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The Crystal Structures of the Two Isomers of Isopropyl *N*-(Methylfuroxan)carbamate, $C_7H_{11}N_3O_4$

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The structures of the positional isomers of the title furoxan derivative were solved by direct methods, and refined by block-diagonal least squares, from diffractometer intensities (Cu $K\alpha$). Isopropyl 3-methyl-4-furoxan carbamate (m.p. 110–112°) is monoclinic, space group $P2_1/c$, with $a = 8{\cdot}915\,(2)$, $b = 12{\cdot}873\,(2)$, $c = 17{\cdot}591\,(3)$ Å, $\beta = 100{\cdot}79\,(1)°$; $Z = 8$ ($R = 4{\cdot}7\%$). Isopropyl 4-methyl-3-furoxancarbamate (m.p. 105–107°) is monoclinic, space group $P2_1/c$, with $a = 4{\cdot}844\,(1)$, $b = 22{\cdot}559\,(4)$, $c = 8{\cdot}962\,(1)$ Å, $\beta = 97{\cdot}98\,(1)°$; $Z = 4$ ($R = 5{\cdot}6\%$). All H atoms, located on difference syntheses, were refined isotropically. The furoxan group is rigorously planar in both the independent molecules, whose bonds and angles are very similar, of the higher-melting isomer, whilst it deviates from strict planarity in the lower-melting isomer. In all three molecules the furoxan and carbamate groups are rotated, to different extents, and no conjugation between the two groups is revealed.

Introduction

After investigating a few disubstituted furoxans and furazans with electron-withdrawing substituents, we carried out an X-ray analysis of the pair of isomers with the electron-releasing isopropyl carbamate function. The title positional isomers were prepared by Gasco, Mortarini, Ruà & Menziani (1972) who assigned structures on the basis of NMR spectroscopy. Their assignment was confirmed by the present analysis: the higher-melting isomer is isopropyl 3-methyl-4-furoxancarbamate and the lower-melting isomer is isopropyl 4-methyl-3-furoxancarbamate. They will be distinguished as isomer *A* and isomer *B* respectively, following Gasco & Boulton (1973).

Structure determination

Experimental results

The compounds, recrystallized from acetone–water or ethanol, yielded prismatic transparent crystals suitable for the X-ray analysis. The space groups were determined from Weissenberg photographs; the cell parameters and intensities were measured, at room temperature, on an automated Siemens AED single-crystal diffractometer (Cu $K\alpha$ β-filtered radiation), by the θ–2θ scanning technique.

Crystal data

Isomer *A*: $C_7H_{11}N_3O_4$, $M_r = 201{\cdot}2$, m.p. 110–112°; monoclinic, $a = 8{\cdot}915\,(2)$, $b = 12{\cdot}873\,(2)$, $c = 17{\cdot}591\,(3)$ Å, $\beta = 100{\cdot}79\,(1)°$; $U = 1983{\cdot}1$ Å^3. Space group $P2_1/c$; $F(000) = 848$; $D_c = 1{\cdot}35$ g cm^{-3}; $Z = 8$. Crystal dimensions: 0·22 × 0·16 × 0·27 mm.

Isomer *B*: $C_7H_{11}N_3O_4$, $M_r = 201{\cdot}2$, m.p. 105–107°; monoclinic, $a = 4{\cdot}844\,(1)$, $b = 22{\cdot}559\,(4)$, $c = 8{\cdot}962\,(1)$ Å, $\beta = 97{\cdot}98\,(1)°$; $U = 969{\cdot}8$ Å^3. Space group $P2_1/c$; $F(000) = 424$; $D_c = 1{\cdot}38$ g cm^{-3}; $Z = 4$. Crystal dimensions: 0·08 × 0·10 × 0·38 mm.

The intensities were measured within the interval $6° < 2\theta < 140°$ for both isomers. For *A*, 3646 independent reflexions were measured, 2809 of which with $I > 2\sigma(I)$ were included in the analysis; for *B* the number of independent reflexions was 1823, 1018 of which were included in the analysis.

The scattering factors were those of Cromer & Mann (1968) for O, N, C and those of Stewart, Davidson & Simpson (1965) for H.

Structure solution and refinement

Both structures were solved by direct methods with the *MULTAN* procedure (Declercq, Germain, Main & Woolfson, 1973). The refinement was carried out by

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*

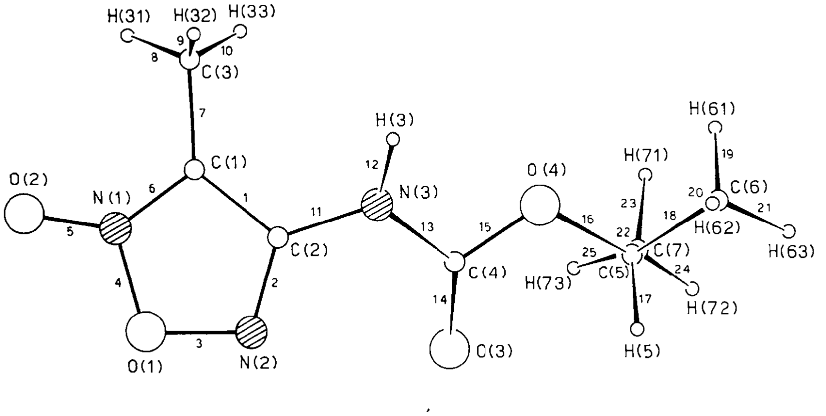
	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	3032 (2)	6973 (1)	3537 (1)	6·19 (6)	2·89 (5)	3·82 (5)	−0·28 (4)	1·09 (4)	−0·05 (4)
O(2)	3637 (2)	6882 (1)	4854 (1)	7·12 (8)	4·30 (6)	3·98 (5)	−0·67 (6)	0·58 (5)	−1·15 (5)
O(3)	2448 (1)	4957 (1)	1682 (1)	4·75 (5)	3·26 (5)	3·37 (4)	0·02 (4)	1·20 (4)	0·19 (4)
O(4)	1640 (2)	3338 (1)	1906 (1)	6·31 (6)	3·21 (5)	3·83 (5)	−0·87 (5)	1·86 (5)	−0·61 (4)
N(1)	3192 (2)	6393 (1)	4245 (1)	4·31 (6)	3·46 (6)	3·30 (6)	0·00 (5)	0·67 (5)	−0·17 (4)
N(2)	2509 (2)	6280 (1)	2934 (1)	5·78 (7)	3·39 (7)	3·42 (6)	−0·32 (5)	0·90 (5)	−0·09 (5)
N(3)	1943 (2)	4474 (1)	2862 (1)	4·71 (6)	3·52 (6)	3·28 (5)	−0·91 (5)	1·43 (5)	−0·30 (4)
C(1)	2806 (2)	5424 (1)	4079 (1)	3·53 (6)	3·12 (7)	3·19 (6)	−0·01 (5)	0·80 (5)	−0·06 (5)
C(2)	2397 (2)	5379 (1)	3263 (1)	3·44 (6)	3·22 (7)	3·32 (6)	−0·01 (5)	1·08 (5)	−0·01 (5)
C(3)	2874 (3)	4614 (2)	4680 (1)	6·98 (11)	4·33 (9)	3·42 (7)	−1·04 (8)	0·44 (7)	0·51 (6)
C(4)	2048 (2)	4314 (1)	2105 (1)	3·46 (6)	3·15 (7)	3·23 (6)	0·15 (5)	0·86 (5)	−0·14 (5)
C(5)	1694 (2)	3023 (1)	1114 (1)	4·79 (8)	3·86 (8)	3·74 (7)	0·05 (6)	1·03 (6)	−0·79 (6)
C(6)	559 (3)	2154 (2)	925 (1)	5·76 (10)	4·92 (10)	6·34 (11)	−0·75 (7)	1·12 (8)	−1·68 (9)
C(7)	3292 (3)	2699 (2)	1064 (2)	5·25 (10)	6·98 (14)	7·36 (13)	−0·38 (9)	2·05 (9)	−2·50 (11)
O(1′)	1867 (2)	9535 (1)	1424 (1)	4·93 (6)	3·39 (6)	6·40 (7)	−0·35 (5)	1·38 (5)	−0·30 (5)
O(2′)	4457 (2)	9611 (1)	1668 (1)	5·14 (7)	5·94 (8)	7·59 (9)	−2·49 (6)	1·65 (6)	−0·61 (7)
O(3′)	−1647 (1)	7418 (1)	1186 (1)	3·54 (5)	3·65 (6)	6·87 (7)	0·36 (4)	0·96 (5)	0·04 (5)
O(4′)	−990 (1)	5747 (1)	1029 (1)	3·72 (5)	3·48 (6)	7·41 (8)	−0·25 (4)	0·93 (5)	−0·60 (5)
N(1′)	3326 (2)	9034 (1)	1556 (1)	4·04 (6)	4·57 (7)	4·45 (6)	−0·77 (5)	1·17 (5)	−0·21 (6)
N(2′)	766 (2)	8757 (1)	1310 (1)	3·97 (6)	3·38 (7)	5·26 (7)	−0·06 (5)	0·89 (5)	−0·33 (5)
N(3′)	834 (2)	6915 (1)	1261 (1)	3·30 (5)	3·07 (6)	4·87 (6)	0·18 (4)	0·56 (5)	0·05 (5)
C(1′)	3122 (2)	8023 (1)	1527 (1)	3·77 (6)	4·11 (8)	3·13 (6)	−0·34 (6)	0·90 (5)	0·17 (5)
C(2′)	1518 (2)	7880 (1)	1367 (1)	3·32 (6)	3·63 (7)	3·04 (6)	0·06 (5)	0·55 (5)	0·14 (5)
C(3′)	4408 (2)	7284 (2)	1611 (1)	3·59 (7)	5·70 (10)	5·54 (9)	0·15 (7)	1·09 (6)	0·93 (8)
C(4′)	−712 (2)	6750 (1)	1164 (1)	3·59 (6)	3·13 (7)	3·78 (7)	0·17 (5)	0·66 (5)	0·25 (5)
C(5′)	−2575 (2)	5394 (2)	950 (1)	3·86 (7)	4·29 (9)	6·05 (10)	−0·62 (6)	0·75 (7)	0·12 (7)
C(6′)	−2834 (4)	5048 (3)	1712 (2)	7·82 (15)	10·18 (21)	6·98 (14)	−1·99 (14)	2·41 (12)	0·63 (14)
C(7′)	−2764 (3)	4536 (2)	348 (2)	7·37 (13)	5·90 (13)	7·29 (14)	−2·09 (10)	1·13 (11)	−1·56 (10)

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
H(3)	148 (3)	394 (2)	311 (1)	6·9 (6)	H(3′)	145 (3)	633 (2)	128 (2)	7·0 (6)
H(31)	359 (3)	476 (2)	513 (1)	6·2 (5)	H(31′)	526 (3)	762 (2)	183 (2)	10·1 (7)
H(32)	181 (3)	454 (2)	482 (2)	9·1 (7)	H(32′)	430 (3)	669 (2)	197 (2)	8·7 (6)
H(33)	324 (3)	397 (2)	451 (2)	10·3 (7)	H(33′)	460 (3)	705 (2)	111 (2)	9·3 (7)
H(5)	132 (3)	362 (2)	73 (1)	6·6 (6)	H(5′)	−334 (2)	598 (2)	73 (1)	5·9 (5)
H(61)	89 (3)	159 (2)	131 (1)	7·2 (6)	H(61′)	−210 (3)	442 (2)	189 (1)	6·7 (6)
H(62)	−43 (3)	238 (2)	99 (2)	7·9 (6)	H(62′)	−258 (3)	561 (2)	210 (2)	7·8 (6)
H(63)	49 (3)	190 (2)	36 (1)	8·0 (6)	H(63′)	−386 (3)	484 (2)	171 (2)	8·7 (7)
H(71)	350 (3)	204 (2)	138 (2)	7·7 (6)	H(71′)	−196 (3)	397 (2)	48 (2)	8·0 (6)
H(72)	345 (3)	257 (2)	53 (1)	7·5 (6)	H(72′)	−389 (3)	424 (2)	28 (2)	8·6 (7)
H(73)	409 (3)	319 (2)	132 (2)	7·9 (6)	H(73′)	−261 (3)	482 (2)	−17 (2)	9·3 (7)

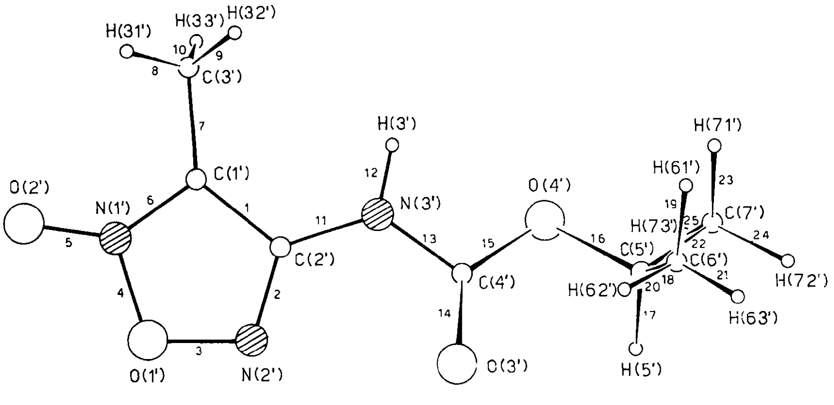
Table 2. *Isomer B: fractional coordinates* ($\times 10^4$ *for* O,N,C; $\times 10^3$ *for* H) *and vibrational parameters with the significant figures of e.s.d.'s in parentheses*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	−2400 (6)	3200 (1)	506 (3)	6·06 (13)	8·07 (16)	3·54 (10)	−0·89 (12)	−0·21 (9)	−0·93 (11)
O(2)	−3578 (6)	4006 (1)	1841 (3)	6·11 (14)	7·38 (17)	6·54 (15)	2·26 (13)	−0·60 (12)	−0·04 (13)
O(3)	−3101 (4)	3610 (1)	4976 (3)	2·85 (8)	6·56 (14)	4·93 (11)	−0·40 (9)	0·73 (8)	−1·34 (10)
O(4)	753 (4)	4012 (1)	6312 (2)	3·45 (9)	5·33 (11)	3·75 (9)	−0·26 (8)	0·91 (8)	−1·35 (9)
N(1)	−352 (7)	2764 (1)	704 (3)	5·85 (16)	5·87 (16)	3·99 (12)	−0·75 (13)	1·10 (12)	−1·00 (12)
N(2)	−1965 (6)	3581 (1)	1810 (3)	4·87 (14)	5·46 (15)	3·98 (12)	0·01 (12)	0·05 (11)	−0·11 (11)
N(3)	1095 (5)	3618 (1)	4092 (3)	3·04 (10)	4·50 (13)	3·51 (11)	−0·51 (10)	0·67 (8)	−0·95 (10)
C(1)	1099 (7)	2854 (1)	2028 (4)	4·37 (15)	4·53 (16)	3·47 (13)	−0·86 (13)	1·50 (12)	−0·49 (12)
C(2)	109 (6)	3357 (1)	2715 (3)	3·17 (12)	4·37 (16)	3·17 (12)	−0·52 (11)	0·44 (10)	−0·03 (11)
C(3)	3405 (8)	2459 (2)	2628 (4)	5·30 (18)	4·55 (17)	5·08 (17)	0·33 (15)	2·01 (14)	−0·54 (14)
C(4)	−656 (6)	3742 (1)	5133 (3)	3·21 (13)	4·38 (15)	3·37 (13)	0·05 (11)	0·27 (11)	−0·53 (12)
C(5)	−858 (7)	4234 (2)	7485 (4)	5·21 (17)	5·05 (18)	3·76 (14)	−0·19 (14)	1·82 (14)	−1·24 (13)
C(6)	−2148 (10)	4812 (2)	6974 (5)	8·02 (25)	6·32 (23)	6·55 (22)	2·50 (20)	1·77 (20)	−0·72 (19)
C(7)	1195 (10)	4273 (2)	8886 (4)	9·12 (28)	6·54 (22)	3·71 (16)	0·59 (21)	1·02 (18)	−0·43 (16)

	x	y	z	B		x	y	z	B
H(3)	307 (7)	377 (2)	437 (4)	6·6 (9)	H(62)	−324 (8)	498 (2)	774 (5)	10·2 (1·2)
H(5)	−246 (7)	389 (1)	761 (4)	6·0 (8)	H(63)	−64 (8)	511 (2)	686 (4)	8·4 (1·0)
H(31)	483 (7)	263 (2)	325 (4)	6·6 (9)	H(71)	40 (8)	440 (2)	967 (4)	7·0 (9)
H(32)	292 (9)	217 (2)	326 (5)	9·4 (1·2)	H(72)	212 (7)	390 (2)	915 (4)	6·6 (9)
H(33)	411 (9)	225 (2)	179 (5)	9·0 (1·1)	H(73)	256 (8)	463 (2)	866 (4)	7·8 (1·0)
H(61)	−356 (7)	482 (2)	599 (4)	7·3 (9)					



molecule (I)



molecule (II)

Fig. 1. Isomer *A*. Projection of the molecules onto the least-squares mean plane of the furoxan ring.

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

Column I refers to the unprimed atoms of Table 1; column II refers to the primed atoms of Table 1.

	I	II		I	II
1	1·415 (3)	1·417 (3)	14	1·211 (2)	1·203 (2)
2	1·308 (2)	1·307 (2)	15	1·336 (2)	1·328 (2)
3	1·398 (2)	1·390 (2)	16	1·460 (3)	1·466 (3)
4	1·436 (2)	1·431 (3)	17	1·04 (2)	1·04 (2)
5	1·242 (2)	1·238 (2)	18	1·503 (3)	1·471 (4)
6	1·312 (2)	1·314 (2)	19	1·00 (2)	1·05 (2)
7	1·478 (3)	1·476 (3)	20	0·96 (3)	0·99 (3)
8	0·94 (2)	0·90 (3)	21	1·04 (2)	0·95 (3)
9	1·03 (3)	1·01 (3)	22	1·503 (4)	1·518 (4)
10	0·96 (3)	0·98 (3)	23	1·01 (3)	1·02 (3)
11	1·383 (2)	1·381 (2)	24	0·99 (2)	1·06 (3)
12	0·95 (2)	0·93 (3)	25	0·99 (3)	1·01 (3)
13	1·368 (3)	1·373 (3)			
1,2	112·7 (1)	112·8 (1)	2,3	105·8 (2)	105·8 (2)
3,4	106·9 (1)	107·1 (1)	4,5	116·6 (1)	116·3 (1)
4,6	108·8 (2)	109·0 (2)	5,6	134·6 (2)	134·7 (2)
6,1	105·8 (1)	105·3 (1)	6,7	122·5 (2)	122·4 (2)
7,1	131·7 (1)	132·3 (1)	7,8	113 (2)	108 (2)
7,9	109 (2)	113 (2)	7,10	111 (2)	112 (2)
8,9	109 (2)	106 (3)	8,10	103 (3)	105 (3)
9,10	112 (2)	113 (2)	11,1	123·2 (1)	123·2 (1)
11,2	124·1 (2)	124·0 (2)	11,12	119 (1)	119 (2)
11,13	123·8 (1)	124·3 (1)	12,13	117 (1)	117 (2)
13,14	125·3 (1)	124·8 (1)	13,15	109·4 (1)	108·8 (1)
14,15	125·4 (2)	126·4 (2)	15,16	117·1 (1)	117·6 (2)
16,17	111 (1)	111 (1)	16,18	106·1 (1)	108·7 (2)
17,18	107 (1)	111 (1)	18,19	107 (1)	108 (1)
18,20	110 (2)	111 (2)	18,21	111 (1)	113 (2)
19,20	108 (2)	108 (2)	19,21	112 (2)	109 (2)
20,21	109 (3)	108 (2)	22,16	109·5 (2)	105·7 (2)
22,17	111 (1)	107 (1)	22,18	112·8 (2)	113·6 (3)
22,23	106 (2)	112 (2)	22,24	114 (2)	109 (2)
22,25	114 (2)	110 (2)	23,24	110 (2)	112 (2)
23,25	104 (2)	105 (2)	24,25	109 (2)	108 (2)

block-diagonal least-squares calculations with the non-hydrogen atoms refined anisotropically. All H atoms were located on difference syntheses and refined isotropically. Unit weights were used for A; the weighting scheme for B was $1/w = A + B|F_o| + C|F_o|^2$, with $A = 0{\cdot}52273, B = 0{\cdot}01099, C = 0{\cdot}00005776$.

At convergence R was 0·047 for isomer A and 0·056 for isomer B.† The asymmetric unit of A is formed by two molecules whose atoms have been distinguished (Table 1) by primed and unprimed numbers; the corresponding bond lengths and angles are given in Table 3 under columns I and II. The parameters of B are given in Table 2 and the bond angles and distances in Table 4. The thermal parameters B_{ij}, Tables 1 and 2, are the coefficients of the expression: $\exp(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}\,h_i\,h_j\,a_i^*\,a_j^*)$.

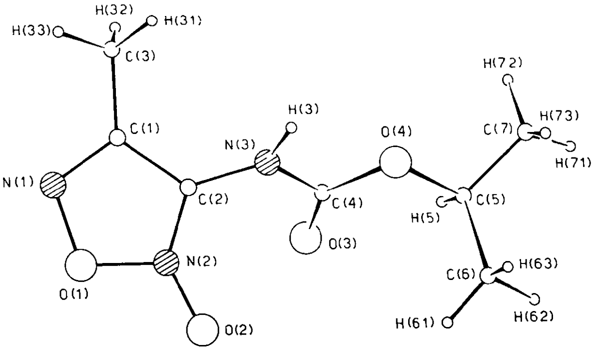


Fig. 2. Isomer B. Projection of the molecule onto the least-squares mean plane of the furoxan ring.

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

1	1·407 (4)	8	0·91 (4)	14	1·210 (4)	20	1·00 (4)
2	1·308 (5)	9	0·92 (4)	15	1·324 (3)	21	1·01 (4)
3	1·391 (4)	10	0·99 (4)	16	1·481 (4)	22	1·492 (5)
4	1·442 (4)	11	1·391 (4)	17	1·11 (3)	23	0·89 (4)
5	1·240 (4)	12	1·01 (4)	18	1·490 (6)	24	0·97 (4)
6	1·302 (4)	13	1·374 (4)	19	1·04 (4)	25	1·08 (4)
7	1·471 (5)						
1,2	110·4 (3)	2,3	106·9 (2)	3,4	107·3 (2)	4,5	117·2 (3)
4,6	106·7 (2)	5,6	136·1 (3)	6,1	108·7 (3)	7,1	128·1 (3)
7,2	121·5 (3)	7,8	116 (3)	7,9	114 (3)	7,10	110 (3)
8,9	99 (4)	8,10	111 (3)	9,10	106 (4)	11,1	129·3 (3)
11,6	121·9 (2)	11,12	124 (2)	11,13	121·4 (2)	12,13	114 (2)
13,14	123·9 (3)	13,15	109·7 (2)	14,15	126·4 (3)	15,16	117·3 (2)
16,17	106 (2)	16,18	108·5 (3)	17,18	112 (2)	18,19	118 (3)
18,20	111 (3)	18,21	110 (2)	19,20	103 (3)	19,21	108 (3)
20,21	106 (3)	22,16	105·2 (3)	22,17	110 (2)	22,18	114·1 (4)
22,23	112 (2)	22,24	113 (2)	22,25	104 (2)	23,24	109 (3)
23,25	105 (4)	24,25	115 (3)				

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32065 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Figs. 1 and 2 show the projections of the *A* and *B* molecules on to the least-squares planes of their furazan rings. The figures also show the numbering scheme adopted by us for describing the disubstituted furoxans (see, for example, Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1976).

Description and discussion

In both the independent molecules of *A* the furoxan moiety is planar, the average distance from the plane being 0·003 Å; N(3) is 0·024 Å out of the plane for molecule I and 0·058 Å for molecule II (Table 6). The group N(3)C(4)O(3)O(4) also is planar in both molecules, although more rigorously so in I; C(5) is at 0·011 Å and C(5′) at 0·078 Å from the respective plane. The structural parameters of the two molecules are not significantly different except for some small deviations in the isopropyl group (Table 3); the atoms of this group, and particularly C(6′) (Table 1), are affected by a large vibrational motion which may alter the apparent lengths of the bonds involved. The only relevant difference concerns the dihedral angle between the furazan ring and the carbamate group, whose values are 21 and 9° for molecules I and II respectively. The interactions of H(3) and H(3′) can explain the different conformation of the two molecules. H(3) approaches atoms O(3′) and N(2′) in such a way that it can be considered as forming a weak bifurcated intermolecular hydrogen bond (Fig. 3 and Table 5). H(3′) is involved in a simple hydrogen bond N(3′)–H(3′)···O(3). These slight packing differences are seemingly sufficient to alter significantly the mutual orientation of the furoxan and carbamate groups. This suggests an absence of conjugation between the two groups, although the bonds 11 are somewhat shorter (Table 3) than the presumably single bond C_{sp^2}–N, 1·42–1·43 Å (Service d'Analyse des Structures Cristallines, Bordeaux, 1976). The absence of conjugation is confirmed by the geometry of the furoxan groups. In fact the difference between bonds 2 and 6 is among the smallest found so far and so is that between 3 and 4 (Calleri *et al.*, 1976). Bond distances in the N(2)C(2)C(1)N(1) fragment indicate the π-delocalization characteristic of the furoxan group. The length of 5 is greater than the expected N=O length corrected for the electronegativity difference effect, 1·20 Å (Pauling, 1960); this suggests an appreciable polarization of this bond, both here and in isomer *B* (Tables 3 and 4). The endocyclic angles fit well the

Table 5. *Relevant intermolecular contacts*

Isomer *A*

N(3)···O(3′)^i	3·169 (2) Å	N(3)–H(3)–O(3′)^i	151 (3)°
H(3)···O(3′)^i	2·31 (3)		
N(3)···N(2′)^i	3·182 (3)	N(3)–H(3)–N(2′)^i	137 (3)
H(3)···N(2′)^i	2·42 (3)		
N(3′)···O(3)	2·928 (2)	N(3′)–H(3′)–O(3)	158 (3)
H(3′)···O(3)	2·04 (3)		
N(3′)···N(2)	3·149 (3)		
H(3′)···N(2)	2·89 (3)		

(i) $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$.

Isomer *B*

N(3)···O(3)^i	2·813 (4) Å	N(3)–H(3)–O(3)^i	150 (4)°
H(3)···O(3)^i	1·89 (3)		

(i) $1+x, y, z$.

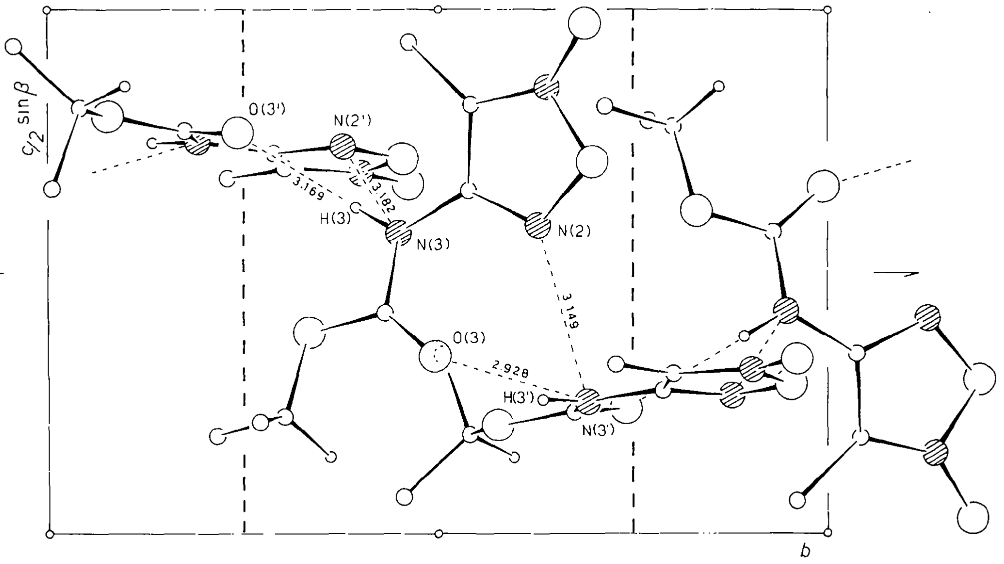

Fig. 3. Isomer *A*. Projection of the network of hydrogen bonds on (100). For clarity methyl hydrogens have been omitted.

trend found for the disubstituted furoxans (Calleri *et al.*, 1975).

Similar considerations apply to the lower-melting isomer *B*, where, however, the angle 1,6 is significantly larger than the average, 107°. Neither the furoxan nor the furazan group is strictly planar (Table 6), as previously found; the furoxan group of the lower-melting isomer of a pair is often less planar than that of the higher-melting isomer (Calleri *et al.*, 1976). N(3) is 0·016 Å out of the furazan plane which makes a dihedral angle of 54° with the C(4)N(3)O(3)O(4) group. The value of this angle can be justified by the steric hindrance between O(3) and O(2), which reach their minimum-energy distance at a value of 2·927 (4) Å, corresponding to the sum of the van der Waals radii. Fig. 4 shows the hydrogen bonding between molecules of isomer *B* projected on (010).

In conclusion, the dimensions of the furoxan moieties of the present *A* and *B* isomers are much closer than for the other pairs. In particular, bond 2 of isomer *B* is here slightly longer than 6, whilst usually it is much shorter, and these two bonds are not very different in all three molecules. Therefore the X-ray analysis does not reveal any influence of the electron-releasing carbamate function on the geometry of the furoxan moiety.

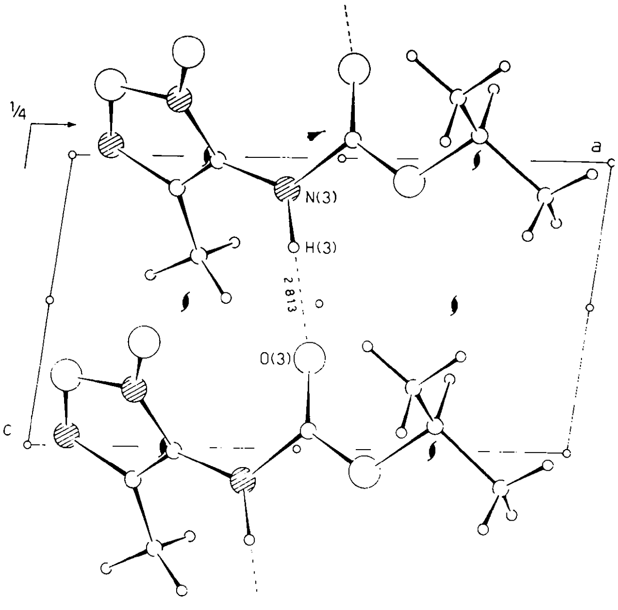

Fig. 4. Isomer *B*. Projection on (010) of molecules joined by hydrogen bonds.

Table 6. *Equations of least-squares planes and distances* (Å) *from these planes*

Atoms not included in the least-squares plane equations are starred. The transformation matrix from monoclinic *x*,*y*,*z* to orthogonal *X*, *Y*, *Z* coordinates is
$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}.$$

Furazan ring

Isomer *A*	molecule I	$0\cdot9753X - 0\cdot2122Y - 0\cdot0612Z = -0\cdot7824$
	molecule II	$0\cdot1890X + 0\cdot0176Y - 0\cdot9818Z = -1\cdot9742$
Isomer *B*		$0\cdot6935X + 0\cdot5760Y - 0\cdot4327Z = 3\cdot1286$

	Isomer *A*		
	Molecule I	Molecule II	Isomer *B*
N(1)	−0·001	0·002	0·014
C(1)	−0·001	−0·004	−0·005
C(2)	0·004	0·004	−0·007
N(2)	−0·005	−0·003	0·013
O(1)	0·003	0·000	−0·015
*O(2)	−0·008	0·009	0·009
*C(3)	0·022	0·048	−0·026
*N(3)	0·028	0·053	0·016

Carbamate group

Isomer *A*	molecule I	$-0\cdot9120X + 0\cdot2945Y - 0\cdot2854Z = -0\cdot4355$
	molecule II	$0\cdot1038X + 0\cdot1549Y - 0\cdot9825Z = -0\cdot7296$
Isomer *B*		$-0\cdot1669X + 0\cdot8842Y - 0\cdot4362Z = 5\cdot6307$

	Isomer *A*		
	Molecule I	Molecule II	Isomer *B*
N(3)	0·000	0·002	−0·002
C(4)	0·000	−0·006	0·006
O(3)	0·000	0·002	−0·002
O(4)	0·000	0·002	−0·002
*C(2)	−0·103	0·074	0·062
*C(5)	−0·011	−0·078	0·142

The fact that form *A* is very strongly favoured at equilibrium for all the carbamate derivatives (Gasco *et al.*, 1972; Gasco & Boulton, 1973) can only be explained by an intramolecular interaction involving O(3) and N(2); indeed the distance between these two atoms is significantly shorter than the sum of the van der Waals radii. This interaction, which of course cannot be present in the less stable isomer *B*, produces a polarization of electronic charge from O to N. The polarization is stronger in molecule II [2·733 (2) Å] where it is involved in the above mentioned bifurcated hydrogen bond, and weaker [2·777 (2) Å] in molecule I, where hydrogen bonding with H(3) involves O(3) only.

In all three molecules bond 7 is among the shortest in disubstituted furoxans and is shorter than the expected $C_{sp^2}-C_{sp^3}$ bond, 1·51 Å; the methyl groups at C(3) and C(3′), therefore, possibly show a hyperconjugation effect.

Within the carbamate groups bond 15 is considerably shorter than bond 16, as found in other carbamates, esters and lactones when the bridging O atom forms a single $O-C_{sp^3}$ bond and an $O-C_{sp^2}$ bond which shows an additional shortening owing to some conjugation with the —C(—N)=O system.

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The Crystal and Molecular Structure of 1,4-Diethoxybenzene

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The crystal structure of 1,4-diethoxybenzene has been determined from visually estimated Cu $K\alpha$ X-ray data. The crystals are monoclinic, space group $P2_1$, with $a = 9{\cdot}518\,(6)$, $b = 7{\cdot}61\,(1)$, $c = 7{\cdot}137\,(6)$ Å, $\beta = 110{\cdot}40\,(6)°$ and $Z = 2$. The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations to $R = 0{\cdot}069$ for 672 non-zero reflexions. The molecule is nearly centrosymmetric and planar. The ethoxy groups take *trans* conformations. The benzene ring seems to adopt a Kekulé structure. The C(aromatic)—O bond lengths, 1·378 (7) and 1·377 (7) Å, are longer than the C(sp^2)—O length in aromatic esters, while the C(aliphatic)—O lengths, 1·416 (8) and 1·426 (8) Å, are shorter than the corresponding length in the esters. The C—O—C angles, 119·4 (5) and 118·9 (5)° are close to the sp^2 angle. The molecules related by a twofold screw axis are stacked with a dihedral angle of 75·5° to form a chevron in a similar manner to 1,4-dimethoxybenzene and terphenyl. The molecular sheets parallel to (100) are stacked through H · · · O and loose $CH_3 \cdots CH_3$ contacts.

Introduction

The dialkyl ethers of *p*-hydroquinone have a residual dipole moment; in benzene solution the moments of the dimethyl and diethyl ethers are 1·70 and 1·80 D respectively (Mizushima, Morino & Okazaki, 1938). Goodwin, Przybylska & Robertson (1950) have established, however, that the molecule of 1,4-dimethoxybenzene is centrosymmetric in the crystalline state. This apparent discrepancy may be ascribed to the rotation of the alkyl group about the ring C—O bond in phenyl alkyl ethers. This sort of rotation is considered to play an important role in the β-blocking adrenergic action (Fukui, Nagata & Imamura, 1970; Petrongolo & Tomasi, 1975) or in the nematic aggregate in liquid crystals (Bryan, 1967).

As an extension of the structural study of bis(2-hydroxyethyl) terephthalate (Kashino & Haisa, 1975), this paper reports the conformation of ethoxy groups attached to the benzene ring and the stacking mode of the molecules in the crystal, and compares the geometry of the ethereal linkage in ethers and esters.

Experimental

The crystals were grown from an acetone solution by slow evaporation as colourless plates with developed (100).

Crystal data

1,4-Diethoxybenzene, $C_{10}H_{14}O_2$, $M_r = 166{\cdot}2$, m.p. 70–71 °C. Monoclinic, space group $P2_1$, $a = 9{\cdot}518\,(6)$, $b = 7{\cdot}61\,(1)$, $c = 7{\cdot}137\,(6)$ Å, $\beta = 110{\cdot}40\,(6)°$, $V = 484{\cdot}5\,(8)$ Å^3, $D_m = 1{\cdot}14$ (by flotation in aqueous solution of KI), $D_x = 1{\cdot}139$ g cm^{-3} for $Z = 2$, $\mu = 6{\cdot}4$ cm^{-1} for Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å), $F(000) = 180$. Systematic absences $0k0$ with k odd. The higher symmetry was ruled out by the determination of the structure.

By using specimens with dimensions $0{\cdot}18 \times 0{\cdot}29 \times 0{\cdot}70$ and $0{\cdot}15 \times 0{\cdot}60 \times 0{\cdot}38$ mm in glass capillaries, intensity data were collected on Weissenberg photographs for the layers $hk0$ to $hk5$ and $h0l$ to $h5l$ respectively. Visually estimated intensities were corrected for