

The Crystal Structures of the Two Isomers of Methylfuroxancarbohydrazide, $C_4H_6N_4O_3$

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3-Methyl-4-furoxancarbohydrazide is the lower melting isomer (124–126°) of the title compounds. It crystallizes in space group $P\bar{1}$, with two molecules in a unit cell having $a=9.092$, $b=6.733$, $c=6.987$ Å, $\alpha=69.91$, $\beta=117.72$, $\gamma=117.40^\circ$. The higher melting isomer (129–131°) is 4-methyl-3-furoxancarbohydrazide, which has the space group $P2_1/c$ and four molecules in the unit cell with $a=12.151$, $b=7.531$, $c=7.236$ Å, $\beta=94.11^\circ$. Both structures were solved by direct methods and refined to $R=6.2\%$ (for 1205 non-zero reflexions) and to $R=4.9\%$ (for 932 non-zero reflexions) respectively, using diffractometer data (Mo $K\alpha$ radiation). The coordinates of all the hydrogen atoms were obtained from difference syntheses and refined. In both molecules non-hydrogen atoms deviate significantly from planarity and even the furoxan rings are not strictly planar. Several intra- and intermolecular contacts occur.

Gasco, Mortarini, Ruà & Menziani (1972) and Gasco, Mortarini, Ruà, Nano & Menziani (1972) have synthesized several pairs of isomers of asymmetrically substituted furoxans. They have also proposed a n.m.r. method for the structural assignment of isomers following the suggestion of Mallory & Cammarata (1966). In order to confirm their assignments and to study the influence of the different substituents on the furoxan ring, we have undertaken an X-ray analysis of a few of these compounds.

The present article illustrates the crystal structures of 3-methyl-4-furoxancarbohydrazide (lower melting isomer: LMI hereinafter) and of 4-methyl-3-furoxancarbohydrazide (higher melting isomer: HMI). A concise report of these structures has been published (Germain & Viterbo, 1972; Calleri, Chiari & Viterbo, 1972).

Experimental

Crystal data and intensity measurement

The compounds prepared by Gasco *et al.* (1972) were recrystallized from ethanol to give prismatic crystals suitable for X-ray investigation. The crystal classes and space groups were determined from Weissenberg photographs (Cu $K\alpha$ radiation). The unit-cell constants and relative intensities of the reflexions were measured, at room temperature, by a Hilger and Watts 4-circle diffractometer using the θ - 2θ step scanning technique. Molybdenum $K\alpha$ radiation (0.7107 Å) was used with a β -filter and pulse-height analyser. The crystal data are:

LMI: $C_4H_6N_4O_3$, $M=158.124$, m.p. 124–126°C; triclinic, $a=9.092$ (1), $b=6.733$ (8), $c=6.987$ (6) Å, $\alpha=69.91$ (2), $\beta=117.72$ (2), $\gamma=117.40$ (2)°; $U=331.58$ Å³. Space group chosen: $P\bar{1}$ (confirmed by the subsequent analysis); $F(000)=164e$, $D_{calc}=1.584$ cm⁻³, $Z=$

2. Crystal dimensions: 0.3 × 0.3 × 0.5 mm, rotation axis: [001].

HMI: $C_4H_6N_4O_3$, $M=158.24$, m.p. 129–131°C; monoclinic, $a=12.151$ (3), $b=7.531$ (2), $c=7.236$ (2) Å, $\beta=94.11$ (2)°; $U=660.5$ Å³. Space group: $P2_1/c$ (C_{2h}^5 , No. 14), $F(000)=328e$, $D_{calc}=1.590$ g cm⁻³, $Z=4$. Crystal dimensions: 0.2 × 0.3 × 0.6 mm; rotation axis: [010].

For LMI, 1710 reflexions were measured, 505 of which were considered as 'unobserved'; for HMI 1810 reflexions were measured, 932 of which were used throughout the analysis. The 'unobserved' reflexions were periodically checked during the refinement and no abnormal F_c value was noticed. The observations were corrected for Lorentz-polarization effects, but not for absorption. The computation of atomic scattering factors was by linear interpolation of the values for neutral atoms recommended in *International Tables for X-ray Crystallography* (1962).

Structure determination and refinement

Both structures were solved by direct methods. For HMI the solution proceeded straightforwardly using the *MULTAN* program of Germain, Main & Woolfson (1971). For LMI, however, no E map gave a plausible solution. Four peaks were chosen from the map obtained using the most consistent set of phases; with this starting model the phase refinement was attempted by the tangent formula assuming a $P1$ symmetry (*cf.* Karle, 1968). Despite the fact that one of the said peaks was spurious, the structure improved showing two molecules related by a centre of symmetry. To return to the $P\bar{1}$ symmetry, the origin was then translated to the inversion centre.

From Fourier syntheses the molecule of LMI

turned out to be that of 3-methyl-4-furoxancarbohydrazide, while that of HMI showed the configuration of 4-methyl-3-furoxancarbohydrazide in accordance with the conclusion of Gasco *et al.* (1972).

The refinement was by least-squares full-matrix methods. For LMI two isotropic followed by three anisotropic cycles reduced R to 0.097. A difference synthesis computed at this stage permitted the location of all the hydrogen atoms. The introduction of these atoms, whose coordinates alone were refined, improved the agreement ($R=0.090$) and four further cycles lowered R to 0.062 for the 1205 non-zero reflexions. The final average shift/error value for *all* the parameters was 0.09. The last cycles were computed using the *ORFLS* program of the X-RAY System, version 1970, edited by J. McD. Stewart of Maryland University, U.S.A.

The weighting scheme was:

$$\sigma^2 = 1 + \left(\frac{F_o - B}{A} \right)^2$$

where $A=8$ and $B=4$. It yielded a reasonably good sequence of $w\Delta^2$ values for reflexions batted in groups of increasing F_o 's and $\sin \theta$ values.

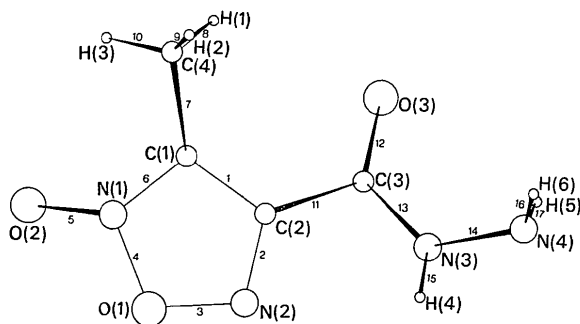


Fig. 1. Atom and bond numbering scheme for LMI.

The positional and vibrational parameters are listed in Table 1, with the numbering scheme shown in Fig. 1.

The refinement of HMI proceeded in the same way. Starting from the coordinates of the E map, one cycle of refinement on coordinates alone, followed by two isotropic and three anisotropic cycles, lowered R to 0.077. A difference synthesis showed, in this case also, all the hydrogen atoms, and their introduction produced a very large decrease in R to 0.056. Four final cycles, using *ORFLS* program and refining the coordinates of the hydrogen atoms, yielded a final $R=0.049$ for the 932 non-zero reflexions.* The average shift/error value for *all* the variables was 0.03. The weighting scheme was used in the last cycles with $A=15$ and $B=8.5$. These values gave a very good constancy of $w\Delta^2$ versus F_o and a satisfactory trend versus the $\sin \theta$ values.

The parameters of HMI are listed in Table 2 with the numbering scheme of Fig. 2.

Description and discussion of the structures

The bond distances and interbond angles of LMI and HMI are listed in Tables 3 and 4. Figs. 1 and 2 represent the orthographic projections of the LMI and HMI molecules, respectively, onto the mean planes through the five atoms of the furoxan groups (the only planar part in both molecules); the figures also show the numbering scheme adopted for atoms, bonds and angles.

For LMI, the mean plane through all the non-hydrogen atoms excepting N(3) and N(4) has, in fractional coordinates, the equation:

$$-3.506x + 6.670y - 1.511z = 0.645.$$

* The final F_o, F_c tables are available from the first two authors and have also been deposited with the National Library, England as Supplementary Publication No. SUP30096. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ.

Table 1. Fractional coordinates and vibrational parameters ($\times 10^4$) of LMI with the significant figures of the standard deviations in parentheses

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	6332 (4)	3211 (5)	4875 (5)	124 (5)	242 (9)	209 (8)	55 (5)	51 (5)	-38 (7)
C(2)	4669 (5)	2288 (5)	5112 (5)	136 (5)	222 (9)	195 (8)	57 (5)	68 (5)	-34 (6)
C(3)	2878 (4)	1751 (5)	3316 (5)	135 (5)	269 (9)	194 (8)	70 (6)	68 (5)	-14 (7)
C(4)	6851 (6)	3963 (8)	2934 (7)	168 (7)	436 (16)	274 (11)	72 (9)	121 (7)	2 (10)
N(2)	4850 (4)	1914 (5)	7158 (4)	148 (5)	421 (12)	205 (7)	98 (6)	57 (5)	-67 (7)
N(1)	7545 (4)	3366 (5)	6870 (5)	129 (5)	328 (10)	253 (8)	64 (5)	53 (5)	-71 (7)
N(3)	1500 (4)	970 (6)	3927 (5)	117 (5)	425 (12)	171 (7)	59 (6)	56 (5)	-48 (7)
N(4)	-262 (4)	444 (7)	2454 (5)	131 (5)	480 (14)	213 (8)	65 (7)	62 (5)	-44 (8)
O(1)	6624 (5)	2553 (5)	8371 (4)	153 (5)	501 (11)	205 (6)	102 (6)	39 (4)	-97 (6)
O(2)	9180 (3)	3999 (5)	7672 (5)	120 (5)	538 (12)	330 (9)	73 (6)	31 (5)	-12 (8)
O(3)	2746 (3)	2008 (5)	1431 (4)	160 (5)	560 (12)	184 (6)	61 (6)	76 (4)	-67 (7)
H(2)	6102 (61)	2911 (75)	1925 (74)	$B=3.0 \text{ \AA}^2$					
H(1)	6592 (56)	5367 (76)	2204 (72)	$B=3.0$					
H(3)	8104 (65)	4376 (71)	3414 (72)	$B=3.0$					
H(4)	1538 (59)	801 (76)	5013 (78)	$B=3.0$					
H(6)	-465 (58)	-738 (78)	1909 (75)	$B=3.0$					
H(5)	-302 (60)	1597 (80)	1564 (83)	$B=3.0$					

The estimated standard deviations of the 9 atoms from this plane are, however, 0.028 Å with C(4), O(2) and O(3) at about 0.04 Å from the plane. With a very large $\chi^2=342$ this group of atoms is certainly non-planar; the furoxan ring, excluding O(2), is possibly non-planar ($\bar{\sigma}=0.003$, $\chi^2=2.22$). The equation of the latter mean plane is:

$$-3.446x + 6.672y + 1.538z = 0.706;$$

atom O(2) is at 0.02 Å from this plane.

The equation of the mean plane passing through all the non-hydrogen atoms of HMI excepting N(3) and N(4), is:

$$-5.059x - 0.179y + 6.776z = -2.230.$$

With $\chi^2=52.2$ and $\bar{\sigma}=0.008$ HMI also is significantly non-planar. Atoms O(1) and O(3) are about 0.01 Å out of the plane. The equation of the plane passing through the five atoms of the furoxan ring, excepting O(2), is:

$$-5.121x - 0.233y + 6.760z = -2.285.$$

With $\chi^2=0.33$ ($\bar{\sigma}=0.0008$) this ring can be considered significantly planar; atom O(2) is 0.01 Å out of the plane.

The planarity, therefore, is altogether more marked in the higher melting isomer than in the lower melting one; a similar trend had been found in another pair of isomers studied by us (Calleri, Ferraris & Viterbo, 1969*a, b*).

Inspection of bond distances and interbond angles in both furoxan moieties of the title hydrazides shows that they are similar to those of the other furoxans whose structures have been studied so far. Bond 1 has a marked double-bond character (over 30%) as in the other aryl-alkyl furoxans (Calleri *et al.*, 1969*a, b*; Viterbo & Ferraris, 1970; Battaglia, Dondoni, Panattoni, Bondoli & Clemente, 1971) and benzofuroxans (Cady, Larson & Cromer, 1966; Britton & Noland, 1972; Prout, Hodder & Viterbo, 1972) in agreement with the lengthening of bonds 2 and 6; bond 5 has the

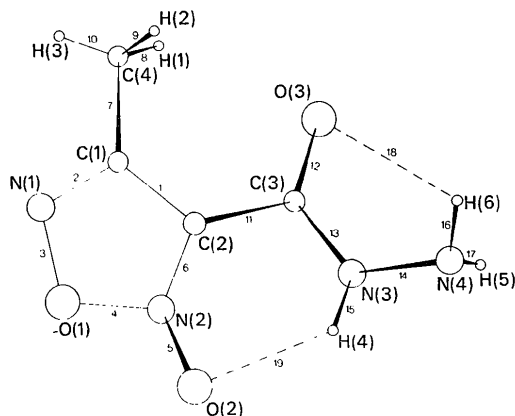


Fig. 2. Atom and bond numbering scheme for HMI.

usual very high double-bond character. Bond 4 is much longer than bond 3 and this is a rule for all the quoted furoxans with the remarkable exception of 4,6-dinitrobenzofuroxan (Prout, Hodder & Viterbo, 1972,) where the presence of a nitro group next to the furoxan ring allows the contribution of resonance forms implying a tautomeric interconversion different from the usual one *via* a dinitroso compound. However, the magnitude of the said difference, highly significant in most cases, does not seem to be directly correlated either to the electronegativity of the substituents or to the length of the extranuclear N → O bonds. As regards this latter bond, it must be remembered that the difference between the largest value (1.221 (6) Å, Calleri *et al.*, 1969*a*), and one of the smallest (1.204 (4) Å, Britton & Noland, 1972) found in structures determined with a comparable degree of accuracy, is certainly significant on the basis of the *t* test. The distribution of the differences of bonds 4–3, *versus* the corresponding N → O values, is apparently of a Gaussian nature around the mid-point at ~1.22 Å.

Bond 2 is significantly shorter than bond 6 in both hydrazides; the same situation obtains in all the other

Table 2. Fractional coordinates and vibrational parameters ($\times 10^4$) of HMI with the significant figures of the standard deviations in parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	6630 (2)	3548 (4)	1764 (4)	49 (2)	168 (6)	164 (7)	2 (3)	7 (3)	3 (5)
C(2)	7534 (2)	2460 (3)	2411 (4)	49 (2)	113 (5)	149 (6)	-3 (2)	7 (3)	-1 (4)
C(3)	8634 (2)	2987 (3)	3240 (4)	51 (2)	106 (4)	133 (6)	-5 (2)	8 (3)	-1 (4)
C(4)	6557 (3)	5525 (5)	1758 (7)	72 (3)	161 (7)	274 (10)	31 (4)	-14 (4)	21 (7)
N(1)	5800 (2)	2581 (4)	1104 (5)	56 (2)	196 (6)	269 (8)	-1 (3)	-21 (3)	-2 (5)
N(2)	7221 (2)	791 (2)	2118 (4)	56 (2)	142 (4)	201 (6)	-16 (2)	-2 (3)	-11 (4)
N(3)	9324 (2)	1686 (3)	3777 (4)	53 (2)	103 (4)	209 (6)	-1 (2)	-12 (2)	-1 (4)
N(4)	376 (2)	2059 (4)	4659 (4)	53 (2)	131 (5)	217 (7)	4 (2)	-21 (3)	-3 (4)
O(1)	6121 (2)	817 (3)	1283 (4)	61 (2)	184 (5)	295 (7)	-27 (2)	-25 (3)	-23 (4)
O(2)	7659 (2)	-664 (3)	2420 (4)	87 (2)	102 (4)	330 (7)	-4 (2)	-10 (3)	-16 (4)
O(3)	8846 (2)	4572 (2)	3416 (3)	67 (2)	108 (4)	264 (6)	-5 (2)	-3 (2)	-2 (4)
H(1)	7205 (58)	5982 (88)	1003 (98)	$B=3.0 \text{ \AA}^2$					
H(2)	6711 (38)	5923 (61)	3098 (76)	$B=3.0$					
H(3)	5862 (43)	5858 (62)	1269 (68)	$B=3.0$					
H(4)	9116 (30)	575 (49)	3746 (51)	$B=3.0$					
H(5)	847 (40)	2012 (66)	3835 (73)	$B=3.0$					
H(6)	332 (31)	3162 (56)	5049 (60)	$B=3.0$					

quoted compounds except bis-*p*-chlorophenylfuroxan (Battaglia *et al.*, 1971, *loc. cit.*) and 5-methylbenzofuroxan (Britton & Noland, 1972), but this difference is seldom significant.

The furoxan moiety, in conclusion, appears to have well defined characteristics more likely to be slightly influenced by the crystal field than by the presence of different substituents.

The configuration of the hydrazide groups of LMI and HMI, including the hydrogen atoms, is quite comparable to that found in several other hydrazides (*cf. e.g.* Jensen, 1956; Chesnut & Marsh, 1958; Jensen & Lingafelter, 1961). The shortening of bond 14 with respect to twice the single-bond radius of nitrogen (0.74 Å) is significant and could be explained by the slight difference in electronegativity between N(4) and N(3). However, the electron-diffraction study of hydrazine (Morino, Iijima & Murata, 1960) showed that the single-bond value for nitrogen in this kind of compound is really shorter (1.45 Å) than the expected one; it is therefore probable that no particular meaning need be attributed to the length of bond 14 [*cf.* also the study by Shintani (1960) of the centrosymmetric molecule of diacetylhydrazine; N-N = 1.40 Å].

In Table 5 the shortest intra- and intermolecular approaches, occurring in the crystals of LMI and HMI, are listed with reference to the assumed asymmetric units (*cf.* Tables 1 and 2). Some of these contacts would suggest the existence of hydrogen bonds, but, after looking at the bond distances and angles involving the hydrogen atoms also, one may conclude that no

real bonding takes place. The two intramolecular interactions in HMI (dashed lines in Fig. 2) are reported in detail in Table 4; although in this case the distances O(2)---H(4) and O(3)---H(6) are significantly shorter than the sum of the van der Waals radii, the values of angles 15, 19 and 16, 18, very different from 180°, simply suggest the presence of weak interactions. These interactions, practically absent in the LMI molecule, are in agreement with thermodynamic data on the interconversion equilibrium of these two hydrazides: a free-energy difference $\Delta G = 700 \text{ cal mole}^{-1}$ was assessed in favour of HMI (Boulton & Gasco, 1973). On the other hand, for other pairs of furoxan isomers (Boulton & Gasco, 1973), the isomer having a methyl group adjacent to the *N*-oxide oxygen was found to be the favoured one and recent investigations of Boulton and coworkers (personal communication) lead to the general conclusion that 'The *N*-oxide oxygen prefers to occupy the less hindered site adjacent to the smaller group except for some fused-ring cases or when, as in the case of amino-furoxans, electronic effects are of overriding importance' (*cf.* also Gagneux & Meier, 1970).

The energy difference between the isomers is in any case rather small and, furthermore, one should not expect a strict correspondence between molecules in dilute solution and in the solid state where packing energy may play a major role.

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Table 3. Bond distances and interbond angles of LMI with *e.s.d.*'s in parentheses

1	1.413 (5) Å	6	1.317 (4) Å	10	0.95 (5) Å	14	1.395 (4) Å
2	1.306 (5)	7	1.490 (7)	11	1.492 (4)	15	0.71 (6)
3	1.358 (3)	8	0.98 (5)	12	1.223 (5)	16	0.90 (6)
4	1.450 (5)	9	0.96 (5)	13	1.328 (6)	17	0.81 (5)
5	1.229 (4)						
1,2	111.9 (2)°	4,5	117.0 (3)°	8,9	107 (4)°	13,14	123.2 (3)°
1,6	105.9 (3)	4,6	107.7 (3)	8,10	107 (5)	13,15	126 (4)
1,7	133.0 (3)	5,6	135.3 (4)	9,10	117 (4)	14,15	110 (4)
1,11	126.5 (3)	6,7	121.1 (3)	11,12	120.1 (4)	14,16	104 (3)
2,3	107.2 (3)	7,8	104 (4)	11,13	115.7 (3)	14,17	106 (3)
2,11	121.6 (3)	7,9	111 (3)	12,13	124.2 (3)	16,17	115 (5)
3,4	107.3 (2)	7,10	109 (3)				

Table 4. Bond distances and interbond angles of HMI with *e.s.d.*'s in parentheses

1	1.422 (4) Å	6	1.326 (4) Å	11	1.480 (4) Å	16	0.88 (4) Å
2	1.307 (4)	7	1.492 (5)	12	1.226 (3)	17	0.86 (5)
3	1.388 (4)	8	1.05 (7)	13	1.329 (4)	18	2.34 (4)
4	1.427 (3)	9	1.02 (5)	14	1.416 (4)	19	2.16 (4)
5	1.231 (3)	10	0.93 (5)	15	0.87 (4)		
1,2	110.9 (3)°	4,6	107.6 (2)°	8,10	114 (5)°	14,15	117 (3)°
1,6	106.7 (2)	5,6	134.5 (2)	9,10	112 (4)	14,16	105 (2)
1,7	128.4 (3)	5,19	91 (1)	11,12	118.7 (2)	14,17	108 (3)
1,11	129.2 (2)	6,11	124.0 (2)	11,13	116.9 (2)	15,19	130 (3)
2,3	107.2 (2)	7,8	106 (4)	12,13	124.3 (2)	16,17	109 (4)
2,7	120.7 (3)	7,9	106 (3)	12,18	76 (1)	16,18	109 (3)
3,4	107.6 (2)	7,10	109 (3)	13,14	121.0 (2)		
4,5	117.9 (2)	8,9	108 (5)	13,15	122 (2)		

Table 5. Shortest intra- and intermolecular distances

LMI		HMI	
Intramolecular		Intramolecular	
O(2)···C(4)	2.988 Å	O(2)···N(3)	2.811 Å
O(2)···H(3)	2.62	O(2)···H(4)	2.16
O(3)···C(4)	3.089	O(3)···N(4)	2.758
O(3)···H(2)	2.69	O(3)···H(6)	2.34
O(3)···N(4)	2.784	O(3)···C(4)	3.035
O(3)···H(5)	2.70	O(3)···H(2)	2.78
O(3)···H(6)	2.75	O(3)···H(1)	2.77
Intermolecular		Intermolecular	
O(3)···N(4) at (\bar{x} , \bar{y} , \bar{z})	3.023 Å	O(3)···N(4) at ($1-x$, $1-y$, $1-z$)	3.014 Å
O(3)···H(6) at (\bar{x} , \bar{y} , \bar{z})	2.39	O(3)···H(6) at ($1-x$, $1-y$, $1-z$)	2.23
N(4)···N(3) at (\bar{x} , \bar{y} , $1-z$)	2.928	N(4)···N(3) at ($1-x$, \bar{y} , $1-z$)	3.051
N(4)···H(4) at (\bar{x} , \bar{y} , $1-z$)	2.28	N(4)···H(4) at ($1-x$, \bar{y} , $1-z$)	2.35

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References

- BATTAGLIA, A., DONDONI, A., PANATTONI, C., BONDOLI, G. & CLEMENTE, D. A. (1971). *Tetrahedron Lett.* **31**, 2907–2908.
- BOULTON, A. J. & GASCO, A. (1973). Abstracts, The Chemical Society, Heterocyclic Group Meeting, Queen Elizabeth College, London.
- BRITTON, D. & NOLAND, W. (1972). *Acta Cryst.* **B28**, 1116–1121.
- CADY, H. H., LARSON, A. C. & CROMER, D. T. (1966). *Acta Cryst.* **20**, 336–341.
- CALLERI, M., CHIARI, G. & VITERBO, D. (1972). *Cryst. Struct. Commun.* **1**, 407–410.
- CALLERI, M., FERRARIS, G. & VITERBO, D. (1969a). *Acta Cryst.* **B25**, 1126–1133.
- CALLERI, M., FERRARIS, G. & VITERBO, D. (1969b). *Acta Cryst.* **B25**, 1133–1139.
- CHESNUT, D. B. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 413–419.
- GAGNEUX, A. R. & MEIER, R. (1970). *Helv. Chim. Acta*, **53**, 1883–1890.
- GASCO, A., MORTARINI, V., RUÀ, G. & MENZIANI, E. (1972). *J. Heterocycl. Chem.* **9**, 837–841.
- GASCO, A., MORTARINI, V., RUÀ, G., NANO, G. M. & MENZIANI, E. (1972). *J. Heterocycl. Chem.* **9**, 577–580.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GERMAIN, G. & VITERBO, D. (1972). *Cryst. Struct. Commun.* **1**, 411–414.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JENSEN, L. H. (1956). *J. Chem. Soc.* **78**, 3993–3999.
- JENSEN, L. H. & LINGAFELTER, E. C. (1961). *Acta Cryst.* **14**, 507–520.
- KARLE, J. (1968). *Acta Cryst.* **B24**, 182–186.
- MALLORY, F. B. & CAMMARATA, A. (1966). *J. Amer. Chem. Soc.* **88**, 61–66.
- MORINO, S. M., IJIMA, T. & MURATA, Y. (1960). *Bull. Chem. Soc. Japan*, **33**, 46–48.
- PROUT, C. K., HODDER, D. J. R. & VITERBO, D. (1972). *Acta Cryst.* **B28**, 1523–1526.
- SHINTANI, R. (1960). *Acta Cryst.* **13**, 609–618.
- VITERBO, D. & FERRARIS, G. (1970). *J. Chem. Soc. (B)*, pp. 223–227.