Crystal Structure of Methyl 5-Bromo-2-oxo-Δ^2-1,3,4-oxadiazolin-3-carboxylate

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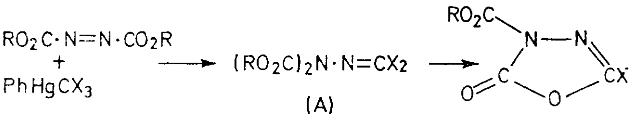
Summary An *X*-ray crystal structure determination of the title compound has confirmed the cyclic structure and has demonstrated a strong charge-transfer interaction between the carbonyl oxygen and the bromine atoms of adjacent molecules; the medium-dependent i.r. spectra of this molecule are discussed in the light of this finding.

THE reaction of phenyl(trihalogenomethyl)mercury compounds with dialkyl azodicarboxylates gives hydrazonodihalogenomethanes (A) as final products.[1] Pyrolysis of the latter gives in high yield products believed to be alkyl 5-halogeno-2-oxo-Δ^2-1,3,4-oxadiazoline-3-carboxylates, (I)—(IV).

The unusually high i.r. stretching frequencies of the ring C=O groups and the variation with medium of one of the bands attributable to a C=O vibration (Table) were of special interest. To confirm the proposed cyclic structure of (I)—(IV) and to obtain structural information which



(I) R = Me; X = Br
(II) R = Me; X = Cl
(III) R = Et; X = Br
(IV) R = Et; X = Cl

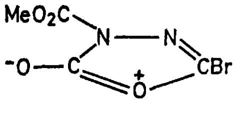
might serve to explain the spectroscopic properties, an *X*-ray crystal structure analysis of (I) was undertaken.

Single crystals of (I)(orthorhombic) were obtained from chloroform (m.p. 119—120°). Crystal data: $a = 9{\cdot}12(6)$, $b = 4{\cdot}82(3)$, $c = 16{\cdot}04(8)$ Å, $D_m = 2{\cdot}09$ g cm^{-3}, $Z = 4$, $D_c = 2{\cdot}10$ g cm^{-3}, space group $Pca2_1$, Mo-K_α radiation 664 diffractometer intensities. With anisotropic temperature factors for the bromine and isotropic values for all other atoms, *R* is currently 13·6%. The Figure shows that the structure is indeed that of a 1,3,4-oxadiazolin-5-one. The ester group is disordered with respect to rotation about the N(2)–C(3) bond. It is not unusual in solids of molecules containing both electron-donating and electron-accepting atoms to observe strong charge-transfer (CT) interaction between neighbouring molecules. In this case the CT interaction is very strong. The distance between the Br in one molecule and O(2) in the molecule related by the *c* glide is 2·796(4) Å, 0·55 Å less than the sum of the van der Waals radii (3·35 Å) and also much shorter than the O–Br distances seen in other cases of CT interactions, *e.g.* 3·16Å in *N*-(*p*-bromophenyl)sydnone;[2] 3·27 Å in oxalyl bromide.[3] The distance is comparable to that found in the addition complex of methanol and Br_2 (2·80 Å)[4] or of acetone and Br_2 (2·82 Å).[5] The effect of this strong CT interaction can be seen in the rest of the structure. The C(2)–O(2) distance (1·29 Å) is longer than that (1·19—1·22 Å) in similar systems.[6] The C(1)–Br distance (1·997 Å) is longer than expected, with concomitant shortening of the C(1)–N(1) double bond. In addition, in order for O(2) to interact with an adjacent Br, it is tipped out of the plane of the five membered ring by 0·36 Å.

Solvent effect on carbonyl frequencies of (I) (*cm*$^{-1}$)

CCl_4	$CHCl_3$		KBr or Nujol	
1870s 1860s	1870s 1860s	1813w	1870w 1850w	1820

The existence of this strong CT interaction in (I) in the solid state suggests that the molecule is highly polarizable, with a significant contribution from (V) in a polar medium. Such a contribution would diminish the C=O bond order and decrease the C=O frequency. Thus the bands at 1813—1820 cm^{-1} are probably due to the C=O group undergoing this CT interaction. In the solid state, such intermolecular CT predominates; hence the band at 1820 cm^{-1} is very intense. In dilute solution, however, such intermolecular interactions are much diminished.[7] In a non-polar solvent (CCl_4) thus there are no strong interactions between molecules of (I) nor between (I) and solvent molecules. Hence no band in the 1813—1820 cm^{-1} region is observed. In a solvent of moderate polarity ($CHCl_3$), some interaction occurs, and a weak band at 1813 cm^{-1} is seen. In solution the absorption due to the unperturbed C=O group is intense; in the solid state it is, as expected, weak.



(V)

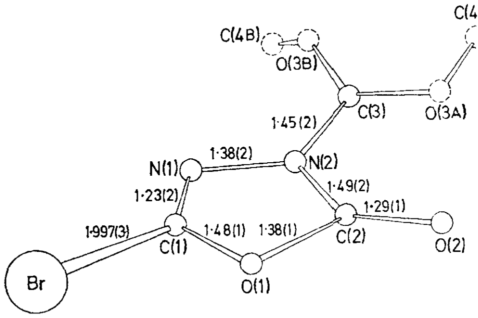


Figure. *Bond distances* (Å) *and atom numbering in structure* (I).

By this new route, 5-substituted alkyl 2-oxo-Δ^2-1,3,4-oxadiazoline-3-carboxylates are readily accessible. Their reactive *C*-halogen linkage provides entry to other derivatives. For instance, the C–Br bond of (I) may be reduced to C–H by tri-n-butyltin hydride. A large number of Δ^2-1,3,4-oxadiazolin-5-ones have tuberculostatic activity;[8] thus useful application of this new chemistry may be possible.

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