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Structure of 6-Chloro-3-ethoxycarbonyl-2-methylquinoxaline 1,4-Dioxide

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Abstract. $C_{12}H_{11}ClN_2O_4$, $M_r = 282\cdot68$, monoclinic, $B2_1/a$, $a = 7\cdot491\,(2)$, $b = 13\cdot598\,(5)$, $c = 24\cdot547\,(7)$ Å, $\beta = 91\cdot34\,(1)°$, $Z = 8$, $D_c = 1\cdot502$ Mg m^{-3}, [λ(Mo $K\alpha$) = 0·71069 Å]. The structure was solved by direct methods and refined to an R value of 0·045 for 2179 reflections. The quinoxaline ring is planar, but the substituents deviate slightly from planarity. Some of the bond lengths differ from the other substituted quinoxalines. There are no short intermolecular distances.

Introduction. Among the biologically active quinoxalines, the 3-substituted 2-methylquinoxaline 1,4-dioxides have high antibacterial activity as potent bacteriocides. Since no accurate study on 2,3-substituted quinoxaline 1,4-dioxides has been carried out, an X-ray analysis of 6-chloro-3-ethoxycarbonyl-2-methylquinoxaline 1,4-dioxide was performed. The compound was kindly supplied by Dr Celmer of Pfizer Inc. Yellow needle-shaped crystals were grown from ethanol. A needle of 0·2 × 0·2 × 0·3 mm mounted along the a axis was used for intensity data collection on a Syntex $P2_1$ four-circle computer-controlled diffractometer with a graphite monochromator [λ(Mo $K\alpha$) = 0·71069 Å] and pulse-height analyser. Systematic absences indicated space group $B2_1/a$. This space group can be reduced to a primitive space group $P2_1/a$ by the use of transformation matrix $100/0\bar{1}0/\bar{\tfrac{1}{2}}0\bar{\tfrac{1}{2}}$. The cell dimensions in the primitive space group are $a = 7\cdot491\,(2)$, $b = 13\cdot598\,(5)$, $c = 12\cdot748\,(5)$ Å, $\beta = 105\cdot74°$ and $Z = 4$. The intensities of 4449 reflections with $2\theta < 50\cdot0°$ were scanned using the θ–2θ technique, with a variable scan rate (0·5°–29·3° min^{-1}), scan range of 2·0° and background to scan ratio of 0·8. The intensities were corrected for Lorentz and polarization effects. 2179 reflections with $I > 3\sigma(I)$ were considered observed.

The structure was solved by the direct-method program *MULTAN* (Germain, Main & Woolfson, 1971). The E map revealed all the non-H atoms. First isotropic and then anisotropic refinement of non-H atoms reduced R from 0·28 to 0·075. At this stage all the H atoms were located from the difference Fourier map. Further refinement of non-H atoms (anisotropic) and H atoms (isotropic) reduced R to a final value of 0·045. The refinement was based on F_o, the quantity minimized being $\sum w(F_o - F_c)^2$. The weighting scheme used was based on counter statistics as defined by Corfield, Doedens & Ibers (1967); the value of p was 0·04. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1964).*

Discussion. The final atomic coordinates are given in Table 1. The bond lengths and angles in the molecule are given in Tables 2 and 3 respectively. Fig. 1 shows the thermal-ellipsoid plot of the molecule. The dihedral angle between the carbon ring and the heterocyclic ring is 0·7°, which indicates that the quinoxaline part is planar. Atoms O(4) and C(10) deviate significantly [−0·101 (2) and 0·130 (2) Å] from the least-squares plane through the heterocyclic ring. The plane through C(9), O(2) and O(3) is approximately perpendicular to the heterocyclic ring plane.

Table 1. *Atomic coordinates* (×10^4) *and* B_{eq} *values for non*-H *atoms with e.s.d.'s in parentheses*

$B_{eq} = 8\pi^2(U_{11}.U_{22}.U_{33})^{1/3}$, where U_{11}, U_{22}, U_{33} are the amplitudes along the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq} (Å^2)
Cl	9121 (1)	5965 (1)	5819 (1)	4·38 (9)
O(1)	1313 (2)	6773 (1)	4560 (1)	4·20 (9)
O(2)	4305 (3)	4739 (1)	2897 (1)	4·71 (9)
O(3)	5400 (2)	6255 (1)	2768 (1)	3·90 (9)
O(4)	7438 (2)	5341 (1)	3770 (1)	4·05 (9)
N(1)	2791 (3)	6449 (1)	4365 (1)	3·00 (9)
N(4)	5979 (2)	5721 (1)	3964 (1)	2·93 (9)
C(2)	2924 (3)	6234 (1)	3832 (1)	2·95 (9)
C(2*a*)	4284 (3)	6312 (1)	4715 (1)	2·73 (9)
C(3)	4527 (3)	5855 (1)	3643 (1)	2·82 (9)
C(3*a*)	5899 (3)	5967 (1)	4511 (1)	2·68 (9)
C(5)	7414 (3)	5873 (2)	4853 (1)	3·10 (9)
C(6)	7252 (3)	6098 (1)	5389 (1)	3·20 (9)
C(7)	5647 (4)	6414 (2)	5607 (1)	3·47 (9)
C(8)	4159 (3)	6527 (1)	5270 (1)	3·32 (9)
C(9)	4731 (3)	5531 (2)	3058 (1)	3·15 (9)
C(10)	1338 (4)	6433 (2)	3469 (1)	4·05 (9)
C(11)	5745 (4)	6054 (2)	2195 (1)	4·23 (9)
C(12)	6876 (4)	6852 (3)	1996 (1)	5·60 (9)

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* Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35976 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

Cl–C(6)	1·744 (3)	C(2)–C(3)	1·396 (3)
O(1)–N(1)	1·294 (2)	C(2)–C(10)	1·493 (3)
O(2)–C(9)	1·189 (3)	C(2*a*)–C(8)	1·399 (3)
O(3)–C(9)	1·321 (3)	C(3)–C(9)	1·512 (3)
O(3)–C(11)	1·461 (3)	C(3*a*)–C(5)	1·401 (3)
O(4)–N(4)	1·308 (2)	C(3*a*)–C(2*a*)	1·401 (3)
N(1)–C(2)	1·348 (3)	C(5)–C(6)	1·358 (3)
N(1)–C(2*a*)	1·406 (3)	C(6)–C(7)	1·395 (4)
N(4)–C(3)	1·341 (3)	C(7)–C(8)	1·381 (3)
N(4)–C(3*a*)	1·387 (3)	C(11)–C(12)	1·467 (4)

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

Cl–C(6)–C(5)	118·3 (3)	N(1)–C(2*a*)–C(8)	120·0 (3)
Cl–C(6)–C(7)	119·1 (3)	N(4)–C(3)–C(2)	123·2 (2)
O(1)–N(1)–C(2)	121·1 (2)	N(4)–C(3)–C(9)	114·8 (2)
O(1)–N(1)–C(2*a*)	119·6 (2)	C(3)–N(4)–C(3*a*)	118·9 (2)
O(2)–C(9)–O(3)	126·7 (2)	N(4)–C(3*a*)–C(5)	120·3 (2)
O(2)–C(9)–C(3)	123·2 (2)	N(4)–C(3*a*)–C(2*a*)	119·0 (2)
O(3)–C(9)–C(3)	110·1 (2)	C(2)–C(3)–C(9)	122·0 (2)
C(9)–O(3)–C(11)	117·3 (2)	C(3)–C(2)–C(10)	123·2 (2)
O(3)–C(11)–C(12)	107·4 (3)	C(3*a*)–C(5)–C(6)	118·0 (3)
O(4)–N(4)–C(3)	120·8 (2)	C(5)–C(3*a*)–C(2*a*)	120·7 (3)
O(4)–N(4)–C(3*a*)	120·3 (2)	C(3*a*)–C(2*a*)–C(8)	119·7 (3)
N(1)–C(2)–C(3)	119·1 (2)	C(5)–C(6)–C(7)	122·6 (3)
N(1)–C(2)–C(10)	117·1 (2)	C(6)–C(7)–C(8)	119·7 (3)
C(2)–N(1)–C(2*a*)	119·3 (2)	C(7)–C(8)–C(2*a*)	119·2 (3)
N(1)–C(2*a*)–C(3*a*)	120·5 (2)		

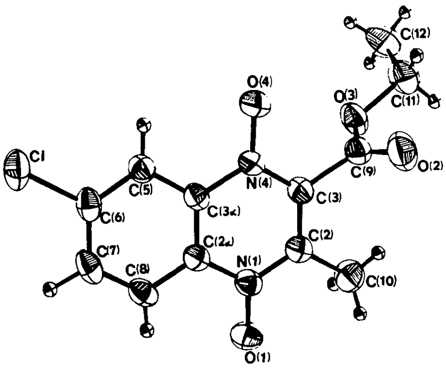

Fig. 1. Thermal-ellipsoid plot of the molecule.

The bond distances and angles agree well with those calculated by Tinland (1967). The C(2)–C(3) bond distance of 1·396 (3) Å comes much closer to the calculated value of 1·421 Å (Tinland, 1967) than to 1·480 (3) Å in 2,3-di-*tert*-butylquinoxaline (Visser & Vos, 1971), 1·522 (2) Å in 1,4-dihydro-2,3-quinoxalinedione (Svensson, 1976) and 1·515 (3) Å in 7-amino-5-chloro-2,3-dihydroxyquinoxaline (Stępień, 1977). The argument that in other compounds substitution at the 2- and 3-position of quinoxaline lengthens the C(2)–C(3) bond does not hold true in this case. The other bond distances in the heterocyclic ring agree well with those in the above compounds. The bonds C(5)–C(6) and C(7)–C(8) are shorter than other bonds in the carbon ring. This also agrees with Tinland's (1967) prediction. The N(1)–O(1) and N(4)–O(4) distances of 1·294 (2) and 1·308 (2) Å are very close to the expected values. The C–H distances have an average value of 0·92 (3) Å. The distances and angles in the side chain are normal. Fig. 2 shows the packing of the molecules in the cell. The molecules are partially stacked, the stacking distance being 3·52 Å. There are no intermolecular distances less than 3·4 Å.

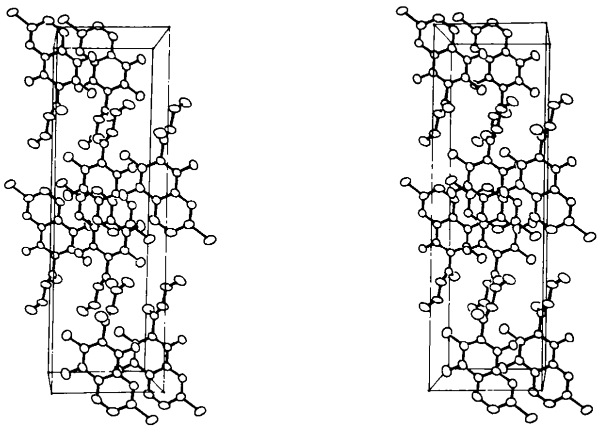

Fig. 2. Packing of the molecules in the unit cell.

The conformation of the side chain at the 3-position approximately resembles the similar part (except O replaced by N) in *N*-tetramethyltriostin *A* (Kennard, Cruse, Viswamitra, Sheldrick & Jones, 1980), a quinoxaline antibiotic which biintercalates DNA. The mode of action of 2,3-substituted quinoxaline dioxides may be that of intercalation.

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