·16 (4)	16	1·390 (4)	22	1·02 (4)
4	1·423 (4)	11	1·765 (3)	17	1·375 (5)	23	1·06 (4)
5	1·224 (4)	12	1·436 (3)	18	1·386 (5)	24	1·04 (4)
6	1·325 (4)	13	1·431 (3)	19	1·380 (4)	25	1·02 (4)
7	1·509 (5)						

⟨C–C⟩ in the phenyl ring: 1·386 (2) Å.

The S–C_{ph} distances are not significantly different in the two isomers and agree with those observed in other compounds (Table 6). Their values seem to indicate some degree of π-conjugation (Ammon, Watts & Stewart, 1970) in agreement also with the fact that S nearly lies in the phenyl plane and that the phenyl ring is approximately perpendicular to the C(2)SC(4) plane: the angle between these planes is 83° and 79° for LMI and HMI respectively, *i.e.* not far

Table 4 (*cont.*)

1,2	110·8 (3)°	7,10	95 (2)°	12,14	109·0 (2)°	17,18	120·5 (3)°
2,3	107·8 (3)	8,9	96 (4)	13,14	110·1 (1)	17,22	128 (2)
3,4	107·2 (2)	8,10	122 (3)	14,15	118·3 (2)	17,23	123 (2)
4,5	117·8 (2)	9,10	126 (3)	14,20	119·8 (3)	18,19	120·8 (3)
4,6	107·1 (2)	11,1	132·1 (2)	15,16	118·5 (3)	18,23	116 (2)
5,6	135·1 (3)	11,6	120·6 (2)	15,20	121·9 (2)	18,24	122 (2)
6,1	107·1 (2)	11,12	107·8 (1)	15,21	120 (2)	19,20	118·2 (3)
7,1	127·8 (3)	11,13	104·5 (1)	16,17	120·2 (3)	19,24	116 (2)
7,2	121·3 (3)	11,14	103·5 (2)	16,21	121 (2)	19,25	123 (2)
7,8	108 (2)	12,13	120·5 (2)	16,22	112 (2)	20,25	119 (2)
7,9	108 (2)						

Mean tetrahedral angle at sulphur: 109·2 (2)°

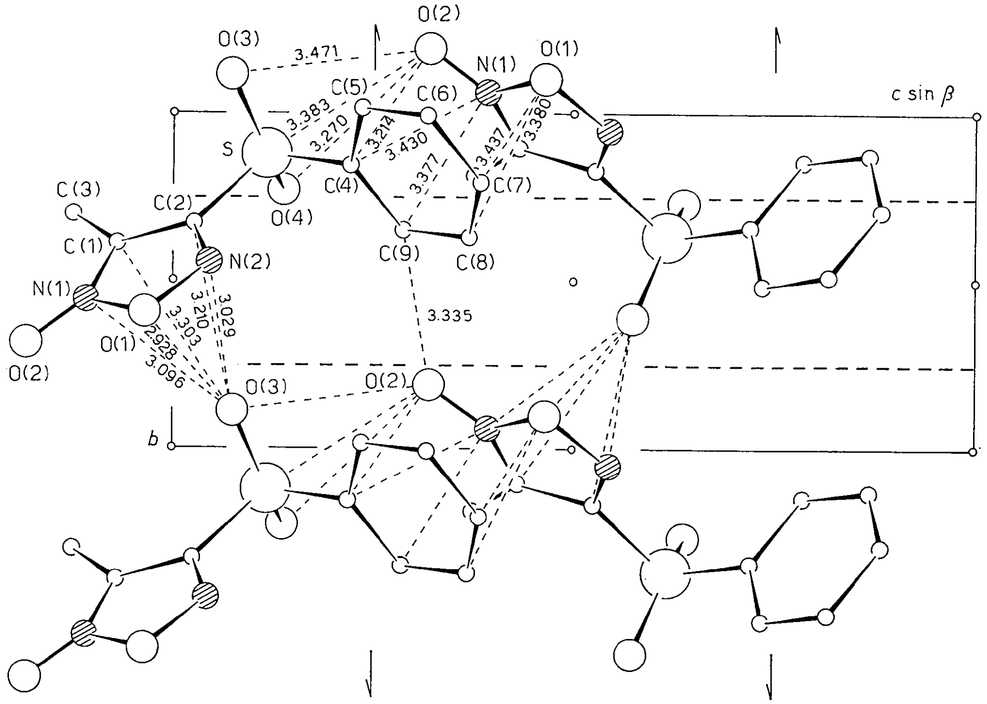


Fig. 3. LMI. Projection of the structure on (100). For clarity, the molecules related by the screw axes and centres of symmetry have been omitted.

Table 5. *Least-squares mean planes, in fractional coordinates, referred to the unit-cell axes*

$\langle\delta\rangle$ = mean distance of the atoms from their planes; $\chi^2 = \sum(\delta/\sigma)^2$.

LMI
(1) Plane through C(2), S, C(4)
$8{\cdot}134x - 4{\cdot}108y - 7{\cdot}048z = 0{\cdot}211$
(2) Plane through the phenyl ring C(4) to C(9)
$-8{\cdot}933x - 3{\cdot}069y + 9{\cdot}932z = -0{\cdot}917$
$\langle\delta\rangle = 0{\cdot}001$ Å, $\chi^2 = 0{\cdot}45$, S at $-0{\cdot}010$ Å
(3) Plane through the furazan ring C(1), C(2), N(1), N(2), O(1)
$-7{\cdot}508x + 3{\cdot}947y + 8{\cdot}329z = -0{\cdot}102$
$\langle\delta\rangle = 0{\cdot}007$ Å, $\chi^2 = 71{\cdot}45$, S at $0{\cdot}136$, O(2) at $0{\cdot}049$, C(3) at $-0{\cdot}059$ Å
(4) Plane through O(3), S, O(4)
$0{\cdot}710x - 2{\cdot}092y + 11{\cdot}941z = 1{\cdot}237$
Angles: 1,2 = 82°40′ 1,3 = 7°4′ 1,4 = 82°46′
2,3 = 79°45′ 2,4 = 46°32′ 3,4 = 82°46′

HMI
(1) Plane through C(2), S, C(4)
$4{\cdot}349x + 1{\cdot}498y - 11{\cdot}444z = -0{\cdot}123$
(2) Plane through the phenyl ring C(4) to C(9)
$11{\cdot}256x - 3{\cdot}547y - 2{\cdot}993z = 0{\cdot}440$
$\langle\delta\rangle = 0{\cdot}005$ Å, $\chi^2 = 16{\cdot}20$, S at $0{\cdot}086$ Å
(3) Plane through the furazan ring C(1), C(2), N(1), N(2), O(1)
$-11{\cdot}403x - 3{\cdot}643y - 1{\cdot}714z = -0{\cdot}836$
$\langle\delta\rangle = 0{\cdot}005$ Å, $\chi^2 = 9{\cdot}51$, S at $-0{\cdot}072$, O(2) at $-0{\cdot}044$, C(3) at $-0{\cdot}009$ Å
(4) Plane through O(3), S, O(4)
$16{\cdot}341x - 0{\cdot}706y + 2{\cdot}451z = 1{\cdot}039$
Angles: 1,2 = 79°20′ 1,3 = 74°50′ 1,4 = 88°24′
2,3 = 84°50′ 2,4 = 45°34′ 3,4 = 54°21′

from the 90° value predicted by Koch & Moffitt (1951) as suitable for overlap of the S 3*d* and the trigonal C 2*p* orbitals.

A lower degree of π-conjugation between S and furoxan is indicated by the S–C_{fur} distance in the HMI isomer where the angle formed by the furazan ring and the C(2)SC(4) plane is 75°, *i.e.* not far from the theoretical requirements for conjugation. On the other hand π-conjugation is particularly unfavoured in the LMI isomer where the angle between the C(2)SC(4) plane and the furazan ring is only 7° and S shows a larger displacement from the furazan plane. This situation is supported by the value of the S–C_{fur} distance which in LMI corresponds well to that (1·78 Å) assumed for a C_{sp2}–S^{VI} single bond (Andreetti, Bocelli & Sgarabotto, 1974).

The trend of bond distances and angles in the furoxan moieties of the two isomers is similar to that found in other substituted furoxans and in general the considerations developed on this argument in connexion with the methylfuroxancarboxamide isomers (Calleri *et al.* 1975) are valid also in the present case. The difference between bonds 3 and 4, which is always greater for the isomer in which the methyl group is next to the *N*-oxide function (*i.e.* LMI for all the pairs of Table 7 excepting the amide derivatives, in which the isomer with the methyl group next to the *N*-oxide function is HMI) takes here for LMI one of the largest values. HMI shows a remarkable difference between bonds 2 and 6: bond 2 is in the lower part of the range of the values quoted in Table 7.

In both isomers the deformations of the phenyl ring caused by the sulphonyl group are in agreement with the rules of Domenicano, Vaciago & Coulson (1975). In particular the endocyclic angle α at the C atom to which the electron-withdrawing sulphonyl group is attached is a little larger than the theoretical trigonal value, while the two endocyclic angles β at the adjacent C atoms are a little narrower than the theoretical value. Since conjugation between the sulphonyl group and the phenyl ring is rather small, the corresponding effect on the endocyclic angle α, which should be opposite to that produced by the electron-withdrawing group, must be small.

The reciprocal orientation of the planes through O(3)SO(4) and the phenyl ring is indicated by the angle formed by these two planes, 47° and 46° in LMI and HMI respectively. This orientation is influenced by the contacts H(5)···O(3) which are 2·59 (4) and 2·49 (4) Å in LMI and HMI respectively, as required by normal van der Waals contacts.

The molecular conformation of HMI is particularly influenced by the interactions between the exocyclic O and the sulphonyl group [O(2)···O(3) = 3·038 (4) Å]. The absence of this interaction in LMI can justify the fact that this isomer is slightly favoured at equilibrium (Gasco & Boulton, 1973), as the sulphonyl group exerts a repulsion on the O entering at N(2) and therefore the addition at N(1) is favoured.

The molecules are packed in the two isomers as illustrated in Figs. 3 and 4; other contacts less than 3·5 Å are shown in Table 8.

We thank Dr A. Gasco for suggesting this work and providing the samples, and Professors L. Cavalca and M. Nardelli for their interest.

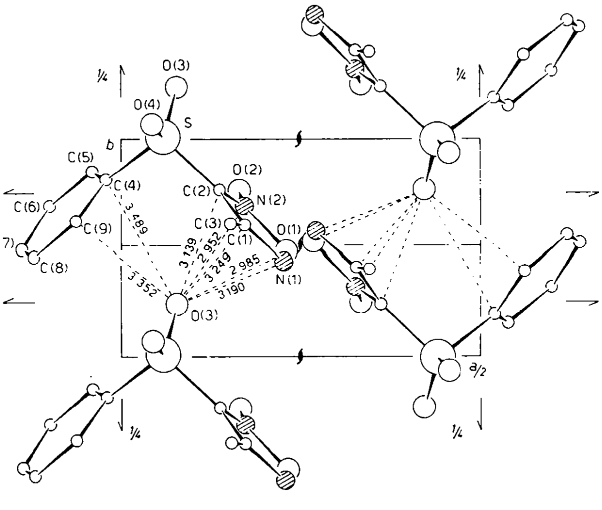
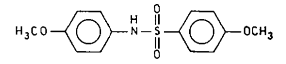
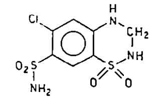
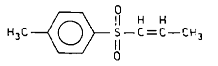
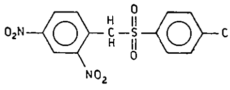
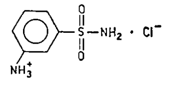
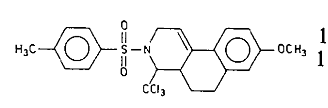
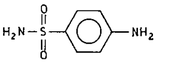
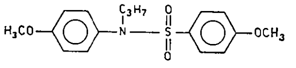
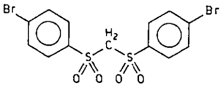
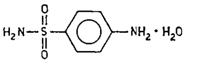
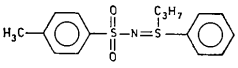
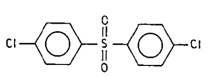
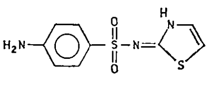
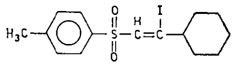
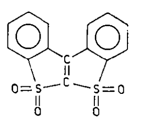
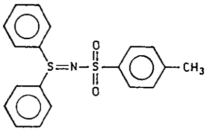


Fig. 4. HMI. Projection of the structure on (001). For clarity, the molecules related by the screw axes parallel to **a** and **b** have been omitted.

Table 6. *Comparison of the* $S–C_{ph}$ *distances in sulphones*

Compound	$S–C_{ph}$(Å)	Ref.	Compound	$S–C_{ph}$ (Å)	Ref.	Compound	$S–C_{ph}$ (Å)	Ref.
LMI HMI	1·754 (2) 1·747 (3)	*a*		1·756 (6)	*g*		1·754 (11)	*n*
	1·766 (3)	*b*		1·753 (4)	*h*		1·765 (4)	*o*
	1·75 (2) 1·78 (2)	*c*		1·750 (18)	*i*		1·766 (6)	*p*
	1·73 (2)	*d*		1·748 (12)	*j*		1·763 (8)	*q*
	1·765 (6)	*e*		1·748 (10) 1·745 (5) 1·769 (6) 1·749 (9)	*k*		1·78	*r*
	1·779 (5) 1·784 (4)	*f*		1·759 (3)	*l*			
				1·756 (8)	*m*			

(*a*) This work; (*b*) Klazinga & Vos (1973); (*c*) Van der Meer (1973); (*d*) Berthou, Jéminet & Laurent (1972); (*e*) Sime & Abrahams (1960); (*f*) Goldberg & Shmueli (1971); (*g*) Pokrywiecki, Weeks & Duax (1973*a*); (*h*) Harlow, Simonsen, Pfluger & Sames (1974); (*i*) O'Connell & Maslen (1967); (*j*) Alléaume & Decap, (1968); (*k*) Kruger & Gafner (1972); (*l*) Kruger & Gafner (1971); (*m*) Kálmán, Duffin & Kucsman (1971), (*n*) Dupont & Dideberg (1972); (*o*) Le Bars, Alléaume & Hauw (1973); (*p*) Pokrywiecki, Weeks & Duax (1973*b*); (*q*) Kálmán & Sasvári (1972); (*r*) Ohrt, Parthasarathy, Wolf & Truce (1975).

Table 7. *Endocyclic and exocyclic bond distances of the furoxan group of* $CH_3(C_2N_2O_2)R'$ *furoxans*

Bond	R′ = sulphone¹		R′ = amide²		R′ = dimethylamide³˒⁴		R′ = hydrazide⁵		R′ = nitro⁶
	LMI	HMI	LMI	HMI	LMI	HMI	LMI	HMI	
2	1·307 (3) Å	1·288 (4) Å	1·304 (2) Å	1·307 (2) Å	1·299 (2) Å	1·301 (3) Å	1·306 (4) Å	1·307 (5) Å	1·288 (6) Å
6	1·313 (4)	1·325 (4)	1·324 (2)	1·324 (3)	1·310 (3)	1·311 (3)	1·317 (4)	1·326 (4)	1·332 (6)
3	1·372 (3)	1·380 (4)	1·384 (2)	1·375 (3)	1·368 (3)	1·384 (3)	1·358 (3)	1·388 (4)	1·367 (5)
4	1·465 (3)	1·423 (4)	1·428 (2)	1·445 (2)	1·447 (3)	1·436 (3)	1·450 (5)	1·427 (3)	1·479 (5)
1	1·417 (3)	1·409 (4)	1·423 (2)	1·419 (3)	1·411 (3)	1·424 (3)	1·413 (5)	1·422 (4)	1·401 (6)
5	1·237 (3)	1·224 (4)	1·232 (2)	1·240 (2)	1·242 (3)	1·232 (3)	1·229 (4)	1·231 (3)	1·220 (5)
7	1·481 (4)	1·509 (5)	1·487 (3)	1·477 (4)	1·480 (4)	1·474 (4)	1·490 (7)	1·492 (5)	1·476 (8)

(1) Present work; (2) Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo (1975); (3) Chiesi Villa, Guastini, Calleri & Chiari (1974); (4) Calleri, Viterbo, Gaetani Manfredotti & Guastini (1974); (5) Calleri, Chiari, Germain & Viterbo (1973); (6) Cameron & Freer (1974).

Table 8. *Contacts less than* 3·5 Å

LMI		HMI			
C(3)···O(2ⁱ)	3·357 (3) Å	O(2)···C(6ⁱ)	3·322 (5) Å	C(7)···N(1ⁱⁱⁱ)	3·376 (5) Å
C(3)···O(4ⁱⁱ)	3·330 (4)	O(2)···C(7ⁱ)	3·285 (4)	O(3)···O(2ⁱᵛ)	3·436 (4)
		N(1)···C(7ⁱⁱ)	3·416 (5)		

LMI		HMI			
(i)	$\bar{x}, y-\frac{1}{2}, \bar{z}-\frac{1}{2}$	(i)	$\bar{x}, \frac{1}{2}+y, \bar{z}-\frac{1}{2}$	(iii)	$x-\frac{1}{2}, \bar{y}-\frac{1}{2}, \bar{z}$
(ii)	$\bar{x}, 1-y, \bar{z}$	(ii)	$\frac{1}{2}+x, \bar{y}-\frac{1}{2}, \bar{z}$	(iv)	$\bar{x}, 1+y, z$

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The Crystal Structure of Diisothiocyanatodiethoxy-(1,3-diphenylpropane-1,3-dionato)-niobium(V)

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The structure of $Nb(OC_2H_5)_2(NCS)_2(C_6H_5COCHCOC_6H_5)$ has been determined by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final R of 0·034 for 2353 independent reflexions. The crystals are triclinic, space group $P\bar{1}$, with $a = 11{\cdot}085$ (4), $b = 12{\cdot}688$ (5), $c = 8{\cdot}690$ (3) Å, $\alpha = 94{\cdot}07$ (5), $\beta = 97{\cdot}72$ (5), $\gamma = 77{\cdot}40$ (5)°, $Z = 2$. Nb is involved in distorted octahedral coordination; the donor atoms are the N atoms of the isothiocyanato groups, and the O atoms of the ethoxy and of the dibenzoylmethane (dbm) groups.

Introduction

An X-ray analysis of diisothiocyanatodiethoxy-(1,3-diphenylpropane-1,3-dionato)niobium(V) was undertaken after the structural study by n.m.r. and infrared spectroscopy (Kergoat, Tocquer, Guerchais & Dahan, 1976) in order to confirm the monomeric structural unit and to determine the coordination of the Nb atom.