

Table 3. Equations of mean planes and deviations (Å) of relevant atoms from the planes

$X, Y,$ and Z are in Å referred to orthogonal axes $a, b',$ and c^* .

Plane (1): C(1)–C(6)							
$-0.204X - 0.730Y - 0.652Z + 3.697 = 0$							
C(1)	-0.001	C(2)	0.015	C(3)	-0.018	C(4)	0.009
C(5)	0.019	C(6)	-0.021	C(7)	-0.023	C(8)	0.113
C(9)	0.058	C(10)	-0.055	C(11)	-0.065	C(12)	-1.420
C(13)	-1.403	C(14)	-1.621	C(15)	-2.557		
Plane (2): C(3), C(11), C(12), O(3)							
$0.080X + 0.650Y - 0.756Z + 6.484 = 0$							
C(3)	0.002	C(11)	-0.006	C(12)	0.002	O(3)	0.002
Plane (3): C(1), C(7), O(1), O(2)							
$-0.759X + 0.611Y - 0.226Z + 1.461 = 0$							
C(1)	0.005	C(7)	-0.023	O(1)	0.009	O(2)	0.010
Angles between planes							
				Plane(1)–plane(2)	89.9°		
				Plane(1)–plane(3)	81.7		

acid with the more bulky trimethylbenzoic acid group one would expect an even larger value; however, this particular angle is found to be 119.5 (3)°. This does not preclude the possibility that this angle may increase in the racemization process in solution.

The carboxylic acid group has an unusual feature in that both the C–O lengths are equal, within the limits of error. This is possibly due to disorder, where some of the molecules have crystallized with the acid group rotated through approximately 180° with respect to the other molecules; the elongation of the oxygen thermal ellipsoids in the direction of rotation thus possibly results from non-coincidence of the two orientations. As the molecules form hydrogen-bonded dimers the orientation of one half of the dimer necessarily fixes the orientation of the other half. The O...O distance is 2.642 Å.

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2-(3'-Bromophenyl)-4-acetoxy-6H-1,3-oxazin-6-one

BY HERMAN L. AMMON

Department of Chemistry, University of Maryland College Park, Maryland 20742, U.S.A.

AND ARNOLD J. GORDON* AND RICHARD L. EHRENKAUFER†

Department of Chemistry, Catholic University of America, Washington, D.C. 20017, U.S.A.

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Abstract. C₁₂H₈NO₄Br; M.W. 310.12; monoclinic, space group, $P2_1/c$; $a = 8.490$ (2), $b = 16.797$ (2), $c = 8.381$ (1) Å, $\beta = 95.09$ (1)°; $D_m = 1.716$ g cm⁻³; $D_c = 1.732$ g cm⁻³ for $Z = 4$. Mo $K\alpha$ diffractometer data. $R = 0.035$. The identification of the N and O atoms in

the oxazinone ring is described. Bond lengths show evidence for an α -pyrone type of resonance interaction.

Introduction. A preliminary X-ray diffraction study of the 2-phenyl derivative *Ia* showed that the compound crystallized in the orthorhombic space group $Fdd2$. Since a phase solution in this acentric space group could be difficult, we turned our attention to the *m*-bromophenyl derivative, *Ib*, which crystallized from

* Present address: Pfizer Pharmaceuticals, 235 E. 42nd St. N.Y., New York 10017, U.S.A.

† Present address: Brookhaven National Laboratory, Dept. of Chemistry, Upton, N.Y. 11973, U.S.A.

Et₂O in the monoclinic space group, $P2_1/c$. A colourless needle, *ca.* 0.3 mm in cross-section, was cut to a length of 0.4 mm and mounted in a thin-walled capillary parallel to the needle axis. (The capillary was necessary because of the compound's sensitivity to H₂O.) A Picker FACS-I diffractometer and monochromatic Mo radiation (graphite monochromator, $K\alpha\lambda=0.71069$ Å) were used for the lattice parameter and intensity measurements (\mathbf{a}^* was parallel to the instrument's φ axis). The cell constants given in the abstract were obtained by a least-squares fit to 14 2θ 's obtained from manually centered values at $\pm 2\theta$ (av. $|2\theta_o - 2\theta_c| = 0.005^\circ$). The intensity data were measured with the $2\theta-\theta$ method at a 2θ scan rate of $0.5^\circ \text{ min}^{-1}$ and with two 40 sec backgrounds. Three standards were measured at 60 reflexion intervals. 2476 reflexions were collected to a 2θ maximum of 50° . There were 2102 unique data, 1403 of which were more than 3σ above background and coded 'observed'.

The structure was solved in an automatic way with the X-RAY System's (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) direct methods subprogram PHASE. Three origin phases were pyramided to 607 phases (306+, 301-), and a subsequent E map revealed the 18 nonhydrogen atoms. The structure refinement was carried out by full-matrix least-squares minimization of the function $\sum [1/\sigma(F)]^2 [F_o - F_c]^2$.

Hydrogen atoms were located from a difference map. The C, N, O and Br atoms were refined with anisotropic temperature factors, the H's with isotropic terms. Corrections were applied for Br dispersion and for isotropic secondary extinction ($r^* = 0.022(2) e^{-2}$; equation 22 in Larson, 1970).† The atomic parameters are listed in Table 1 and an ORTEP drawing including

bond lengths and angles is given in Fig. 1. Atomic scattering factors: C, N, O (Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal, 1955); Br (*International Tables for X-ray Crystallography*, 1968); H (Stewart, Davidson & Simpson, 1965). The final values of R ($\sum |F_o - F_c| / \sum F_o$) and weighted R ($[\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$, $w = [1/\sigma(F)]^2$) are 0.035 and 0.038.

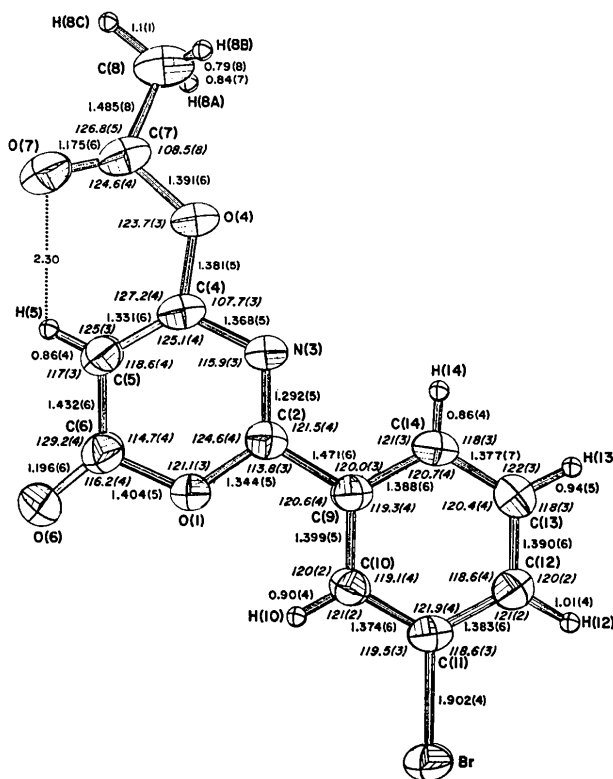


Fig. 1. Bond lengths (Å) and angles ($^\circ$) superimposed on an ORTEP drawing with 45% probability ellipsoids. (0.1 Å spheres for H). The viewing direction is normal to the oxazone ring.

† A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30177. Copies of this table may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates, temperature factors (\AA^2) and estimated standard deviations (in parentheses)

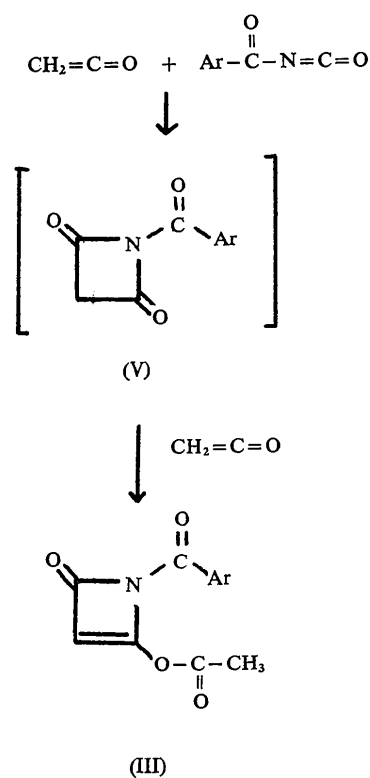
The form of the U 's is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	-0.2648 (5)	-0.0196 (2)	0.5251 (5)	0.043 (2)	0.044 (2)	0.038 (2)	0.002 (2)	0.002 (2)	-0.001 (2)
C(4)	-0.4339 (5)	-0.0915 (3)	0.3597 (5)	0.040 (2)	0.053 (3)	0.038 (2)	0.004 (2)	-0.003 (2)	-0.010 (2)
C(5)	-0.4366 (6)	-0.1528 (3)	0.4600 (6)	0.053 (3)	0.042 (3)	0.052 (2)	-0.004 (2)	-0.010 (2)	-0.004 (2)
C(6)	-0.3473 (5)	-0.1473 (3)	0.6128 (6)	0.048 (3)	0.047 (3)	0.057 (3)	-0.004 (2)	-0.009 (2)	0.002 (2)
C(7)	-0.6118 (5)	-0.1438 (3)	0.1392 (6)	0.048 (3)	0.063 (3)	0.048 (3)	0.000 (2)	-0.007 (2)	-0.017 (2)
C(8)	-0.657 (1)	-0.1217 (6)	-0.0302 (7)	0.089 (5)	0.095 (5)	0.051 (3)	-0.008 (5)	-0.020 (3)	-0.006 (4)
C(9)	-0.1633 (4)	0.0493 (2)	0.5695 (4)	0.041 (2)	0.043 (2)	0.036 (2)	0.001 (2)	-0.002 (2)	-0.002 (2)
C(10)	-0.0708 (5)	0.0511 (3)	0.7162 (5)	0.049 (2)	0.040 (2)	0.036 (2)	0.004 (2)	-0.002 (2)	0.001 (2)
C(11)	0.0240 (5)	0.1159 (3)	0.7531 (4)	0.043 (2)	0.050 (2)	0.036 (2)	0.002 (2)	-0.003 (2)	-0.006 (2)
C(12)	0.0310 (5)	0.1797 (3)	0.6494 (5)	0.050 (3)	0.046 (2)	0.044 (2)	-0.006 (2)	0.001 (2)	-0.003 (2)
C(13)	-0.0616 (6)	0.1775 (3)	0.5041 (6)	0.069 (3)	0.049 (3)	0.047 (3)	-0.007 (3)	-0.001 (2)	0.007 (2)
C(14)	-0.1585 (5)	0.1134 (3)	0.4655 (5)	0.055 (3)	0.058 (3)	0.036 (2)	-0.003 (2)	-0.008 (2)	0.003 (2)
O(1)	-0.2613 (3)	-0.0764 (2)	0.6383 (3)	0.056 (2)	0.043 (2)	0.041 (2)	-0.006 (1)	-0.011 (1)	0.003 (1)
O(4)	-0.5120 (4)	-0.0852 (2)	0.2085 (3)	0.061 (2)	0.063 (2)	0.040 (2)	-0.009 (2)	-0.014 (1)	-0.003 (1)
O(6)	-0.3363 (4)	-0.1944 (2)	0.7204 (4)	0.086 (2)	0.060 (2)	0.064 (2)	-0.019 (2)	-0.026 (2)	0.023 (2)
O(7)	-0.6536 (4)	-0.2001 (2)	0.2067 (4)	0.071 (2)	0.065 (2)	0.064 (2)	-0.013 (2)	-0.018 (2)	-0.009 (2)
N	-0.3477 (4)	-0.0233 (2)	0.3884 (4)	0.047 (2)	0.048 (2)	0.034 (2)	-0.003 (2)	-0.005 (2)	-0.002 (2)
Br	0.14491 (6)	0.12052 (3)	0.95515 (5)	0.0634 (3)	0.0593 (3)	0.0462 (3)	-0.0024 (3)	-0.0183 (2)	-0.0031 (2)

Table 1 (cont.)

	x	y	z	U
H(5)	-0.492 (5)	-0.195 (3)	0.442 (5)	0.05 (1)
H(8A)	-0.567 (8)	-0.120 (4)	-0.065 (8)	0.11 (3)
H(8B)	-0.693 (9)	-0.078 (5)	-0.036 (9)	0.12 (3)
H(8C)	-0.74 (1)	-0.162 (6)	-0.06 (1)	0.20 (4)
H(10)	-0.079 (4)	0.111 (2)	0.787 (5)	0.04 (1)
H(12)	0.109 (5)	0.225 (3)	0.672 (5)	0.06 (1)
H(13)	-0.057 (5)	0.222 (3)	0.435 (6)	0.07 (1)
H(14)	-0.220 (5)	0.116 (3)	0.378 (6)	0.05 (1)

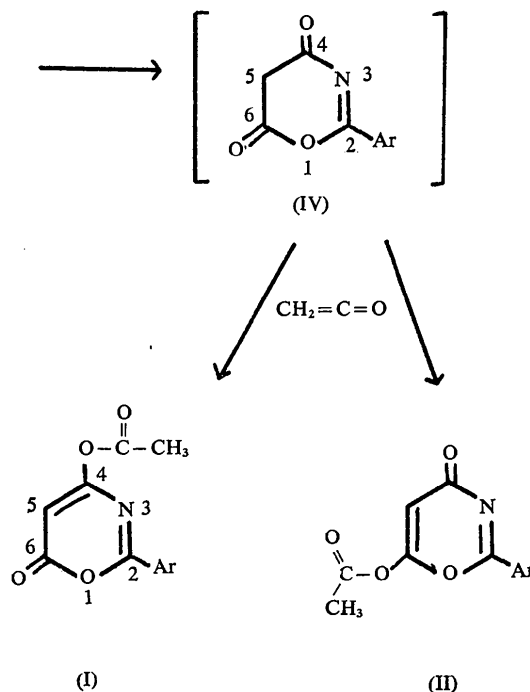
Discussion. The reaction of an excess of ketene with benzoylisocyanate gave a pale yellow 2:1 ketene-benzoylisocyanate adduct (Ehrenkauf, 1972). An extensive spectroscopic investigation of the product, as well as chemical degradation studies, narrowed the structural possibilities to I, II and III. The reaction mechanism leading to I or II might involve a [4+2] cycloaddition to IV followed by enolization at C(4) or C(6) and reaction with a second ketene molecule. On the other hand, reaction leading to III has precedence (Mundlos & Graf, 1964) and would probably occur *via* a [2+2] cycloaddition to V, again followed by enol acetate formation. The spectroscopic data suggested but could not confirm Ia as the most likely of the three possibilities. Therefore, an X-ray crystallographic analysis of Ib, prepared from *m*-bromobenzoylisocyanate and excess ketene, was carried out. Except for minor changes due to the Br substituent, the spectroscopic and chemical properties of Ia and Ib were the same.



The original *E* map showed that the adduct had the oxazinone structure, I or II. These two possibilities are quite similar, differing only in the locations of the O and N, and the N double bond in the heterocyclic ring. That is, the two compounds are enol acetate tautomers at C(4) and C(6). A preliminary structure refinement with isotropic temperature factors, in which N form factors were assigned to both N and O, was used to determine these atomic identities. The assignment of atom types was based on the temperature factor magnitudes: the smaller t.f. for the 1-position atom (structure I) was associated with O whereas the normal t.f. for the 3-position atom was associated with N.

The O *vs.* N assignment was again checked during the latter stages of the least-squares structure refinement. The calculations, which included unit weights, anisotropic t.f.'s for C, N, O and Br, isotropic t.f.'s for H, Br dispersion and isotropic secondary extinction corrections, gave *R* values of 0.036 and 0.042 for the assignments corresponding to structures I and II, respectively. Hamilton's (1965) *R* index significance test indicated that the structures were different at the 99.5% level.

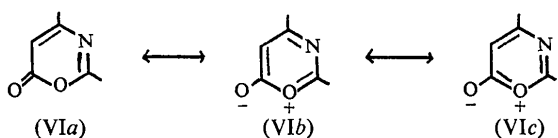
Bond distances in the oxazinone ring indicate that structures VIb and VIc make a contribution to the resonance hybrid. These distances are in consonance with the observed direction of enol acetate formation in IV yielding an α -pyrone analog (VIa or I) rather than a cross-conjugated γ -pyrone analog (II). The ring



a: Ar = phenyl

b: Ar = 3'-bromophenyl

O(1)–C(2) bond shortening and concomitant C=N lengthening from normal values (compare O(1)–C(2) with O(1)–C(6); C=N=1.28 Å) are probably responsible for the extremely low $\bar{\nu}_{C=O}$ in the infrared (1550 cm^{-1}) and Raman (1548 cm^{-1}) spectra. The acetoxy, oxazinone and phenyl groups are individually coplanar; the angles between the acetoxy–oxazinone and phenyl–oxazinone planes are 8.40 and 2.9°, respectively. The conformation of the acetoxy group [C(7) and N(3) are *anti* with respect to the C(4)–O(4) bond] is undoubtedly influenced by a stabilizing O(7)···H(5) interaction (2.30 Å, Fig. 1). The conformation of the *m*-bromophenyl moiety is set by intermolecular packing interactions which prevent the Br from trading places with H(13) (see Fig. 1). The unequal pairs of exocyclic angles at C(2), C(4) and C(6) in the oxazinone ring arise from the different electronegativities of the attached atoms and, in the case of C(2) and C(4), to participation in double bonds.



This work establishes unequivocally for the first time the constitution of a 1,3-oxazin-6-one system. In a recent paper (Martin, Burpitt, Gott, Harris & Meen, 1971) it was claimed that benzoylisocyanate and ketene reacted to give a compound whose chemical and spectral properties were nearly identical to those

reported here for Ia. However, the authors gave the structure as II, an assignment which must now be considered erroneous.

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The Crystal Structure of Ammonium Hexachloroantimonate(V) Monohydrate and the Crystal Data of the Anhydrous Compound

BY H. HENKE, E. BUSCHMANN AND H. BÄRNIGHAUSEN

Institut für Anorganische Chemie der Universität Karlsruhe (TH), 75 Karlsruhe, Englerstrasse 11, Germany (BRD)

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Abstract. $\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$ crystallizes in the orthorhombic space group *Immm* (No. 71) with the lattice dimensions $a=7.113$ (2), $b=9.049$ (3), and $c=8.049$ (3) Å. The unit cell contains 2 formula units giving a density D_x of 2.375 g cm^{-3} . The structure is built up from SbCl_6^- octahedra and $(\text{NH}_4 \cdot \text{OH}_2)^+$ groups which involve hydrogen bonding. Single-crystal photographs of NH_4SbCl_6 show monoclinic symmetry, possible space groups *Cc* (No. 9) or *C2/c* (No. 15). The lattice parameters are $a=12.062$ (6), $b=6.310$ (3), $c=15.220$ (6) Å, and $\beta=129.11$ (9)°. With 4

formula units per cell the density D_x is 2.605 g cm^{-3} .

Structure determination of $\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$. Suitable crystals of $\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$ were grown from aqueous solutions of the acid HSbCl_6 and an excess of NH_4Cl (Weinland & Feige, 1903). The 'octahedral' crystal that we actually used was bounded by the faces {110} and {011}. The average edge length was 0.4 mm. Intensity data for all 429 unique reflexions in the range $4^\circ < 2\theta < 60^\circ$ were collected on an automatic Picker-FACSI diffractometer. Using monochromatic $\text{Mo K}\alpha$ radiation