International Tables for X-ray Crystallography (1974). C(18) has been assigned the β-position in accord with Lupón *et al.* (1983).

Discussion. Fractional atomic coordinates are given in Table 1.* The numbering scheme, bond lengths, bond angles and intra-annular torsion angles are given in Fig. 1. As can been seen from the molecular drawing in Fig. 2, O(19) is also in the β-position. This confirms the assignment based on NMR-shift experiments (Lupón *et al.*, 1983).

As in other 1,4-dien-3-one steroids the *A* ring is almost planar. C(10) [0·036 (3) Å] and C(5) [−0·034 (3) Å] have the largest deviations from a mean plane through the C atoms of ring *A*. The *B* and *C* rings have the usual chair conformation. Ring *D* may be described as an envelope with C(14) out of the plane. However, a few thermal parameters, in particular at C(16), indicate some disorder in this ring. There is a hydrogen bond from H(19) to O(3) of a neighboring molecule; O(20) is not involved in hydrogen bonding.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42315 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure Analysis of Minaprine Analogs: 3-Morpholinium Ethylamino-5-methyl-6-phenylpyridazinium Oxalate, Oxalic Acid (1/1)*

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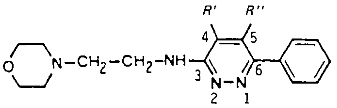
Abstract. $C_{17}H_{24}N_4O^{2+}.C_2O_4^{2-}.C_2H_2O_4$, $M_r = 478·5$, triclinic, $P\bar{1}$, $a = 9·949$ (1), $b = 16·477$ (6), $c = 8·345$ (1) Å, $\alpha = 87·75$ (2), $\beta = 109·88$ (1), $\gamma = 116·59$ (2)°, $V = 1139·9$ (13) Å^3, $Z = 2$, $D_x = 1·39$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0·70$ cm^{-1}, $F(000) = 504$, $T = 293$ K, final $R = 0·037$ for 1268 observed reflections. By comparison with the previously studied 4-demethyl and 4-phenyl analogs, the presence of a methyl group on position 5 results in an important torsion of the phenyl ring with regard to the adjacent pyridazine, but has no influence on the bond lengths and angles.

Introduction. This work is part of a general study on structural and molecular properties of a series of analogs of minaprine (commercial name: Cantor–Clin-Midy, France), an antidepressant drug belonging to the aminopyridazine family (Wermuth, 1985). The crystal structure of the title compound, hereafter abbreviated as the '5-methyl' analog, has been studied by X-ray diffraction and compared with those of the 4-demethyl and 4-phenyl analogs (Michel, Gustin, Evrard & Durant, 1982*a,b*). The comparison has been undertaken in order to ascertain the influence of the substituent on the phenyl torsion and the bond length between pyridazine and phenyl rings, in correlation with the activity evolution.



$R' = CH_3$, $R'' = H$: Minaprine

$R' = H$, $R'' = CH_3$: 5-Methyl analog

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* 4-{2-[(4-Methyl-3-phenyl-6-pyridazinio)amino]ethyl}-morpholinium oxalate–oxalic acid (1/1).

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and* B_{eq} *values with e.s.d.'s in parentheses*

$$B_{\text{eq}} = 8\pi^2 U_{\text{eq}},\ U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
O(1)	11098 (5)	1738 (3)	2984 (5)	7·56 (2)
C(2)	10842 (6)	2465 (5)	3398 (6)	6·80 (3)
C(3)	9138 (6)	2314 (3)	2253 (6)	4·63 (2)
N(4)	7877 (5)	1415 (2)	2394 (5)	3·66 (2)
C(5)	8250 (6)	672 (3)	2027 (6)	4·84 (3)
C(6)	9948 (8)	883 (5)	3183 (8)	7·02 (4)
C(7)	6240 (6)	1237 (3)	1171 (6)	4·33 (2)
C(8)	5563 (6)	1795 (3)	1736 (6)	4·22 (2)
N(9)	4871 (5)	1358 (2)	3031 (5)	4·11 (2)
C(10)	4738 (5)	1805 (3)	4195 (6)	3·30 (2)
C(11)	5279 (6)	2769 (3)	4431 (6)	3·63 (2)
C(12)	5085 (5)	3142 (3)	5682 (6)	3·50 (2)
C(13)	4359 (6)	2552 (3)	6790 (6)	3·58 (2)
N(14)	3836 (5)	1659 (3)	6567 (5)	3·90 (2)
N(15)	4030 (5)	1315 (2)	5275 (5)	3·55 (2)
C(16)	4074 (6)	2903 (3)	8197 (6)	4·13 (3)
C(17)	5329 (6)	3662 (3)	9385 (6)	4·82 (3)
C(18)	5023 (8)	4000 (4)	10641 (6)	5·53 (3)
C(19)	3522 (9)	3598 (5)	10731 (6)	6·64 (4)
C(20)	2298 (8)	2845 (5)	9620 (8)	7·96 (4)
C(21)	2573 (6)	2480 (4)	8345 (6)	5·89 (3)
C(22)	5534 (6)	4139 (3)	5825 (6)	5·11 (3)
O(551)	7346 (4)	538 (2)	5266 (4)	4·86 (1)
C(552)	7363 (6)	910 (3)	6577 (6)	3·66 (2)
C(553)	8111 (6)	1963 (3)	6806 (6)	3·36 (2)
O(554)	8078 (4)	2333 (2)	8049 (4)	4·66 (1)
O(555)	6839 (5)	502 (2)	7665 (5)	6·50 (2)
O(556)	8662 (4)	2362 (2)	5702 (4)	4·74 (1)
O(661)	8426 (5)	4058 (2)	3561 (6)	7·08 (2)
C(662)	9583 (6)	4477 (3)	4823 (8)	4·74 (2)
O(663)	10306 (5)	4122 (2)	6008 (5)	6·75 (2)
O(771)	−1339 (4)	3990 (2)	−1386 (5)	5·78 (2)
C(772)	−67 (6)	4516 (3)	−81 (8)	4·40 (3)
O(773)	860 (5)	4297 (2)	889 (6)	6·85 (2)
H(4)	7895	1392	3580	8·94
H(15)	3468	539	5019	8·61

Experimental. Colorless plate-like crystals obtained by slow evaporation from a methanol/butanol solution. Crystal 0·21 × 0·06 × 0·17 mm, density not measured, four-circle Enraf–Nonius diffractometer (CAD-4 system, graphite monochromator), lattice parameters from least-squares refinement of 22 medium-angle reflections, ω–2θ scan method, $4 \le 2\theta \le 44°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}53$ Å^{-1}, $-10 \le h \le 10$, $0 \le k \le 17$, $-8 \le l \le 8$. No absorption correction. 2786 measured reflections, 1268 observed $[I \ge 2{\cdot}5\sigma(I)]$, no significant variation in intensity of standard reflection. Direct methods [*MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980)]. All 22 non-H atoms of the title compound and the six atoms of the oxalate anion found in the best figure of merit E map. A difference Fourier map revealed the six atoms of the oxalic acid molecule; as this exhibits C_i symmetry (inversion center on the C—C bond), it appeared as two half-molecules with their centers coinciding with the crystallographic centers $0,\frac{1}{2},0$ and $0,\frac{1}{2},\frac{1}{2}$. Full-matrix least-squares refinement on F using *SHELX*76 (Sheldrick, 1976). 22 H atoms located on a difference Fourier map, the other four calculated [H(31),H(32), H(61) and H(62)]. Anisotropic temperature factors (U_{ij}) for C, N and O atoms; isotropic ones for H atoms (corresponding to those of carrier atoms incremented by 0·05). $R = 0{\cdot}037$, $wR = 0{\cdot}041$ given by final least-squares cycle; $w = 1/\sigma^2(F_o) + 0{\cdot}001F^2$, $(\Delta/\sigma)_{\max} = -0{\cdot}690$ [y parameter of N(15)], $S = 0{\cdot}60$, $-0{\cdot}24 \le \Delta\rho \le 0{\cdot}25$ e Å^{-3} in final difference map. Scattering factors from *SHELX*76. Structural analysis by *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Atomic parameters are given in Table 1* while atom numbering, bond lengths and valence angles are shown on Fig. 1.

The experimental results are here compared to those of the dihydrochloride of the 4-demethyl and 4-phenyl analogs previously studied (Michel *et al.*, 1982*a*,*b*). In the 5-methyl derivative, the dihedral angle C(12)—

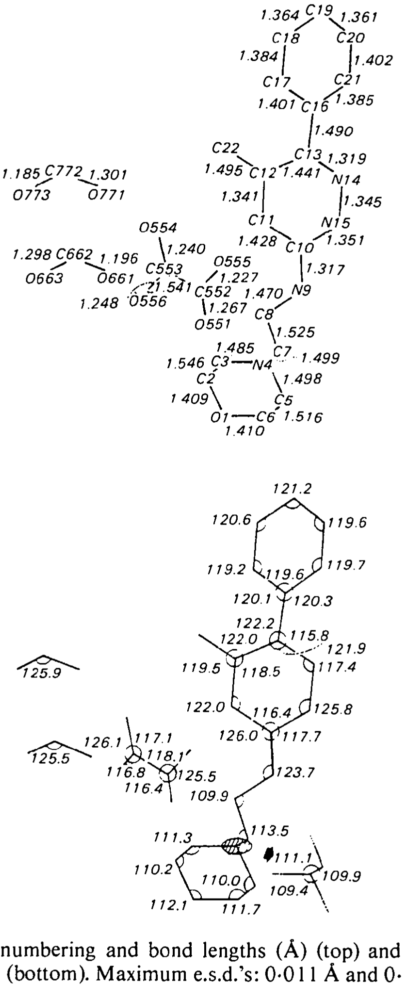

Fig. 1. Atom numbering and bond lengths (Å) (top) and valence angles (°) (bottom). Maximum e.s.d.'s: 0·011 Å and 0·7°.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, main torsion angles and intermolecular hydrogen-bond data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42361 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

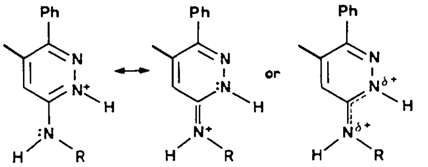
C(13)—C(16)—C(17) between the pyridazine and phenyl rings is much greater than for the other analogs (Table 2), resulting from the steric hindrance between the methyl substituent and the phenyl ring. However, the bond length C(13)—C(16): 1·490 (9) Å, is similar to the values previously observed, and corresponds to the mean value for a single bond between sp^2 C atoms. This latter observation seems to confirm the lack of conjugation between these two rings, as earlier suggested for the biphenyl (Hargreaves & Rizvi, 1962). Moreover, the comparison of the structural features of all the analogs studied, reported in Table 2, enables the following comments to be made:

– the two protonated N atoms are N(4) [N(4)—H(4): 0·983 (4) Å] and N(15) [N(15)—H(15): 1·137 (3) Å]. This latter protonation site is also observed for 6-substituted 3-aminopyridazine derivatives (Makoto, 1964; Cookson & Cheeseman, 1972). The N(4) atom is the most basic site, characterized by an sp^3 hybridization, as indicated by the bond-angle values around N(4): H(4)—N(4)—C(7) = 110·2 (5), H(4)—N(4)—C(3) = 110·2 (3), H(4)—N(4)—C(5) = 105·9 (4)°. The N(15) atom is sp^2 hybridized: H(15)—N(15)—N(14) = 116·5 (4) and H(15)—N(15)—C(10) = 117·6 (4)°.

– the N(9) atom is characterized by an sp^2 hybridization: the sum of the valence angles around N(9) is close to 360·0° (358·2°) and the dihedral angle C(8)—N(9)—C(10)—C(11) is close to 0° [–2·3 (7)°]. Moreover, the bond length N(9)—C(10): 1·317 (8) Å, is intermediate between that of a single C—N bond: 1·47 Å and that of a double C=N bond: 1·27 Å.

– the bond-length modifications compared to unsubstituted pyridazine (Almenningen, Bjornsen, Ottersen, Seip & Strand, 1977) are similar for the three analogs.

All these observations can be explained by the following resonance scheme:



– the valence angle N(14)—C(13)—C(16): 115·8 (5)° is clearly smaller than the opposite one C(12)—C(13)—C(16): 122·2 (4)° (Fig. 1). Unexpectedly, this difference of 6·4° is similar to those observed for the 4-demethyl (6·3°) and 4-phenyl (7·0°) analogs (Table 2), in spite of the more important steric hindrance of the methyl substituent on position 5 compared with that of an H atom. In contrast with those two H-substituted molecules, the torsion of the phenyl ring is here more important [–50·8 (7)°] to avoid excessive van der Waals interactions between H(17) and the methyl substituent.

Table 2. *Comparison of the values of the main structural features in the unsubstituted pyridazine* (*Almenningen et al.,* 1977), *the* 4-*demethyl and* 4-*phenyl analogs* (*Michel et al.,* 1982*a,b*), *and the title compound, with e.s.d.'s in parentheses*

	Pyridazine	4-Demethyl analog	4-Phenyl analog	5-Methyl analog
Bond distances (Å)				
C(13)—C(16)	—	1·491 (10)	1·476 (9)	1·490 (9)
N(9)—C(10)	—	1·323 (10)	1·340 (9)	1·317 (8)
C(10)—C(11)	1·39	1·423 (9)	1·453 (9)	1·428 (7)
C(11)—C(12)	1·38	1·347 (11)	1·357 (9)	1·341 (9)
C(12)—C(13)	1·39	1·429 (14)	1·416 (14)	1·441 (7)
C(13)—N(14)	1·34	1·308 (8)	1·320 (8)	1·319 (7)
N(14)—N(15)	1·33	1·364 (9)	1·366 (8)	1·345 (7)
N(15)—C(10)	1·34	1·336 (13)	1·335 (13)	1·351 (7)
Sum of bond angles around N(9) (°)	—	359·7	358·6	358·2
Bond angles (°)				
C(12)—C(13)—C(16)	—	122·3 (5)	123·3 (4)	122·2 (4)
N(14)—C(13)—C(16)	—	116·0 (4)	115·8 (3)	115·8 (5)
Torsion angles (°)				
C(8)—N(9)—C(10)—C(11)	—	179·4 (5)	–170·6 (5)	–2·3 (7)
C(12)—C(13)—C(16)—C(17)		2·9 (8)	0·2 (6)	–50·8 (7)

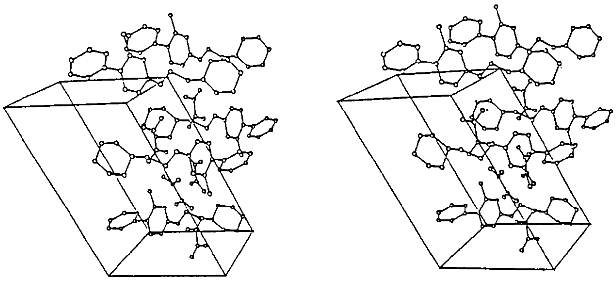


Fig. 2. Stereoview of the molecular conformation and crystal packing.

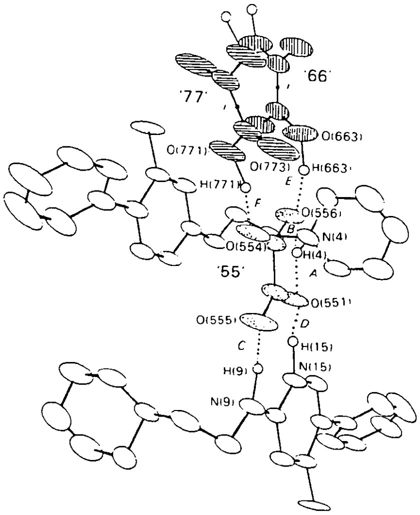


Fig. 3. Representation of the intermolecular hydrogen bonds (dotted lines) between the oxalic acid molecules ('66' and '77'), the oxalate ion ('55'), and the 5-methyl analog.

– the valence angle C(10)—N(15)—N(14) is 8·4° greater than N(15)—N(14)—C(13) (Fig. 1). The replacement of the lone pair on N(15) by an N—H$^+$ bond results in a diminution of repulsions and an opening of the angle C(10)—N(15)—N(14), according to the Gillespie (1972) theory.

The morpholino ring is in the chair form and the side-chain methylene groups 7 and 8 are in *synclinal* conformation, with N(4)—C(7)—C(8)—N(9): −80·7 (4)°.

Crystal cohesion is assumed by a dense network of intermolecular hydrogen bonds between two oxalate moieties, the protonated N(4) and N(15) and the exocyclic N(9) atoms of the 5-methyl analog. The hydrogen bonds are constituted by the alternation of oxalate ions ('55') and oxalic acid molecules ('66' and '77'), to form a zigzag chain (Figs. 2 and 3). The dihedral angles between the least-squares mean planes through the heavy atoms of the ion '55' and the molecules '66' and '77' are 63·3 and 74·1° respectively. The dihedral angle between planes of '66' and '77' is 16·3°. The terminal ions are linked to two 5-methyl analog molecules *via* four different N—H···O bonds, with the N(4), N(9) and N(15) atoms. N(4) participates in a bifurcated hydrogen bond: N(4)—H···O(551): 2·831 (5) Å and N(4)—H···O(556): 2·906 (6) Å (Fig. 3). Such a situation has been described for the dimethylammonium hydrogen oxalate (Thomas & Pramatus, 1975). As shown in Fig. 1, there are differences in the internal geometry of the oxalic acid molecule and oxalate anion. This can be explained by the sensitive response of the geometry to changes in the surrounding H atoms: the molecules '66' and '77' are planar, experimental errors excepted; the anion '55' is slightly distorted (dihedral angle between COO$^-$ planes: 2·43°).

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Structure of the *N*-Tritylalanine Anhydride:Diethyl Ether (1:1) Inclusion Complex

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Abstract. $C_{44}H_{40}N_2O_3.C_4H_{10}O$, $M_r = 718·9$, monoclinic, $P2_1$, $a = 9·092\ (3)$, $b = 24·809\ (4)$, $c = 9·135\ (3)$ Å, $\beta = 102·60\ (2)°$, $V = 2010·9\ (9)$ Å^3, $Z = 2$, $D_x = 1·187$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·70$ cm^{-1}, $F(000) = 768$, room temperature. $R = 0·090$ for 1663 observed reflections. The observed structure represents a crystalline inclusion complex of the channel type. The host lattice consists of loosely packed layers of *N*-tritylalanine anhydride molecules, and has a higher symmetry than the entire crystal. The Et_2O guest species are included between adjacent layers of the hosts. In view of the noncomplementary steric fit

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