Acta Cryst. (1975). B31, 2384

The Crystal Structures of the Two Isomers of Methylfuroxancarboxamide, $C_4H_5N_3O_3$

BY M. CALLERI AND G. CHIARI
Istituto di Mineralogia dell'Università, Via San Massimo 24, 10123 *Torino, Italy*

A. CHIESI VILLA, A. GAETANI MANFREDOTTI AND C. GUASTINI
Istituto di Strutturistica Chimica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via Massimo d'Azeglio 85, 43100 *Parma, Italy*

AND D. VITERBO
Istituto di Chimica Fisica dell'Università, Corso Massimo d'Azeglio 48, 10125 *Torino, Italy*

(*Received* 25 *March* 1975; *accepted* 1 *April* 1975)

The structures of the positional isomers of methylfuroxancarboxamide have been solved by direct methods and refined by full-matrix least-squares methods with diffractometer-collected intensities. 4-Methyl-3-furoxancarboxamide (m.p. 134–135 °C) is monoclinic, space group $C2/c$, with $a=11\cdot82$ (1), $b=14\cdot37$ (1), $c=7\cdot31$ (1) Å, $\beta=95\cdot30$ (2)°, $Z=8$, $R=4\cdot9$%. 3-Methyl-4-furoxancarboxamide (m.p. 145 °C) is monoclinic, space group $P2_1/n$, with $a=12\cdot64$ (1), $b=12\cdot17$ (1), $c=3\cdot94$ (2) Å, $\beta=92\cdot10$ (3)°, $Z=4$, $R=5\cdot6$%. The H atoms, located on difference syntheses, have been refined isotropically. The carboxamide group is nearly coplanar with the furazan ring in 4-methyl-3-furoxancarboxamide, where a weak hydrogen-bonding interaction takes place between the extranuclear O atom and the amide group, whilst the two fragments make an angle of 18° in 3-methyl-4-furoxancarboxamide where this kind of interaction is not present. Weak intermolecular hydrogen bonds occur in both isomers. A comparison of the dimensions of the furoxan rings of several asymmetrically substituted furoxans is given.

Introduction

The title positional isomers were synthesized by Gasco, Mortarini, Ruà, Nano & Menziani (1972), who assigned structures on the basis of n.m.r. spectroscopy and also studied the isomerization reaction and the equilibration rate of several pairs of furoxan isomers (Gasco & Boulton, 1973). These authors assigned to the higher-melting isomer of the pair the formula 3-methyl-4- and to the lower-melting isomer 4-methyl-3-furoxancarboxamide, following the convention of regarding the N atom of the *N*-oxide function as the 2-position of the furoxan group; their assignment has been confirmed by the present investigation.

We have undertaken the X-ray analysis of these two isomers as part of a study of variously substituted methylfuroxans and furazans. For most of the isomer pairs investigated so far the lower-melting isomer has turned out to be the compound with the methyl group next to the *N*-oxide function, so we have become accustomed to distinguish the isomers by their respective melting points (*cf.* the references quoted in this article). Here, however, we find an inversion of the melting points: hence we prefer to name 3-methyl-4-furoxancarboxamide (the higher-melting isomer) 'isomer *A*', and 4-methyl-3-furoxancarboxamide (the lower-melting isomer) 'isomer *B*', following the notation proposed by Gasco & Boulton (1973).

Structure determination

Experimental results

The compounds prepared by Gasco *et al.* (1972) were recrystallized from aqueous alcoholic solutions. *A* yielded transparent colourless prisms, markedly elongated in the direction chosen as **c**; *B* crystallized as transparent colourless squat prisms with lozenge section, exhibiting an easy cleavage parallel to the form {100}, the most developed. The space groups were determined from Weissenberg photographs. The cell parameters and intensities were measured, at room temperature, on an automatic Siemens AED single-crystal diffractometer (Cu $K\alpha$, β-filtered radiation), by the θ–2θ scan technique.

Crystal data

Isomer *A*: $C_4H_5N_3O_3$, $M=143\cdot1$; m.p. 145 °C; monoclinic, $a=12\cdot64$ (1), $b=12\cdot17$ (1), $c=3\cdot94$ (2) Å, $\beta=92\cdot10$ (2)°; $U=605\cdot7$ Å^3. Space group: $P2_1/n$. $F(000)=296$; $D_c=1\cdot57$ g cm^{-3}; $Z=4$; μ(Cu $K\alpha$)= $11\cdot97$ cm^{-1}.

Isomer *B*: $C_4H_5N_3O_3$, $M=143\cdot1$; m.p. 134–135 °C; monoclinic, $a=11\cdot82$ (1), $b=14\cdot37$ (1), $c=7\cdot31$ (1) Å, $\beta=95\cdot30$ (2)°; $U=1236\cdot5$ Å^3. Space group: $C2/c$. $F(000)=592$; $D_c=1\cdot54$ g cm^{-3}; $Z=8$; μ(Cu $K\alpha$)= $11\cdot71$ cm^{-1}.

The reflexions were measured within the interval $6° \le 2\theta \le 140°$ for both compounds. For *A* 1149 reflexions were measured, 41 of which with $I \leq 2\sigma(I)$ were given zero weight; for *B* the number was 1176; 57 of these had $I \leq 2\sigma(I)$ and were given zero weight. Correction for absorption was neglected in view of the very low $\mu\bar{r}$ values for the crystals ($\mu\bar{r}=0{\cdot}13$ for *A* and 0·15 for *B*). There was no evidence of secondary extinction. The scattering factors were those of Cromer & Mann (1968) for O, N, C and those of Stewart, Davidson & Simpson (1965) for H.

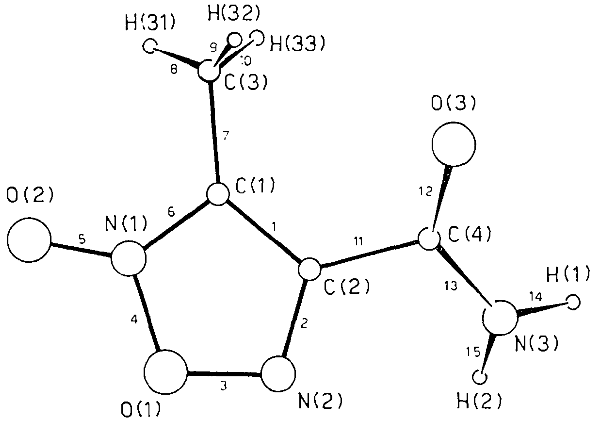

Fig. 1. Isomer *A*: projection of the molecule onto the least-squares mean plane of the furazan ring.

Structure solution and refinement

Both structures were solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971), and Fourier syntheses which showed that isomer *A* is 3-methyl-4- and isomer *B* 4-methyl-3-furoxancarboxamide.

The refinement was carried out by block-diagonal least-squares calculations and completed by full-matrix cycles refining anisotropically the non-hydrogen atoms. All H atoms were located on difference syntheses and refined isotropically. The weighting scheme for both refinements was: $1/w=A+BF_o+CF_o^2$. The coefficients were deduced from the $\langle|\Delta F|\rangle$ *vs* $|F|$ distribution (Stout & Jensen, 1968); for isomer *A*: $A=0{\cdot}0524$, $B=0{\cdot}0227$, $C=0{\cdot}0025$; for isomer *B*: $A=0{\cdot}1076$, $B=0{\cdot}0399$, $C=0{\cdot}0031$.

The final *R* was 0·064 for *A* or 0·056 on excluding the

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

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	2520 (1)	8081 (1)	2224 (5)	2·63 (5)	4·01 (6)	7·21 (9)	−0·18 (5)	−0·90 (6)	−0·95 (6)
O(2)	1550 (1)	9522 (1)	4204 (5)	4·55 (7)	3·47 (7)	6·85 (9)	−0·19 (5)	−1·29 (7)	−1·43 (6)
O(3)	−90 (1)	6374 (1)	−3678 (4)	3·72 (6)	3·42 (6)	6·16 (9)	0·37 (5)	−1·45 (6)	−0·40 (6)
N(1)	1528 (1)	8655 (1)	2549 (5)	2·97 (6)	3·12 (7)	4·88 (8)	−0·06 (5)	−0·60 (6)	−0·02 (6)
N(2)	2308 (1)	7132 (1)	430 (6)	2·89 (7)	3·62 (7)	6·31 (9)	0·05 (6)	−0·46 (6)	−0·40 (7)
N(3)	1329 (1)	5293 (1)	−2506 (5)	3·97 (8)	3·15 (7)	6·28 (9)	0·68 (6)	−1·37 (7)	−0·58 (7)
C(1)	775 (1)	8071 (1)	973 (5)	2·73 (7)	2·85 (7)	3·83 (8)	−0·19 (5)	−0·29 (6)	0·23 (6)
C(2)	1291 (1)	7129 (1)	−297 (5)	2·77 (7)	2·86 (7)	3·97 (8)	−0·12 (6)	−0·16 (6)	0·46 (6)
C(3)	−342 (2)	8430 (2)	877 (6)	3·02 (7)	3·97 (8)	5·45 (9)	0·66 (7)	−0·40 (7)	−0·68 (8)
C(4)	782 (1)	6215 (1)	−2295 (5)	3·10 (7)	2·78 (7)	4·02 (8)	−0·01 (8)	−0·13 (6)	0·34 (6)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H(1)	104 (4)	468 (4)	−352 (13)	6 (1)	H(32)	−57 (4)	865 (4)	−143 (13)	6 (1)
H(2)	187 (4)	518 (4)	−131 (13)	6 (1)	H(33)	−83 (4)	783 (4)	168 (13)	6 (1)
H(31)	−49 (4)	889 (4)	235 (14)	6 (1)					

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

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	2704 (1)	1947 (1)	7679 (2)	6·29 (6)	4·92 (5)	6·44 (6)	2·30 (5)	−0·52 (5)	0·66 (4)
O(2)	1015 (1)	1917 (1)	5920 (2)	6·73 (7)	4·12 (5)	7·32 (7)	0·07 (5)	−1·16 (6)	−0·37 (4)
O(3)	1339 (1)	4851 (1)	6471 (2)	4·16 (4)	3·89 (4)	7·95 (7)	−0·01 (4)	−2·15 (4)	0·20 (4)
N(1)	3415 (1)	2630 (1)	8471 (2)	4·74 (6)	6·13 (7)	5·79 (6)	1·85 (6)	−0·91 (5)	0·48 (6)
N(2)	1751 (1)	2409 (1)	6738 (2)	4·54 (5)	4·25 (5)	5·22 (6)	1·03 (5)	−0·29 (4)	0·36 (4)
N(3)	200 (1)	3736 (1)	5105 (2)	3·91 (5)	3·77 (5)	6·23 (7)	0·10 (4)	−1·44 (5)	−0·05 (4)
C(1)	2951 (1)	3436 (1)	8063 (2)	3·66 (6)	5·47 (8)	4·93 (7)	1·04 (5)	−0·37 (5)	0·55 (5)
C(2)	1904 (1)	3316 (1)	6961 (2)	3·52 (5)	4·01 (6)	4·73 (6)	0·57 (4)	−0·20 (5)	0·23 (5)
C(3)	3495 (2)	4317 (2)	8753 (3)	4·52 (7)	6·79 (9)	7·98 (9)	−0·15 (8)	−2·36 (7)	0·20 (9)
C(4)	1108 (1)	4033 (1)	6139 (2)	3·15 (5)	3·92 (6)	5·14 (6)	0·30 (5)	−0·64 (4)	0·42 (5)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H(1)	−19 (5)	409 (4)	467 (9)	6 (2)	H(32)	369 (5)	471 (5)	761 (9)	8 (2)
H(2)	10 (5)	323 (4)	491 (8)	5 (1)	H(33)	290 (5)	470 (4)	976 (8)	7 (2)
H(31)	397 (5)	425 (4)	942 (9)	6 (2)					

41 zero-weight reflexions; for *B*, *R* was 0·058 (0·049).†

The final positional and vibrational parameters are listed in Tables 1 and 2, for *A* and *B* 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

The projections of *A* and *B* onto the least-squares mean planes of the furazan group are shown in Figs. 1 and 2, which also show the numbering scheme. Tables 3 and 4 list the bond distances and interbond angles, and Table 5 reports the equations of the least-squares planes through the furazan ring and the molecular fragment C(2), C(4), O(3), N(3) with their mutual angles.

In both isomers the furazan group can be considered planar even if the displacements of the atoms from the mean plane (which are less than 0·004 Å) are statistically significant (Table 5), since residual effects of uncorrected systematic and model errors can be present.

Table 3. *Isomer A: bond distances* (Å) *and interbond angles* (°) *with the e.s.d.'s in parentheses*

For the numbering scheme, see Fig. 1.

1	1·419 (3)	6	1·324 (3)	11	1·495 (5)
2	1·307 (2)	7	1·477 (4)	12	1·227 (3)
3	1·375 (3)	8	0·83 (5)	13	1·322 (3)
4	1·445 (2)	9	0·98 (5)	14	0·92 (5)
5	1·240 (2)	10	1·01 (5)	15	0·83 (5)
1, 2	112·4 (2)	4, 6	108·1 (1)	9, 10	109 (4)
1, 6	105·5 (2)	5, 6	134·8 (2)	11, 12	118·6 (2)
1, 7	132·9 (2)	6, 7	121·5 (2)	11, 13	116·7 (2)
1, 11	126·3 (2)	7, 8	115 (3)	12, 13	124·7 (2)
2, 3	106·7 (2)	7, 9	111 (3)	13, 14	121 (3)
2, 11	121·2 (2)	7, 10	112 (3)	13, 15	122 (3)
3, 4	107·3 (1)	8, 9	113 (5)	14, 15	115 (5)
4, 5	117·1 (1)	8, 10	96 (4)		

Table 4. *Isomer B: bond distances* (Å) *and interbond angles* (°) *with the e.s.d.'s in parentheses*

For the numbering scheme, see Fig. 2.

1	1·423 (2)	6	1·324 (2)	11	1·484 (2)
2	1·304 (2)	7	1·487 (3)	12	1·226 (2)
3	1·384 (2)	8	0·71 (6)	13	1·325 (2)
4	1·428 (2)	9	1·05 (7)	14	0·74 (6)
5	1·232 (2)	10	1·20 (6)	15	0·75 (6)
1, 2	110·3 (1)	4, 6	107·8 (1)	9, 10	115 (5)
1, 6	106·9 (1)	5, 6	135·0 (1)	11, 12	117·7 (1)
1, 7	128·4 (1)	6, 11	124·0 (1)	11, 13	117·2 (1)
1, 11	129·1 (1)	7, 8	114 (5)	12, 13	125·1 (1)
2, 3	107·9 (1)	7, 9	108 (4)	13, 14	118 (5)
2, 7	121·3 (1)	7, 10	110 (3)	13, 15	122 (4)
3, 4	107·1 (1)	8, 9	113 (6)	14, 15	120 (6)
4, 5	117·2 (1)	8, 10	96 (6)		

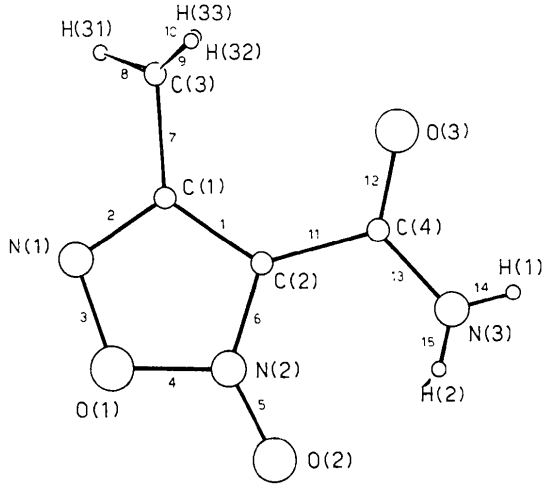

Fig. 2. Isomer *B*: projection of the molecule onto the least-squares mean plane of the furazan ring.

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; $\chi^2=\sum(\delta/\sigma)^2$.

Isomer *A*

1. Plane through the furazan ring: C(1), C(2), N(1), N(2), O(1)	$2{\cdot}395x+5{\cdot}919y-3{\cdot}386z=4{\cdot}630$	$\langle\delta\rangle=0{\cdot}003$ Å $\chi^2=12{\cdot}29$	O(2) at −0·046 Å from 1
2. Plane through C(2), C(4), O(3), N(3)	$5{\cdot}836x+4{\cdot}087y-3{\cdot}299z=3{\cdot}762$	$\langle\delta\rangle=0{\cdot}004$ Å $\chi^2=27{\cdot}01$	H(1) at −0·08 Å H(2) at −0·12 Å O(2) at −0·353 Å from 2

Angle 1,2 = 18°

Isomer *B*

1. Plane through the furazan ring: C(1), C(2), N(1), N(2), O(1)	$6{\cdot}621x+0{\cdot}527y-6{\cdot}402z=-3{\cdot}024$	$\langle\delta\rangle=0{\cdot}002$ Å $\chi^2=15{\cdot}69$	O(2) at 0·007 Å from 1
2. Plane through C(2), C(4), O(3), N(3)	$6{\cdot}969x+0{\cdot}563y-6{\cdot}270z=-2{\cdot}851$	$\langle\delta\rangle=0{\cdot}0004$ Å $\chi^2=0{\cdot}50$	H(1) at 0·02 Å H(2) at 0·02 Å O(2) at −0·046 Å from 2

Angle 1,2 = 2°

---

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31030 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

From Table 5 an important difference between the two molecules is apparent: in *B*, the furazan ring and the fragment C(2), C(4), N(3), O(3) are nearly coplanar, while in *A* they make an angle of 18°. This appears to be the main structural difference between the two compounds and it can be accounted for by the internal hydrogen-bonding interaction involving N(3)–H(2)···O(2) in *B* [N(3)···O(2) = 2·831 (2) Å; N(3)–H(2)···O(2) = 133°]. This interaction seems responsible for the coplanarity of the two parts of the molecule, since coplanarity is not observed in the less stable *A*, where this interaction is absent. This situation compares well with that found for the isomers of methylfuroxancarbohydrazide (Calleri, Chiari, Germain & Viterbo, 1973), and agrees with the results of Gasco & Boulton (1973). These authors found that *B* is appreciably favoured at equilibrium both for the amide and hydrazide derivatives and suggested that 'presumably hydrogen-bonding plays a role in stabilizing form *B* for the amides and hydrazides'. In the dimethylamide derivatives (Chiesi Villa, Guastini, Calleri & Chiari, 1974; Calleri, Viterbo, Gaetani Manfredotti & Guastini, 1974), where there is no possibility of intramolecular hydrogen bonding for both *A* and *B*, distotrions from coplanarity are larger, particularly for the less stable *B* (dihedral angles: 39 and 52° respectively), as a consequence of steric hindrance between the dimethylamide group and the extranuclear O atom.

As regards the amide groups, N(3) can be considered to show sp^2 hybridization, as in the dimethylamides, even though the crude H(1) and H(2) coordinates (Tables 1 and 2) do not allow a detailed analysis; π-delocalization occurs in the O(3), C(4) and N(3) system (Tables 3 and 4), and the effect was found also for the dimethylamide derivatives.

In both the present isomers the length of bond 11 (Tables 3 and 4) corresponds to a C_{sp2}–C_{sp2} single bond and therefore indicates that there is little or no conjugation between the amide substituent and the furoxan moiety. An analogous lack of conjugation has been found for the dimethylamide and hydrazide derivatives, and for 3-methyl-4-nitrofuroxan (Cameron & Freer, 1974).

Within the furoxan rings of *A* and *B*, the dimensions of corresponding bonds do not differ markedly, even though the difference between bonds 4 and 3 is larger for *A*, both here and for most of the asymmetrically substituted furoxans so far studied. This difference is highest, 0·112 Å, for methylnitrofuroxan and it is interesting to note that even for the symmetrically substituted di-(*p*-chlorophenyl)furoxan it is very large, 0·10 Å (Viterbo & Ferraris, 1970). In both isomers bond 4 is significantly longer than the endocyclic N–O bond in furazan, 1·380 (3) Å (Cox & Saegebarth, 1965); this effect obtains for all the furoxans. The difference between bonds 6 and 2 is very similar in the present isomers, and significant. Bond 6 is constantly longer, in the asymmetrically substituted furoxans, than the C=N bond in furazan, 1·300 (3) Å. Therefore, although the dimensions of the furoxan rings are comparable for these *A* and *B* modifications, the degree of electron delocalization throughout the ring, pointed out by Cameron & Freer (1974) for methylnitrofuroxan, appears to be small considering that bonds 2 and 6 have high double-bond character, while the length of bonds 3 and 4, together with the value of the angle at O(1), suggests that O(1) has sp^3 hybridization and that bonds 3 and 4 are essentially single.

The lengths of the six bonds of the furoxan moiety show significant variations in the several compounds with formula $CH_3(C_2N_2O_2)R'$ (*cf.* the references quoted in Table 6). The ranges are: bond 1: 1·401–1·424 Å (the shortest length occurs in form *A* of the nitro-derivative); bond 2: 1·288–1·307 Å (the shortest

Table 6. *Endocyclic and exocyclic interbond angles of the furoxan group of the isomer pairs of* $CH_3(C_2N_2O_2)R'$ *furoxans*

Angle	R′ = amide^1		R′ = dimethylamide^2		R′ = hydrazide^3		R′ = nitro^4	R′ = sulphone^5	
	A	*B**	*A**	*B*	*A*	*B**	*A**	*A**	*B*
1, 2	112·4 (2)°	110·3 (1)°	112·4 (2)°	110·1 (2)°	111·9 (2)°	110·9 (3)°	116·4 (4)°	113·1 (2)°	110·8 (3)°
2, 3	106·7 (2)	107·9 (1)	106·8 (1)	107·9 (2)	107·2 (2)	107·2 (2)	104·7 (4)	106·3 (2)	107·8 (3)
3, 4	107·3 (1)	107·1 (1)	106·9 (1)	107·0 (2)	107·3 (2)	107·6 (3)	107·7 (3)	107·2 (2)	107·2 (2)
4, 6	108·1 (1)	107·8 (1)	108·0 (2)	107·4 (2)	107·7 (3)	107·6 (2)	107·3 (2)	107·9 (2)	107·1 (2)
6, 1	105·5 (2)	106·9 (1)	105·8 (2)	107·5 (2)	105·9 (3)	106·7 (2)	103·7 (4)	105·5 (2)	107·1 (2)
1, 7	132·9 (2)	128·4 (1)	132·7 (2)	127·6 (2)	133·0 (3)	128·4 (3)	135·3 (5)	131·9 (2)	127·8 (3)
6, 7	121·5 (2)		121·5 (2)		121·1 (3)		120·9 (4)	122·6 (2)	
2, 7		121·3 (1)		122·2 (2)		120·7 (3)			121·3 (3)
5, 6	134·8 (2)	135·0 (1)	134·4 (2)	135·9 (2)	135·3 (4)	134·5 (2)	135·3 (4)	135·1 (2)	135·2 (2)
4, 5	117·1 (1)	117·2 (1)	117·6 (2)	116·7 (2)	117·0 (3)	117·9 (2)	117·4 (4)	117·0 (2)	117·8 (2)
1, 11	126·3 (2)	129·1 (1)	124·5 (1)	127·6 (2)	126·5 (3)	129·2 (2)	125·7 (4)	125·3 (2)	132·1 (2)
2, 11	121·2 (2)		122·8 (2)		121·6 (3)		117·7 (4)	121·4 (2)	
6, 11		124·0 (1)		124·3 (2)		124·0 (2)			120·6 (2)

* Modification favoured at equilibrium (Gasco & Boulton, 1973).

References: (1) Present article. (2) Chiesi Villa *et al.* (1974); Calleri *et al.* (1974). (3) Calleri *et al.* (1973). (4) Cameron & Freer (1974). (5) Calleri *et al.* (1975).

length occurs, again, in the nitro-compound and in form *B* of the sulphones); bond 3: 1·358–1·388 Å (the extreme values occur in forms *A* and *B* of the hydrazides); bond 4: 1·424–1·479 Å (the longest bond occurs in the nitro-compound, but longer bonds have been found in fused-ring furoxans (*e.g.* Calleri, Chiari & Viterbo, 1973); bond 5: 1·220–1·242 Å (the shortest length characterizes the nitro-compound and the longest one form *A* of dimethylamides); bond 6: 1·310–1·332 Å (the longest bond was found in the nitro-compound).

The length of bond 7, 1·471–1·511 Å, is not so much shorter than the expected C_{sp3}–C_{sp2} single bond, as to indicate an appreciable hyperconjugation effect.

Comparing bond distances and angles for several methyl-R′ substituted furoxans (Table 6), it appears that the electron distribution in the furoxan moiety is not markedly different (at least when excluding the nitro-derivative). The role played by the different substituents on the equilibrium constants between isomer pairs, and on their conformations is therefore mostly related to steric effects and to hydrogen-bonding interactions in which R′ can be involved.

The lengthening of bond 4 with respect to bond 3 causes angular distortions, mainly for the angle 6,1: the distortions of the endocyclic angles at C(1) and C(2) are in fact large when compared with the expected 120° angle for C_{sp2} atoms, even though they lie within narrow ranges for forms *A* and *B* separately, excluding the nitro-derivative. Angles 1,11 and 2,11 (or 6,11), on the other hand, show larger ranges and, in particular, the large sulphone function is associated with the largest difference between angles 1,11 in the two forms (Table 6 and Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975). While the angles 6,7 (or 2,7) and 5,6 are nearly constant in the several pairs, the angle 1,7 is regularly larger and the angle 1,11 smaller in forms *A*. These large angular distortions are consistent with the requirement of a planar (or nearly planar) furazan ring and with the necessity of keeping apart the methyl group from the adjacent functions; in the nine molecules of Table 6 no appreciable intramolecular interaction occurs between the C(3) methyl group and the neighbouring O atom (*cf.* Cameron & Freer, 1974).

The relief of steric hindrance between the N → O and R′ functions is achieved also through the twisting of the R′ function out of the furazan plane excluding the cases (R′ = amide and hydrazide) where the R′ substituent can interact with the exocyclic O atom, as in the *B* form which is stabilized by this effect. The endocyclic angles at N(2), O(1) and N(1) are nearly constant for the nine compounds of Table 6, excepting the 2,3 angle of nitrofuroxan, and this confirms that the influence of the substituents on the furoxan moiety is, in general, slight.

As shown in Figs. 3 and 4, packing is of the same kind in the two isomers and is mainly determined by the hydrogen-bond system involving the NH_2 groups: isomer *A*: N(3)···O(3^{i}) 2·943 (2) Å, N(3)–H(1)···O(3^{i}) 164 (4)°, N(3)···O(2^{ii}) 3·083 (2) Å, N(3)–H(2)···O(2^{ii}) 164 (5)°; isomer *B*: N(3)···O(3^{i}) 2·894 (2) Å, N(3)–H(1)···O(3^{i}) 177 (4)°, N(3)···N(1^{iii}) 3·044 (3) Å, N(3)–H(2)···N(1^{iii}) 132 (5)°. [i $\bar{x}, 1-y, 1-z$; ii $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; iii $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$.]

In both isomers the N(3)···O(3) hydrogen bonds help to form dimers centred on centres of symmetry. It may be noticed that, owing to the intramolecular interaction, in *B* the NH_2 group forms a bifurcated hydrogen bond (Fig. 4). This packing explains the small differences found in the melting points and densities of the two forms. These differences are also small for the hydrazide derivatives (form *A*: m.p. 124–126°, $D = 1·58$ g cm^{-3}; form *B*: m.p. 129–131°, $D = 1·59$ g cm^{-3}), while for the dimethylamide derivatives the differences are greater (form *A*: m.p. 71–72°, $D = 1·38$ g cm^{-3}; form *B*: m.p. 109°, $D = 1·41$ g cm^{-3}).

We are indebted to Dr A. Gasco for suggesting this work and for providing the samples and to Mr C.

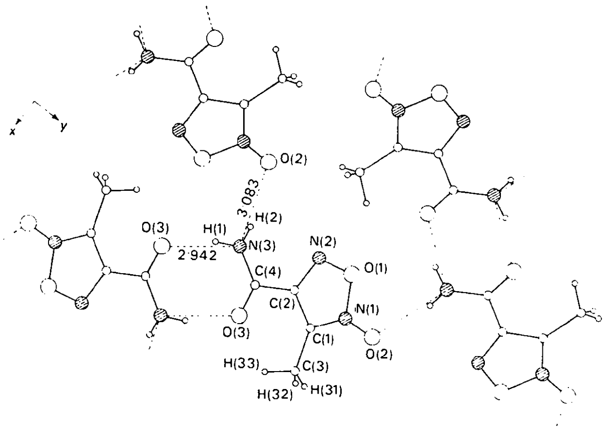

Fig. 3. Isomer *A*: projection of the structure on (001).

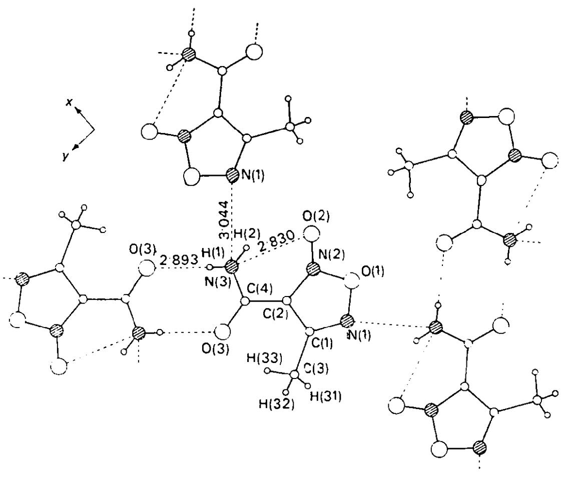

Fig. 4. Isomer *B*: projection of the structure on (001).

Cerutti for his assistance in the preliminary stages of the analysis.

References

CALLERI, M., CHIARI, G., CHIESI VILLA, A., GAETANI MANFREDOTTI, A., GUASTINI, C. & VITERBO, D. (1975). In preparation.

CALLERI, M., CHIARI, G., GERMAIN, G. & VITERBO, D. (1973). *Acta Cryst.* B**29**, 1618–1622.

CALLERI, M., CHIARI, G. & VITERBO, D. (1973). *Cryst. Struct. Commun.* **2**, 335–338.

CALLERI, M., VITERBO, D., GAETANI MANFREDOTTI, A. & GUASTINI, C. (1974). *Cryst. Struct. Commun.* **3**, 269–271.

CAMERON, A. F. & FREER, A. A. (1974). *Acta Cryst.* B**30**, 354–357.

CHIESI VILLA, A., GUASTINI, C., CALLERI, M. & CHIARI, G. (1974). *Cryst. Struct. Commun.* **3**, 265–267.

COX, A. P. & SAEGEBARTH, E. (1965). *Chem. Abs.* **63** 9253C.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

GASCO, A. & BOULTON, A. J. (1973). *J. Chem. Soc. Perkin* II, pp. 1613–1617.

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.* A**27**, 368–376.

STEWART, R. S., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, H. J. & JENSEN, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

VITERBO, D. & FERRARIS, G. (1970). *J. Chem. Soc.* (*B*), pp. 223–227.

Acta Cryst. (1975). B**31**, 2389

The Crystal and Molecular Structure of [3,3]Paracyclophadiyne

BY TOSHIAKI AONO, KIWAKO SAKABE, NORIYOSHI SAKABE, CHUJI KATAYAMA AND JIRO TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464, Japan

(*Received* 28 *January* 1975; *accepted* 18 *March* 1975)

[3,3]Paracyclophadiyne crystallizes in the monoclinic system, space group $P2_1/a$, with lattice parameters $a=14\cdot509$ (2), $b=8\cdot539$ (1), $c=10\cdot623$ (1) Å and $\beta=112\cdot37$ (5)° at 10°C, and $Z=4$. The atomic coordinates and anisotropic temperature factors have been refined by a full-matrix least-squares method to $R=0\cdot087$ based on 1691 structure factors measured on a Hilger–Watts diffractometer. The molecule consists of the benzene and diacetylene groups linked by two trimethylene bridges, one with a rigid conformation and the other with a disordered structure. The diacetylene chain is bent into a bow shape, and the distance between the two groups is about 3·1 Å, which is apparently shorter than normal interatomic distances between the aromatic ring atoms.

The transannular π-electron interactions have been extensively investigated for paracyclophanes by Cram and his coworkers and several interesting features have been reported on the properties of these highly symmetrical and crowded compounds (Cram & Cram, 1971). Evidence of an unusual feature in the aromatic ring has been shown by crystal structure analysis: a significant deformation of the benzene ring has been found in [2,2]paracyclophane (Brown, 1953*a*; Lonsdale, Milledge & Rao, 1960; Hope, Bernstein & Trueblood, 1972) and its tetrahydro- derivative (Coulter & Trueblood, 1963) and similar results have been observed for [2,2]metacyclophane (Brown, 1953*b*) and its derivative (Hanson, 1962) and [3,3]-paracyclophane (Gantzel & Trueblood, 1965), where the distortion of the aromatic ring has also been noticed.

Recently Misumi and coworkers have synthesized a series of paracyclophadiyne derivatives (Matsuoka, Negi, Otsubo, Sakata & Misumi, 1972) and the chemical and spectral properties have been investigated (Kaneda, Ogawa & Misumi, 1973; Takabe, Tanaka & Tanaka, 1974). Detailed analyses of the geometries of these molecules should be important in finding the transannular electron interaction between the benzene and diacetylene groups. In this paper a crystal structure analysis of [3,3]paracyclophadiyne is reported. The present molecule is not as symmetrical as the paracyclophanes; however, it will provide a novel interaction between the different groups through a transannular mode. The structure obtained shows the bent diacetylene group and a partial disorder in one of the trimethylene bridges.