Crystal and Molecular Structure of 2-(*m*-Bromophenyl)-3-methyl-4-(trifluoroacetyl)oxazolium 5-Oxide, a Mesoionic Oxazolone

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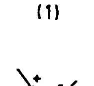
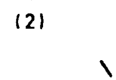
Crystals of the title compound (1) are monoclinic, space group $B2_1/c$, with $Z = 8$ in a unit cell of dimensions: $a = 21.69 \pm 0.03$, $b = 13.32 \pm 0.02$, $c = 8.55 \pm 0.01$ Å, $\beta = 85.4 \pm 0.1°$. The structure was determined by Patterson and Fourier methods from photographic data and refined by full-matrix least-squares techniques to R 0.080 for 748 independent reflections. The *m*-bromophenyl substituent is tilted 44° from the planar oxazolone ring, whereas the trifluoroacetyl group is coplanar with it. Bond angles and distances suggest that an aromatic oxazolium oxide structure is not a good representation.

THERE has been much activity in recent years in the field of mesoionic compounds.[1] Of these, the sydnones [2] and the oxazolium 5-oxides (münchnones) [3] have been studied most extensively. Although much is known about the chemistry of both these systems, investigation of their structures has been confined almost entirely to the sydnones. It therefore appeared of interest to determine the crystal structure of a münchnone. Since the parent münchnones, the simple *N*-substituted oxazolium 5-oxides, are unknown and since compounds with no 4-substituents dimerise rapidly,[4] we chose a derivative containing a stabilizing 4-acyl group, and now report the molecular structure of the title compound (1). This was readily prepared by Singh and Singh's general method,[5] *i.e.* treatment of *N*-(*m*-bromobenzoyl)sarcosine with trifluoroacetic anhydride.



(1)



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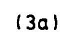

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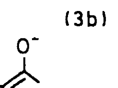

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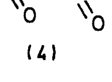

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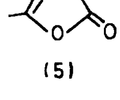

(5)

EXPERIMENTAL

N-(m-*Bromobenzoyl*)*sarcosine*.—A stirred solution of sarcosine (1.78 g) and sodium hydroxide (1.8 g) in water (10 ml) was cooled to 10 °C and *m*-bromobenzoyl chloride (4.4 g, 1 mol equiv) was added during 10 min. Stirring was continued for 4 h and the resulting solution then acidified with concentrated hydrochloric acid. The oil which separated was extracted with chloroform (3 × 5 ml), the combined extracts dried (Na_2SO_4), and solvent removed. The residual oil solidified when triturated with light petroleum; the *product* (4.3 g, 79%) had m.p. 122—122.5 °C (from aqueous ethanol), $\nu_{max.}$ (Nujol) 2 600, 1 723, and 1 599 cm^{-1} (Found: C, 44.4; H, 3.6; N, 5.0. $C_{10}H_{10}BrNO_3$ requires C, 44.15; H, 3.7; N, 5.15%).

Anhydro-2-(m-*bromophenyl*)-5-*hydroxy*-3-*methyl*-4-(*trifluoroacetyl*)*oxazolium Hydroxide* (1).—A solution of *m*-bromobenzoylsarcosine (0.54 g) in dioxan (3 ml) was treated with trifluoroacetic anhydride (0.8 ml). After 5 min light petroleum (b.p. 60—80 °C, 20 ml) was added. The precipitated yellow gum solidified in contact with fresh light petroleum; the *oxazolium oxide* (0.64 gm, 91%) crystallised from benzene–light petroleum as yellow needles suitable for *X*-ray work. It had m.p. 137 °C, $\nu_{max.}$ (Nujol) 1 787, 1 769, and 1 637; $\nu_{max.}$ ($CHCl_3$) 1 799 and 1 638 cm^{-1} (Found: C, 41.1; H, 2.05; N, 4.25. $C_{12}H_7BrF_3NO_3$ requires C, 41.05; H, 2.0; N, 4.0%).

Crystal Data.—$C_{12}H_7BrF_3NO_3$, $M = 350.1$. Monoclinic, $a = 21.69 \pm 0.03$, $b = 13.32 \pm 0.02$, $c = 8.55 \pm 0.01$ Å, $\beta = 85.4 \pm 0.1°$, $U = 2462.4$ Å^3, $D_m = 1.90$ (by displacement), $Z = 8$, $D_c = 1.98$. Space group $B2_{1/c}$ from absences: hkl with $h+l$ odd, and $00l$ with l odd (primitive cell has $a = 11.36$, $b = 13.32$, $c = 8.55$ Å, $\beta = 107.5°$, and $h0l$

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[1] M. Ohta and H. Kato, in 'Non-benzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, p. 117.

[2] F. H. C. Stewart, *Chem. Rev.*, 1964, **64**, 129.

[3] (*a*) R. Huisgen, in 'Aromaticity,' *Chem. Soc. Special Publ. No.* 21, 1967, p. 51; (*b*) G. V. Boyd, in 'Aromaticity, Pseudo-aromaticity, Anti-aromaticity,' The Israel Academy of Sciences and Humanities, Jerusalem, 1971, p. 166.

[4] G. V. Boyd and P. H. Wright, *J.C.S. Perkin I*, 1972, 914.

[5] G. Singh and S. Singh, *Tetrahedron Letters*, 1964, 3789.

absent for l odd). Ni-filtered Cu-K_α radiation, $\lambda = 1.5418$ Å, μ (Cu-K_α) = 55 cm^{-1}.

Unit-cell dimensions were obtained from calibrated zero-layer Weissenberg and precession photographs and refined on the basis of powder data. Intensity data were collected about the c axis which gave a B-centred cell which was not transformed to primitive for the structure determination. The intensities of 754 independent reflections from layers hk0—4 were estimated from multiple-film equi-inclination integrated Weissenberg photographs measured on a Nonius microdensitometer. They were placed on a common scale by comparing intensities from $0kl$ and $h0l$ reflections. Intensities were corrected for Lorentz and polarization effects but not for extinction or absorption (maximum crystal size perpendicular to rotation axis 0.3 mm.).

The bromine atomic co-ordinates were readily determined from a three-dimensional Patterson function map. A Fourier synthesis, computed from the three-dimensional set of signs determined by the bromine co-ordinates, gave an isometric array of peaks from which the complete molecule of (1) could be unambiguously defined. Least-squares refinement of the atomic co-ordinates obtained from the Fourier, with individual isotopic temperature factors and unit weights, gave R 0.097. The bromine atom was given anisotropic temperature factors and further full-matrix least-squares refinement gave a final R of 0.078. Sixteen low-intensity reflections for which $F_o > 2F_c$ or $F_c > 2F_o$ were removed in the later stages of refinement. In the final difference Fourier synthesis the maximum peak electron-density was 0.5 eÅ^{-3}. No attempt was made to locate all hydrogen atoms.

Final atomic co-ordinates and temperature factors are in Table 1. Relevant molecular bond distances and angles are listed in Tables 2 and 3; the atom numbering is shown in the Figure. Structure factor data are listed in Supplementary Publication No. SUP 21353 (5 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates (× 10^4) and thermal parameters (× 10^3), with standard deviations in parentheses

	x/a	y/b	z/c	B/Å^2*
Br	5 992(1)	2 103(2)	5 157(4)	
O(1)	4 270(6)	1 869(9)	198(20)	1 782(296)
C(2)	4 199(9)	1 052(15)	996(33)	1 940(424)
N(3)	3 641(7)	679(11)	732(25)	1 342(331)
C(4)	3 316(8)	1 278(13)	354(31)	1 345(490)
C(5)	3 692(9)	2 073(16)	665(34)	2 368(432)
O(6)	3 684(7)	2 812(12)	1 534(23)	3 335(348)
C(7)	2 694(9)	1 107(14)	1 023(34)	1 895(429)
O(8)	2 356(7)	462(11)	478(25)	3 493(372)
C(9)	2 439(10)	1 722(16)	2 307(37)	2 418(468)
F(10)	2 803(6)	1 741(10)	3 535(21)	4 141(334)
F(11)	1 896(6)	1 352(10)	2 867(21)	4 194(342)
F(12)	2 336(6)	2 677(9)	1 947(20)	3 528(321)
C(13)	3 382(10)	157(16)	1 677(35)	2 670(491)
C(14)	4 731(8)	699(14)	2 157(33)	1 857(438)
C(15)	5 038(9)	1 422(14)	2 888(33)	1 925(486)
C(16)	5 563(10)	1 122(16)	3 904(36)	2 214(434)
C(17)	5 781(10)	111(17)	4 115(37)	2 207(462)
C(18)	5 429(10)	596(16)	2 993(37)	3 058(510)
C(19)	4 916(9)	317(15)	2 073(34)	2 941(512)

* Anisotropic temperature factors of the form: exp − $[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]$, with parameters

B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
15(1)	45(1)	69(19)	−5(1)	−9(1)	−17(3)

All calculations were performed on the London University CDC 6400 computer with a standard set of crystallographic programmes. Atomic scattering factors for neutral atoms were taken from ref. 6.

TABLE 2

Bonded distances (Å), with standard deviations in parentheses

C(16)–Br	1.887(24)	N(3)–C(4)	1.376(28)
C(16)–C(15)	1.433(31)	O(1)–C(5)	1.428(24)
C(15)–C(14)	1.302(28)	C(4)–C(5)	1.374(27)
C(14)–C(19)	1.415(28)	C(5)–O(6)	1.235(27)
C(19)–C(18)	1.360(32)	C(4)–C(7)	1.440(27)
C(18)–C(17)	1.503(35)	C(7)–O(8)	1.242(25)
C(17)–C(16)	1.433(30)	C(7)–C(9)	1.446(35)
C(14)–C(2)	1.538(31)	C(9)–F(12)	1.330(24)
C(2)–N(3)	1.310(23)	C(9)–F(11)	1.331(24)
C(2)–O(1)	1.299(25)	C(9)–F(10)	1.363(29)
N(3)–C(13)	1.510(29)		

Intramolecular contacts <3.4 Å

C(13) ··· O(8)	2.892(29)
C(15) ··· O(1)	2.795(29)

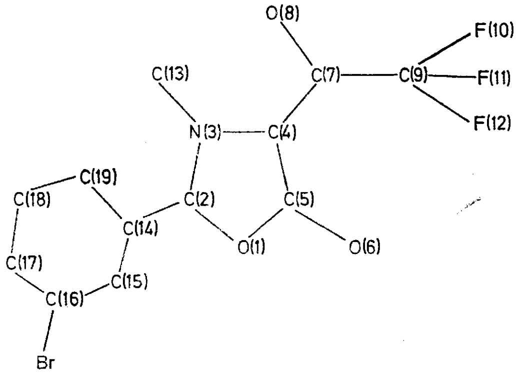
TABLE 3

Interbond angles (deg.), with standard deviations in parentheses

Br–C(16)–C(15)	118.9(1.6)	C(4)–N(3)–C(13)	126.5(1.6)
Br–C(16)–C(17)	116.1(1.8)	O(1)–C(5)–O(6)	115.6(1.7)
C(15)–C(16)–C(17)	124.9(2.1)	O(1)–C(5)–C(4)	105.3(1.9)
C(16)–C(15)–C(14)	115.8(1.9)	O(6)–C(5)–C(4)	138.7(2.1)
C(15)–C(14)–C(19)	126.6(2.0)	N(3)–C(4)–C(5)	107.2(1.7)
C(14)–C(19)–C(18)	117.0(2.1)	C(5)–C(4)–C(7)	126.6(2.0)
C(19)–C(18)–C(17)	123.0(2.1)	N(3)–C(4)–C(7)	126.2(1.8)
C(18)–C(17)–C(16)	111.6(2.2)	C(4)–C(7)–O(8)	121.4(2.2)
C(15)–C(14)–C(2)	114.4(1.8)	C(4)–C(7)–C(9)	120.1(1.9)
C(19)–C(14)–C(2)	117.5(2.0)	C(8)–C(7)–C(9)	118.4(1.9)
C(14)–C(2)–O(1)	118.7(1.6)	C(7)–C(9)–F(10)	112.7(1.9)
C(14)–C(2)–N(3)	129.1(1.9)	C(7)–C(9)–F(11)	115.2(2.5)
O(1)–C(2)–N(3)	112.1(1.9)	C(7)–C(9)–F(12)	109.7(1.9)
C(2)–O(1)–C(5)	107.0(1.5)	F(12)–C(9)–F(11)	106.2(1.7)
C(2)–N(3)–C(13)	124.5(1.9)	F(12)–C(9)–F(10)	106.3(2.3)
C(2)–N(3)–C(4)	108.2(1.7)	F(11)–C(9)–F(10)	106.2(1.9)

Dihedral angles between:

benzene and oxazolone rings	44.2(2.8)
oxazolone ring and plane of O(8), C(7), and C(9)	10.8(1.5)



Atom numbering system for the mesoionic oxazolone (1)

DISCUSSION

The central problem in the chemistry of mesoionic compounds is the problem of their aromaticity, *i.e.*

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[6] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

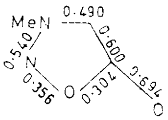
whether a münchnone, for example, is adequately represented by the betaine structure (2), which contains the aromatic 6π-oxazolium cation. Huisgen and coworkers have shown that these compounds can react as 1,3-dipoles (3a and b) [7] and even as valence-tautomeric acylaminoketenes (4).[8] The extent to which the aromatic form contributes to the ground states of these molecules is, however, debatable although i.r. spectroscopy [9] indicates some polarization of the carbonyl group as required by formula (2). In the case of 4-acylmünchnones, such as compound (1), the exocyclic carbonyl group would be expected to stabilise the system by delocalising the negative charge [*cf.* (5)] and, indeed, such compounds exhibit an abnormally low exo- and a high endo-cyclic carbonyl stretching frequency in their i.r. spectra.[4]

The molecular structure determined for the title compound (Figure) does not indicate what most chemists would regard as aromatic character. The angle of twist (44.2°) (Table 3) between the planar oxazolone ring and the bromophenyl group and the resulting long C(2)–C(14) bond indicate that there is little conjugation over the two rings. This means that the aryl substituent perturbs the mesoionic system only slightly; the trifluoroacetyl group, on the other hand, is nearly co-planar with the oxazolone ring, allowing overlap of the *p*-orbitals of the exocyclic carbonyl group with those of the ring atoms. There is a striking deformation of the bond angles round C(5), the angle O(6)–C(5)–C(4) being 138.7°. Similar deformations have been observed in the structures of 3-*p*-bromophenylsydnone,[10] 4,4′-dichloro-3,3′-ethylenebissydnone,[11] and 3,3′-ethylenebissydnone,[11] in which the corresponding angles are 135.7, 136.0, and 136.5°.

The distance (2.89 Å) between the *N*-methyl carbon atom C(13) and O(8) indicates possible hydrogen bonding, which, together with the possibility of extended conjugation, might account for the very slight elongation of the carbonyl bond of the trifluoroacetyl group. The C(4)–C(7) distance (1.44 Å) is somewhat less than that expected of a pure single-bond between two sp^2-hybridised carbon atoms, indicating some contribution from canonical form (5). It is not thought that the presence of the trifluoromethyl group would distort the bonds in its vicinity, since the fluorine atoms in ammonium trifluoroacetate do not affect even the adjacent carbon–carbon bond.[12] The distances within the oxazolone ring are short, indicating considerable double-bond character; a striking exception is the oxygen–carbonyl bond O(1)–C(5) (1.43 Å), which, like the corresponding bonds in sydnones (1.41—1.42 Å),[10,11] is unexpectedly long; comparable bonds in unsaturated γ-lactones,[13] a phthalide,[14] and isoxazolones [15] vary from 1.35 to 1.39 Å. The short C(5)–O(6) carbonyl distance of 1.23 Å, on the other hand, is like those (1.20—1.24 Å) found [13-15] in γ-lactones and, again, is similar to values (1.20—1.215 Å) determined for sydnones.

In the case of sydnones, it has been argued [11] that the normal carbonyl bond-length gives no support for the contribution of aromatic oxide forms and that the deformation round the carbonyl group, together with the abnormally great endocyclic carbon–oxygen distance, indicates an unusually weak σ-bond, though π-overlap may persist. The bond-lengths and -angles in the oxazolone derivative are similar to those of sydnones and the two types of compound clearly have comparable electronic structures, although the presence of the stabilising acyl substituent in our compound must cause some perturbation. The structure of the oxazolone indicates extensive but not full conjugation over the ring and it appears that the system does not possess much aromatic character.

These conclusions are in general agreement with the results of self-consistent $\omega\beta$-calculations [16] on 3-methylsydnone (6), 3-methylmünchnone (7), and 4-formyl-3-methylmünchnone (8).* The bond-orders shown in the formulae indicate the single-bond character of the endocyclic carbonyl–oxygen bond in all three molecules, the double-bond character of the lactone carbonyl groups, and they show the perturbing effect of the 4-acyl substituent.



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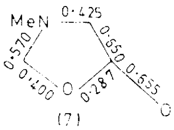

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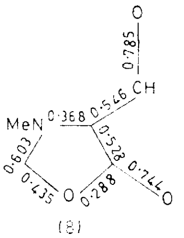

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* The Coulomb integrals used were: $\alpha_{\ddot{\mathrm{N}}\mathrm{Me}} = \alpha_{\mathrm{C}} + 1.5\beta$, $\alpha_{\dot{\mathrm{N}}} = \alpha_{\mathrm{C}} + 0.5\beta$, $\alpha_{\ddot{\mathrm{O}}} = \alpha_{\mathrm{C}} + 2.0\beta$, and $\alpha_{\dot{\mathrm{O}}} = \alpha_{\mathrm{C}} + 1.0\beta$.

[7] E. Funke, R. Huisgen, and F. C. Schaefer, *Chem. Ber.*, 1971, **104**, 1550, and references therein.

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[16] G. V. Boyd and N. Singer, *J. Chem. Soc.* (*B*), 1966, 1017.