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The Crystal and Molecular Structure of 6-Acetyl-8-(acetyloxyimino)-2-phenyl-4-oxo-4,8-dihydro-2*H*,6*H*-pyrazolo[3,4-*f*]-1,2,3-benzotriazole–Dioxane (2:1)

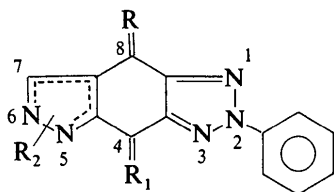By ANNA MARIA MANOTTI LANFREDI, ANTONIO TIRIPICCHIO AND MARISA TIRIPICCHIO CAMELLINI

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Crystals of the title compound are triclinic ($P\bar{1}$) with $a = 10\cdot457\,(5)$, $b = 9\cdot654\,(5)$, $c = 10\cdot207\,(4)$ Å; $\alpha = 78\cdot9\,(1)$, $\beta = 89\cdot9\,(1)$, $\gamma = 110\cdot3\,(1)°$; $Z = 2$. The structure, determined from diffractometer data by direct methods, was refined by block-diagonal least squares to $R = 5\cdot2\%$ for 1880 independent reflexions. The compound is a derivative of the new heterocycle pyrazolo[3,4-*f*]-1,2,3-benzotriazole and the analysis shows that the acetyl substituent is at N(6). Packing is essentially determined by a C—H $\cdots$ O contact, involving the dioxane molecule, which fulfils the geometrical requirements for a hydrogen bond.

Introduction

The reaction of diazomethane with 5-hydroxy-4-phenylbenzofurazan as a synthetic route to derivatives of the new heterocycle pyrazolo[3,4-*f*]-1,2,3-benzotriazole has been investigated by Cerè, Pollicino, Sandri & Scapini (1977), who have synthesized 2-phenyl-5(6)*H*-pyrazolo[3,4-*f*]-benzotriazole-4,8-dione and its mono- and dioximes of general formula

The position of the R_2 substituent was not known, as it was not possible to ascertain by conventional chemical and spectroscopic methods whether N(5) or N(6) was substituted.

The structure of the derivative corresponding to $R = NOAc$, $R_1 = O$, $R_2 = Ac$ has been determined to elucidate the structural features of this class of compound, and in particular to define the position of the R_2 substituent.

Experimental

The title compound was obtained as crystals suitable for X-ray analysis from a toluene–dioxane (1:1) solution. The crystals contain solvent in the dioxane:com-

pound ratio of 1:2, as found from the structural analysis. Unit-cell parameters (Table 1) were obtained from rotation and Weissenberg photographs and refined by least squares from θ, χ and φ values of 16 reflexions measured on an automated single-crystal diffractometer. The intensities were collected on a Siemens AED diffractometer with Ni-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. A prismatic crystal $0.08 \times 0.10 \times 0.22$ mm was mounted with [001] collinear with the φ axis of the instrument and all reflexions with $\theta < 65°$ were recorded. From 3221 independent reflexions, 1880, satisfying the condition $I > 2\sigma(I)$, were used in the analysis.

The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure amplitudes were put on an absolute scale by Wilson's method and normalized structure factors $|E_{hkl}|$ derived. After several attempts with different

Table 1. *Crystallographic data*

$C_{17}H_{12}N_6O_4 \cdot \frac{1}{2}C_4H_8O_2$, F.W. 408.36; triclinic, space group $P\bar{1}$; $a = 10.457$ (5), $b = 9.654$ (5), $c = 10.207$ (4) Å; $\alpha = 78.9$ (1), $\beta = 89.9$ (1), $\gamma = 110.3$ (3)°, $V = 946.1$ Å³, $Z = 2$, $D_x = 1.43$ g cm⁻³, μ(Cu $K\alpha$) = 9.14 cm⁻¹, $F(000) = 424$.

Table 2. *Fractional atomic coordinates for nonhydrogen atoms* ($\times 10^4$) *and thermal parameters with e.s.d.'s*

The anisotropic coefficients are in the form $\exp[-0.25(h^2 a^{*2} B_{11} + \cdots 2klb^* c^* B_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	−2721 (2)	6530 (3)	2869 (3)	3.75 (11)	4.79 (12)	6.61 (15)	2.36 (10)	−0.66 (10)	−1.89 (11)
O(2)	−3395 (3)	1679 (3)	−782 (3)	5.04 (14)	8.59 (18)	8.60 (19)	3.40 (13)	−2.64 (13)	−5.21 (16)
O(3)	2213 (2)	4296 (3)	2894 (3)	3.24 (10)	5.09 (12)	6.57 (14)	2.23 (9)	−2.04 (10)	−3.08 (11)
O(4)	2626 (3)	2215 (4)	2664 (3)	8.78 (19)	8.41 (19)	11.18 (23)	6.11 (16)	−6.85 (17)	−6.24 (18)
O(5)	−47 (2)	8531 (3)	609 (2)	4.66 (11)	3.80 (11)	4.86 (12)	1.88 (9)	−1.48 (10)	−0.98 (9)
N(1)	1518 (3)	6336 (3)	3836 (3)	3.49 (12)	3.42 (12)	4.27 (14)	1.67 (10)	−0.47 (10)	−0.91 (11)
N(2)	1138 (3)	7303 (3)	4372 (3)	3.78 (13)	3.48 (12)	4.02 (14)	1.70 (10)	−0.55 (10)	−0.90 (11)
N(3)	−96 (3)	7365 (3)	4088 (3)	3.67 (12)	3.67 (13)	4.54 (14)	1.78 (10)	−0.55 (11)	−0.62 (11)
N(4)	−3062 (3)	4401 (3)	1135 (3)	3.15 (12)	4.06 (13)	4.76 (15)	1.69 (10)	−0.63 (11)	−0.94 (11)
N(5)	−2763 (3)	3397 (3)	527 (3)	2.99 (11)	4.29 (13)	4.64 (15)	1.53 (10)	−0.87 (10)	−1.16 (12)
N(6)	1044 (3)	3815 (3)	2171 (3)	2.88 (12)	4.71 (14)	5.20 (15)	1.65 (10)	−1.46 (11)	−1.98 (12)
C(1)	−531 (3)	6370 (3)	3300 (3)	3.62 (14)	3.15 (14)	3.87 (16)	1.41 (12)	−0.16 (12)	−0.28 (12)
C(2)	−1851 (3)	6017 (4)	2676 (3)	3.18 (14)	3.63 (15)	4.75 (18)	1.58 (12)	−0.29 (13)	−0.53 (14)
C(3)	−1978 (3)	4917 (4)	1806 (3)	2.86 (13)	3.38 (14)	4.04 (16)	1.23 (11)	−0.17 (12)	−0.31 (12)
C(4)	−986 (3)	4249 (3)	1648 (3)	2.61 (13)	3.38 (15)	3.89 (16)	1.23 (11)	−0.25 (12)	−0.35 (12)
C(5)	282 (3)	4581 (4)	2328 (3)	2.75 (13)	3.50 (15)	4.26 (16)	1.40 (11)	−0.15 (12)	−0.67 (13)
C(6)	459 (3)	5729 (4)	3139 (3)	2.98 (13)	3.45 (14)	3.85 (16)	1.40 (12)	−0.14 (12)	−0.32 (12)
C(7)	−1527 (3)	3270 (4)	824 (3)	3.18 (14)	4.15 (16)	4.07 (17)	1.41 (12)	−0.58 (12)	−0.85 (13)
C(8)	2001 (3)	8208 (4)	5208 (3)	4.09 (16)	3.32 (15)	3.84 (16)	1.34 (12)	−0.32 (13)	−0.70 (13)
C(9)	1608 (4)	9275 (4)	5661 (4)	6.01 (21)	4.37 (18)	5.81 (22)	2.46 (16)	−1.18 (17)	−1.77 (16)
C(10)	2464 (5)	10147 (5)	6466 (4)	7.59 (25)	4.79 (20)	6.02 (24)	2.29 (19)	−0.52 (19)	−2.08 (18)
C(11)	3672 (4)	9928 (4)	6821 (4)	5.96 (21)	4.89 (20)	5.02 (21)	0.82 (16)	−0.43 (17)	−1.62 (17)
C(12)	4042 (4)	8846 (4)	6363 (4)	4.34 (18)	5.29 (19)	5.29 (21)	1.38 (15)	−0.66 (15)	−1.64 (16)
C(13)	3206 (3)	7983 (4)	5542 (4)	3.90 (16)	4.16 (17)	4.53 (18)	1.16 (13)	−0.55 (14)	−1.40 (14)
C(14)	−3720 (4)	2531 (4)	−283 (4)	3.81 (17)	5.66 (20)	5.52 (21)	1.74 (15)	−1.43 (15)	−1.83 (17)
C(15)	−5060 (4)	2771 (6)	−368 (5)	3.91 (18)	9.39 (30)	9.46 (31)	3.12 (19)	−2.64 (20)	−4.77 (26)
C(16)	2938 (4)	3342 (4)	3064 (4)	4.09 (16)	5.86 (20)	5.09 (19)	2.89 (15)	−1.66 (14)	−2.39 (16)
C(17)	4120 (4)	3942 (5)	3858 (4)	4.20 (18)	7.80 (26)	7.57 (26)	3.32 (18)	−3.02 (18)	−3.70 (21)
C(18)	−1212 (3)	8780 (4)	−3 (4)	3.71 (16)	4.55 (18)	5.16 (20)	1.37 (14)	−1.46 (14)	−1.15 (15)
C(19)	750 (4)	9830 (4)	1119 (4)	4.30 (17)	4.25 (17)	4.87 (19)	1.35 (14)	−1.75 (15)	−1.19 (14)

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Discussion

The compound is the acetyloxyimino derivative of 6-acetyl-2-phenyl-4-oxo-4,8-dihydro-2*H*,6*H*-pyrazolo-[3,4-*f*]-1,2,3-benzotriazole. The structure is shown in Fig. 1 with that of the solvating dioxane. As can be seen from Table 4, the structural parameters of the acetylpyrazole and *p*-benzoquinone 4-acetyloxime moieties are in good agreement with those for 1-acetyl-4-bromopyrazole (Lapasset, Escande & Falgueirettes, 1972) and α-2-chloro-*p*-benzoquinone 4-acetyloxime (Fischmann, MacGillavry & Romers, 1961). The only differences are for C(3)—C(4) and C(1)—C(6), which are shorter (1·35 and 1·32 Å) in the quoted work. It is possible that this difference is due to the condensation of the benzoquinone system with the pyrazole and

triazole rings. As in the chlorobenzoquinone derivative, the *p*-benzoquinone 4-acetyloxime moiety is not planar: the O(1)C(1)C(2)C(3)C(6) atoms are nearly coplanar and the plane through them forms an angle of 4·2° with the plane through C(3)C(4)C(5)N(6)O(3) (the
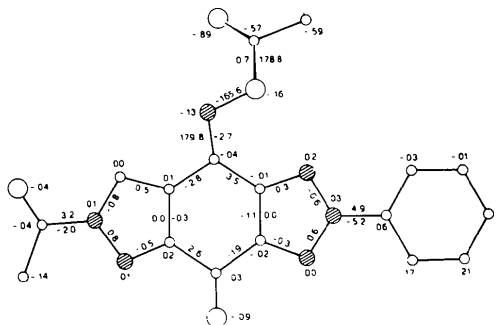

Fig. 2. Displacements (Å) of the atoms from the least-squares plane through the pyrazolo[3,4-*f*]-1,2,3-benzotriazole hetero-cycle, and torsion angles (°).

Fig. 3. Torsion angles in the dioxane ring showing its chair conformation.

Table 3. *Fractional atomic coordinates for hydrogen atoms* (×10³) *and isotropic thermal parameters*

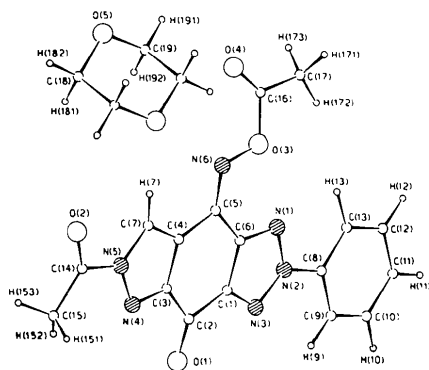|	x	y	z	B (Å²)
H(7)	−112 (3)	269 (3)	40 (3)	5·5 (8)
H(9)	72 (4)	940 (4)	534 (4)	8·1 (10)
H(10)	219 (4)	1093 (4)	682 (4)	9·0 (11)
H(11)	429 (4)	1059 (4)	734 (4)	7·7 (10)
H(12)	493 (4)	872 (4)	656 (4)	7·5 (10)
H(13)	342 (3)	706 (4)	528 (3)	6·1 (8)
H(151)	−530 (4)	311 (5)	46 (4)	9·5 (12)
H(152)	−574 (4)	170 (5)	−42 (4)	11·2 (13)
H(153)	−505 (4)	355 (5)	−120 (4)	11·3 (13)
H(171)	497 (4)	411 (4)	322 (4)	9·1 (11)
H(172)	414 (4)	488 (5)	419 (4)	9·4 (11)
H(173)	422 (4)	315 (5)	455 (4)	10·2 (12)
H(181)	−190 (3)	895 (4)	69 (3)	5·5 (8)
H(182)	−173 (3)	784 (3)	−29 (3)	5·5 (8)
H(191)	156 (3)	963 (4)	145 (3)	5·9 (8)
H(192)	17 (3)	1001 (4)	195 (3)	6·4 (9)

Fig. 1. Projection along [001] of the molecule and of the solvating dioxane, showing the molecular shape and the atomic numbering.
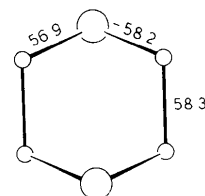
Table 4. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s*

Symmetry code: (i) −x, 2 − y, −z.

C(1)—C(2)	1·479 (5)	C(5)—N(6)	1·289 (6)
C(2)—C(3)	1·483 (6)	N(6)—O(3)	1·413 (4)
C(3)—C(4)	1·422 (5)	O(3)—C(16)	1·370 (6)
C(4)—C(5)	1·462 (5)	C(16)—O(4)	1·176 (6)
C(5)—C(6)	1·469 (6)	C(16)—C(17)	1·486 (6)
C(6)—C(1)	1·402 (5)	N(5)—C(14)	1·440 (5)
C(1)—N(3)	1·331 (5)	C(14)—O(2)	1·186 (6)
N(3)—N(2)	1·342 (5)	C(14)—C(15)	1·498 (7)
N(2)—N(1)	1·335 (6)	N(2)—C(8)	1·431 (5)
N(1)—C(6)	1·338 (5)	C(8)—C(9)	1·386 (7)
C(3)—N(4)	1·321 (5)	C(9)—C(10)	1·390 (6)
N(4)—N(5)	1·365 (6)	C(10)—C(11)	1·389 (7)
N(5)—C(7)	1·369 (5)	C(11)—C(12)	1·388 (7)
C(7)—C(4)	1·363 (5)	C(12)—C(13)	1·388 (6)
C(2)—O(1)	1·209 (5)	C(13)—C(8)	1·384 (5)
C(7)—H(7)	0·97 (3)	C(15)—H(151)	1·02 (4)
C(9)—H(9)	1·02 (4)	C(15)—H(152)	1·04 (5)
C(10)—H(10)	1·02 (4)	C(15)—H(153)	1·02 (4)
C(11)—H(11)	0·98 (4)	C(17)—H(171)	1·05 (4)
C(12)—H(12)	0·99 (4)	C(17)—H(172)	1·02 (5)
C(13)—H(13)	1·07 (4)	C(17)—H(173)	0·97 (5)
O(5)—C(18)	1·442 (4)	C(18)—H(182)	0·98 (3)
C(18)—C(19i)	1·514 (6)	C(19)—H(191)	0·98 (3)
O(5)—C(19)	1·437 (6)	C(19)—H(192)	1·12 (3)
C(18)—H(181)	1·08 (3)		

Table 4 (cont.)

C(2)—C(1)—C(6)	125·4 (3)	N(2)—N(1)—C(6)	103·2 (3)
C(2)—C(1)—N(3)	124·9 (3)	C(3)—N(4)—N(5)	103·3 (3)
N(3)—C(1)—C(6)	109·7 (3)	N(4)—N(5)—C(7)	113·3 (3)
C(1)—C(2)—C(3)	110·8 (3)	N(4)—N(5)—C(14)	121·3 (3)
C(1)—C(2)—O(1)	124·7 (3)	C(7)—N(5)—C(14)	125·4 (3)
C(3)—C(2)—O(1)	124·5 (3)	N(5)—C(7)—C(4)	105·8 (3)
C(2)—C(3)—C(4)	124·2 (3)	C(5)—N(6)—O(3)	108·5 (3)
C(2)—C(3)—N(4)	123·3 (3)	N(6)—O(3)—C(16)	113·8 (3)
N(4)—C(3)—C(4)	112·5 (3)	O(3)—C(16)—C(17)	109·0 (4)
C(3)—C(4)—C(5)	123·4 (3)	O(3)—C(16)—O(4)	124·0 (4)
C(3)—C(4)—C(7)	105·1 (3)	O(4)—C(16)—C(17)	126·9 (4)
C(7)—C(4)—C(5)	131·5 (3)	N(5)—C(14)—C(15)	115·7 (4)
C(4)—C(5)—C(6)	113·2 (3)	N(5)—C(14)—O(2)	117·8 (4)
C(4)—C(5)—N(6)	116·9 (3)	O(2)—C(14)—C(15)	126·6 (4)
C(6)—C(5)—N(6)	129·9 (3)	N(2)—C(8)—C(9)	119·4 (3)
C(1)—C(6)—C(5)	123·0 (3)	N(2)—C(8)—C(13)	118·6 (3)
C(1)—C(6)—N(1)	108·4 (3)	C(9)—C(8)—C(13)	122·0 (3)
C(5)—C(6)—N(1)	128·6 (3)	C(8)—C(9)—C(10)	118·5 (4)
C(1)—N(3)—N(2)	102·6 (3)	C(9)—C(10)—C(11)	120·3 (4)
N(3)—N(2)—N(1)	116·2 (3)	C(10)—C(11)—C(12)	120·3 (4)
N(3)—N(2)—C(8)	122·4 (3)	C(11)—C(12)—C(13)	120·0 (4)
N(1)—N(2)—C(8)	121·5 (3)	C(12)—C(13)—C(8)	119·0 (4)
N(5)—C(7)—H(7)	124 (2)	C(14)—C(15)—H(151)	112 (2)
C(4)—C(7)—H(7)	130 (2)	C(14)—C(15)—H(152)	102 (2)
C(8)—C(9)—H(9)	117 (2)	C(14)—C(15)—H(153)	111 (2)
C(10)—C(9)—H(9)	124 (2)	H(151)—C(15)—H(152)	111 (3)
C(9)—C(10)—H(10)	120 (2)	H(151)—C(15)—H(153)	109 (4)
C(11)—C(10)—H(10)	120 (2)	H(152)—C(15)—H(153)	111 (3)
C(10)—C(11)—H(11)	119 (2)	C(16)—C(17)—H(171)	104 (2)
C(12)—C(11)—H(11)	120 (2)	C(16)—C(17)—H(172)	114 (2)
C(11)—C(12)—H(12)	121 (2)	C(16)—C(17)—H(173)	111 (3)
C(13)—C(12)—H(12)	119 (2)	H(171)—C(17)—H(172)	114 (3)
C(12)—C(13)—H(13)	120 (2)	H(171)—C(17)—H(173)	98 (3)
C(8)—C(13)—H(13)	120 (2)	H(172)—C(17)—H(173)	114 (4)
C(18)—O(5)—C(19)	110·0 (3)	H(182)—C(18)—C(19ⁱ)	115 (2)
O(5)—C(18)—C(19i)	110·4 (3)	O(5)—C(19)—H(191)	106 (2)
O(5)—C(19)—C(18i)	111·4 (3)	O(5)—C(19)—H(192)	112 (2)
O(5)—C(18)—H(181)	113 (2)	H(191)—C(19)—H(192)	110 (2)
O(5)—C(18)—H(182)	106 (2)	H(191)—C(19)—C(18ⁱ)	109 (2)
H(181)—C(18)—H(182)	106 (3)	H(192)—C(19)—C(18ⁱ)	109 (2)
H(181)—C(18)—C(19i)	107 (2)		

angle found by Fischmann *et al.* is 6°). Also the dihedral angle (4·6°) formed by the acetyl group [O(2)-C(14)C(15)] and the pyrazole ring [N(4)N(5)C(7)C(4)-C(3)] agrees with the corresponding one (3·2°) in the acetylbromopyrazole derivative. The pyrazolo[3,4-*f*]-1,2,3-benzotriazole moiety is nearly planar, the maximum deviation being 0·036 Å for C(5). The displacements of the atoms of the rest of the molecule from that plane are shown in Fig. 2 with the torsion angles. The dihedral angles which the pyrazolo[3,4-*f*]-1,2,3-benzotriazole moiety forms with the acetyl group [O(2)C(14)C(15)] the phenyl ring [C(8)—C(13)] and the acetyloxime group [N(6)O(3)C(16)O(4)C(17)] are 4·6, 5·1 and 18·9° respectively. The acetyloxime group is *anti* to the pyrazole ring. The dioxane molecule is centrosymmetric. Its structural parameters and conformation, which is chair (Fig. 3), agree well with those reported (Frey & Monier, 1971; Borel & Leclaire, 1976).

All intermolecular distances are normal, except for H(7)···O(5)(−x, 1 − y, −z) = 2·32 Å which is shorter than the sum of the van der Waals radii (about 2·6 Å) (Weast, 1974). C(7)—H(7) points towards O(5)(−x, 1 − y, − z)|C(7)—H(7)···O(5)(− x, 1 − y, − z) = 175°], so the geometrical requirements for hydrogen bonding are fulfilled. This kind of interaction, even if not common, has been observed in other cases (*e.g.* Allerhand & Schleyer, 1963; Fayos & Garcia-Blanco, 1972, and references therein).

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The Crystal Structure and Conformational Analysis of Acetylcarnitine Hydrochloride Monohydrate

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Acetylcarnitine hydrochloride monohydrate, $C_9H_{17}NO_4 \cdot HCl \cdot H_2O$, is monoclinic, space group $P2_1/c$, with $a = 12 \cdot 037 (1)$, $b = 9 \cdot 509 (1)$, $c = 12 \cdot 449 (1)$ Å, $\beta = 109 \cdot 20 (1)°$, $Z = 4$. Counter data collected with Mo $K\alpha$ radiation were used to derive the structure by direct methods. Refinement by full-matrix least squares led to an R of $0 \cdot 055$ for 2441 reflexions with $I > 0$. Bond distances and angles of the acetylcarnitine cation agree well with those of other β-substituted acetylcholine derivatives. The conformational analysis of the isolated molecule, performed with the force field made up by torsional barriers about single bonds and non-bonded interactions, shows three minima in the energy surface. One of these corresponds to the experimental configuration in the crystal.

Introduction

The role of carnitine (γ-trimethylammonium β-hydroxybutyrate) in fatty-acid metabolism is well documented (Bremer, 1962; Norum & Bremer, 1963; Fritz & Yue, 1963; Bressler & Katz, 1965). The currently held belief is that carnitine serves as a carrier of activated fatty acyl groups, which are transported across the mitochondrial membrane in the form of carnitine esters. The translocation of the active acetyl group of acetyl coenzyme A by acetylcarnitine from intra- to extra-mitochondrial sites has been discussed by Bressler & Katz (1965). More recently, Mueller & Strack (1973) have evaluated the hydrolysis enthalpy of some O-acylcarnitines and betaine esters; the relation between ΔH and the free energy indicated that the ΔG^0 value for all O-acylcarnitines is $-7 \cdot 90$ kcal mol^{-1}. This result confirms the statement of Friedman & Fraenkel (1955), that the ester bond of acetylcarnitine is a high-energy bond comparable to the thioester bond of acetyl coenzyme A.

We have performed an X-ray crystallographic study of acetylcarnitine hydrochloride monohydrate (ACC)

to compare its conformation with that of carnitine (CAR) (Tomita, Urabe, Kim & Fujiwara, 1974). Furthermore, since ACC has muscarinic action in the nervous system (Hosein & Proulx, 1964), its structure can be compared with that of other acetylcholine-like molecules displaying the same action (Baker, Chothia, Pauling & Petcher, 1971).

Experimental

Crystals of ACC were obtained from a dilute methanolic solution of commercial acetylcarnitine hydrochloride by slow evaporation at 275 K. Cell dimensions reported in Table 1 were obtained by a least-squares fit to the $\sin^2 \theta$ values of 45 hkl reflexions measured on a diffractometer. The space group $P2_1/c$ was indicated by the absences $h0l$ with l odd and $0k0$ with k odd. The density was measured by flotation in mixed solvents. For the data collection a crystal $0 \cdot 35 \times 0 \cdot 25 \times 0 \cdot 20$ mm was mounted on a computer-controlled Syntex $P\bar{1}$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å) and