5-Chloro-3-methyl-1,2-benzisoxazole 2-Oxide

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Abstract. $C_8H_6ClNO_2$, monoclinic, $P2_1/n$, $a = 16.329$ (4), $b = 5.668$ (1), $c = 16.957$ (5) Å, $\beta = 91.87$ (2)°, $Z = 8$, $V = 1568.6$ (7) Å³, $D_c = 1.55$ Mg m⁻³, m.p. = 406 K, μ(Mo $K\alpha$) = 0.44 mm⁻¹. The structure has been refined to $R = 0.033$ for 1365 observations measured by diffractometer and 253 parameters. The analysis confirms the structure of 1,2-benzisoxazole N-oxide for the title compound. There are no outstanding differences in the geometry of the two independent molecules. The group formed by the two fused rings is planar in both molecules.

Introduction. Recently, Boulton & Tsoungas (1980) succeeded in preparing a series of 1,2-benzisoxazole N-oxides by oxidation of o-hydroxyaryl ketoximes with lead tetraacetate. A sample of the title compound was sent to us by Dr Boulton in order to confirm the structural assignment by X-ray analysis.

Intensity data were obtained from a crystal mounted in random orientation on a Nicolet $R3$ automatic diffractometer. Reflections in the range $2 \leq 2\theta \leq 40°$ were collected with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the θ–2θ scanning technique at variable speed (from 2° min⁻¹ for very weak reflections to 29.3° min⁻¹ for the strongest ones). No appreciable decrease in the intensity of two standard reflections remeasured at intervals of 50 observations was noted. An experimental absorption correction based on the ψ-scan method (North, Phillips & Mathews, 1968) was applied. 1488 independent reflections were measured in this manner, 1365 of which with $I > 2\sigma(I)$ were considered observed and used in further calculations. The data were corrected for background, Lorentz and polarization effects and were placed on an absolute scale by statistical methods.

For all the computations use was made of the *XTL* (Syntex, 1976) structure determination system supplied with the diffractometer.

The solution was obtained by direct methods with 181 reflections with $E \geq 1.5$, and four general reflections in the starting set. The E map corresponding to

the set with the best figures of merit revealed all 24 non-hydrogen atoms of the two independent molecules.

Refinement of the positional and anisotropic thermal parameters by block-diagonal least-squares cycles led to $R = 0.06$. A subsequent difference Fourier map showed the positions of all the H atoms, whose positional parameters were refined. A fixed average temperature factor ($B = 4.5$ Å² for the H atoms of the methyl groups, and $B = 3.5$ Å² for the remaining H atoms) was assigned on the basis of the indications of two previous least-squares cycles in which they were allowed to vary. In the initial stages of the refinement

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for non-hydrogen atoms* (*e.s.d.'s in parentheses*)

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33} + 4B_{12}\cos\gamma + 4B_{13}\cos\beta + 4B_{23}\cos\alpha).$$

	x	y	z	B_{eq} (Å²)
Cl	3523 (1)	1673 (2)	10013 (1)	5.4 (1)
O(1)	5158 (1)	8170 (4)	7935 (1)	4.5 (1)
O(2)	6467 (1)	7891 (4)	7487 (1)	5.4 (1)
N	5944 (2)	6921 (5)	7898 (2)	4.0 (2)
C(1)	5927 (2)	4978 (6)	8324 (2)	3.3 (2)
C(2)	5141 (2)	4816 (6)	8665 (2)	3.1 (2)
C(3)	4705 (2)	6785 (6)	8415 (2)	3.6 (2)
C(4)	3915 (2)	7229 (7)	8638 (2)	4.5 (2)
C(5)	3570 (2)	5628 (7)	9137 (2)	4.4 (2)
C(6)	3998 (2)	3647 (6)	9390 (2)	3.7 (2)
C(7)	4790 (2)	3191 (6)	9161 (2)	3.4 (2)
C(8)	6648 (2)	3421 (7)	8408 (2)	4.6 (2)
Cl'	3223 (1)	2369 (2)	7202 (1)	4.8 (1)
O(1')	5484 (1)	8143 (3)	5462 (1)	3.9 (1)
O(2')	6838 (1)	7371 (4)	5237 (1)	4.7 (1)
N'	6211 (2)	6636 (5)	5560 (2)	3.7 (1)
C(1')	6043 (2)	4753 (6)	5983 (2)	3.1 (2)
C(2')	5200 (2)	4886 (6)	6187 (2)	2.9 (2)
C(3')	4892 (2)	6956 (6)	5857 (2)	3.1 (2)
C(4')	4088 (2)	7676 (6)	5931 (2)	3.7 (2)
C(5')	3594 (2)	6221 (6)	6350 (2)	3.8 (2)
C(6')	3893 (2)	4145 (6)	6683 (2)	3.2 (2)
C(7')	4693 (2)	3436 (6)	6614 (2)	3.2 (2)
C(8')	6674 (2)	2985 (7)	6175 (2)	4.4 (2)

Table 2. *Atomic coordinates* $(\times 10^3)$ *for hydrogen atoms (e.s.d.'s in parentheses)*

	x	y	z
H(4)	336 (2)	847 (4)	844 (1)
H(5)	303 (2)	585 (4)	929 (1)
H(7)	508 (1)	183 (4)	936 (1)
H(81)	703 (2)	394 (5)	810 (2)
H(82)	679 (2)	337 (6)	891 (2)
H(83)	652 (2)	187 (5)	819 (2)
H(4')	392 (2)	900 (4)	571 (1)
H(5')	303 (1)	661 (4)	642 (1)
H(7')	488 (1)	208 (4)	685 (1)
H(81')	714 (2)	366 (5)	639 (2)
H(82')	689 (2)	233 (5)	572 (2)
H(83')	646 (2)	182 (5)	652 (2)

unit weights were used, whereas in the final full-matrix cycles the weighting function $w = 1/(\sigma_F^2 + q^2 F_o^2)$ was applied; σ_F is the standard deviation of the observed amplitudes estimated from counting statistics, and q is a parameter, the value of which is chosen so as to maintain $w(|F_o| - |F_c|)^2$ as constant as possible over all ranges of $|F_o|$ and $\sin\theta/\lambda$ (in our case $q = 0.004$). Convergence was achieved with $R = 0.033$, error of fit $= 3.28$; a final difference Fourier map yielded no residuals greater than ± 0.15 e Å^{-3}. Refined co-ordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-hydrogen atoms are given in Table 1. The coordinates of the H atoms are reported in Table 2.* Atomic scattering factors were computed with the analytical expression of Cromer & Waber (1974).

Discussion. In the crystal there are no intermolecular contacts other than van der Waals interactions. In both independent molecules the benzisoxazole fragment is planar. The packing is such that the two independent molecules are almost parallel to each other (angle between the two average planes $= 5.9°$). The differences between corresponding bond distances and angles in the two molecules do not exceed 2σ. For this reason, in Fig. 1, where a scheme of the molecule is given together with the unconventional labelling of the atoms, the averages of the interatomic distances and angles, taken over both molecules, are reported. Since the present work is the first crystal structure analysis of a benzisoxazole N-oxide we can only compare our results with those of similar compounds. As pointed out by Boulton & Tsoungas (1980), benzisoxazole N-oxides resemble furoxans both in their mass and their ^{13}C NMR spectra. Both classes of compounds contain the same sequence of atoms,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36200 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
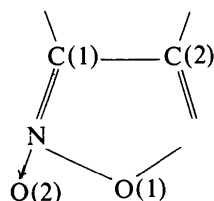
and a comparison can be of interest even though bond lengths and angles are subjected to different constraints in different derivatives. We have considered a series of disubstituted furoxans (Calleri, Ferraris & Viterbo, 1969a,b; Calleri, Chiari, Germain & Viterbo, 1973; Cameron & Freer, 1974; Chiesi Villa, Guastini, Calleri & Chiari, 1974; Calleri, Viterbo, Gaetani Manfredotti & Guastini, 1974; Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1976, 1977; Calvino, Gasco, Serafino & Viterbo, 1981) and of furoxans fused to other five- or six-membered rings (Calleri, Chiari & Viterbo, 1973; Calleri, Viterbo, Chiesi Villa & Guastini, 1975; Calleri & Viterbo, 1976; Calleri, Chawdhury & Viterbo, 1976; Calleri, Bonaccorti & Viterbo, 1977a,b).
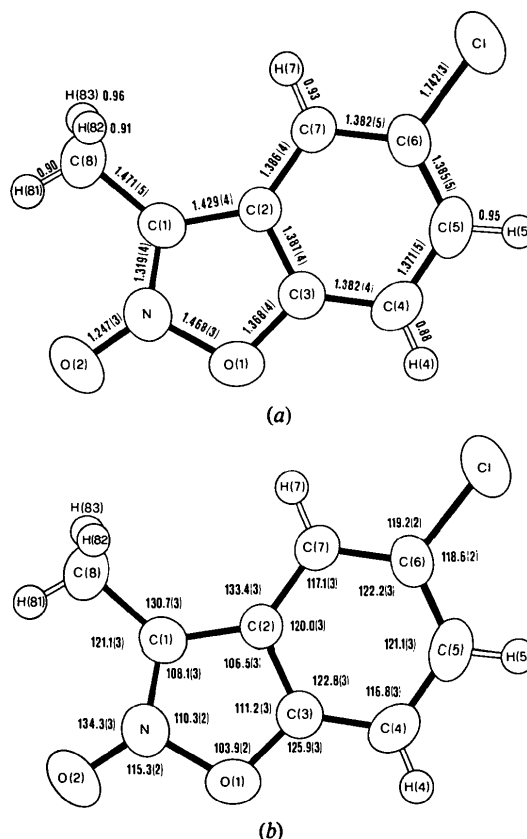

Fig. 1. Drawing of the molecule. Average distances (a) and angles (b) taken over the two independent molecules are shown (e.s.d.'s in parentheses; for bonds involving H, e.s.d. = 0.03 Å). The contours of the non-H atoms are 50% probability thermal ellipsoids as drawn by *ORTEP* II (Johnson, 1965).

There are two important similarities between the title compound and the furoxans quoted above. First of all, bond N—O(1) [1·468 (3) Å] is quite lengthened and compares with the most strained bonds found in some fused furoxans. The N—O distances in the five-membered ring of furazans (Viterbo & Serafino, 1978, and references therein) have an average value of 1·38 Å (σ of the distribution = 0·01 Å) while in furoxans the N—O distance next to the dative N → O bond ranges from 1·425 to 1·501 Å, and corresponds either to a single bond or more often to a strained single bond. A similar lengthening is found in the present N-oxide derivative when compared with the values (1·38–1·42 Å) found in the literature for other compounds containing the same isoxazole ring (Bozopulos, Kokkou & Rentzeperis, 1980, and references therein; Sax, Pletcher, Scholtz, Gerkin & Pinkus, 1971). Secondly, the N—O(2) distance [1·247 (3) Å], although longer than in all studied furoxans, falls just outside the found range (1·204–1·242 Å) and remains almost as short as in nitro groups, and shorter than in pyridine N-oxide, 1·298 Å (Wang, Blessing, Ross & Coppens, 1976).

These similarities may explain the resemblance of the mass and ^{13}C NMR spectra noted above. Some angular differences are noteworthy: for instance, the angle C(1)—N—O(1) of 110·3 (2)° in the title compound is significantly larger than the value of 107·5° obtained by averaging 14 corresponding angles in disubstituted furoxans ($\sigma = 0·9°$). On the other hand, the angle N—O(1)—C(3) of 103·9 (2)° is smaller than the corresponding average of 107·4° ($\sigma = 0·4°$) obtained for the same compounds. Other benzisoxazole N-oxides should first be analysed in order to make a more systematic comparison with the furoxan derivatives.

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