Formation and Crystal Structure of 3-(4-Bromophenyl)-2-hydroxyimino-6,7-dihydro-4(5*H*)-benzofuranone. Michael Addition of Cyclohexane-1,3-dione to 4-Bromo-ω-nitrostyrene

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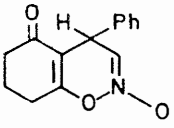
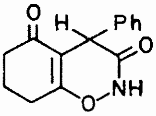
Summary The structure of the abnormal Michael adduct named in the title has been established by spectra and *X*-ray crystallography.

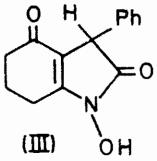
MICHAEL ADDITION of cyclohexane-1,3-dione to ω-nitrostyrene to produce an abnormal adduct was first reported by Stetter, who assigned to it the 1,2-benzoxazine- 2-oxide structure (I).[1] Recently, publications of three groups, appearing independently, have been concerned with the structure of this adduct.[2-4] Alternative structures assigned were cyclic hydroxamic acid ester (II)[2] and hydroxamic acid (III),[3] principally on the basis of spectral evidence which excludes (I). Definitive chemical data supporting a single structure are lacking. The present study indicates that Stetter's compound has the oxime structure (IV).



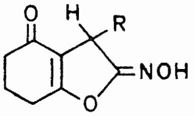
(I)



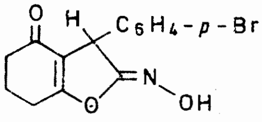
(II)



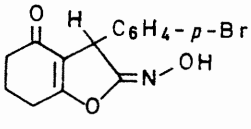
(III)



(IV) R = Ph
(V) R = C_6H_4-*p*-Br



(VA)



(VB)

The 4-bromo-derivative (V) was prepared by reaction of 4-bromo-ω-nitrostyrene[5] with cyclohexane-1,3-dione (0·01 mole of each) in 20 ml of 0·1 M-methanolic sodium methoxide; after 40 h at 0° there was obtained a 55% yield of (V), m.p. 157—170° (mixture of *syn*- and *anti*-forms).

Crystals of (V) obtained from methanol (m.p. 174—178°; 2 : 1 isomer ratio by n.m.r. assay) are orthorhombic with $a = 17{\cdot}37$, $b = 7{\cdot}89$, $c = 19{\cdot}76$ Å. Space group *Pbca* from systematic absences, $D_c = 1{\cdot}53$ g cm^{-3}, $D_m = 1{\cdot}53$ g cm^{-3} (by displacement from water), $Z = 8$.

795 statistically significant reflections were collected on a diffractometer using Ni-filtered Cu-K_α radiation and a scintillation counter. The structure was solved by the heavy-atom technique and application of Fourier syntheses and least-squares structure-factor calculations. The Fouriers revealed that the structure is disordered, with *syn*- and *anti*-forms of the oxime present. Position O(3′) (Figure) showed less electron density than O(3) in the Fouriers. Full-matrix least-squares refinement with anisotropic temperature factors for bromine, isotropic for all other atoms and occupancies of 2/3 and 1/3 for N(1), O(3) and N(1′), O(3′), respectively, gave an *R* value of 0·07 and bond lengths and angles shown in the Figure. Hydrogen positions were included at computed positions but not refined. Bond lengths and angles in the C–N–OH portion of the two forms of the oxime indicate the uncertainty of the true N(1) and N(1′) positions. The average C–N and N–O values of 1·29 and 1·38 Å do, however, show remarkably good agreement with corresponding bonds in known oxime structures.[6] C(10) and C(11) appear to occupy average positions created by cyclohexenone ring inversion.

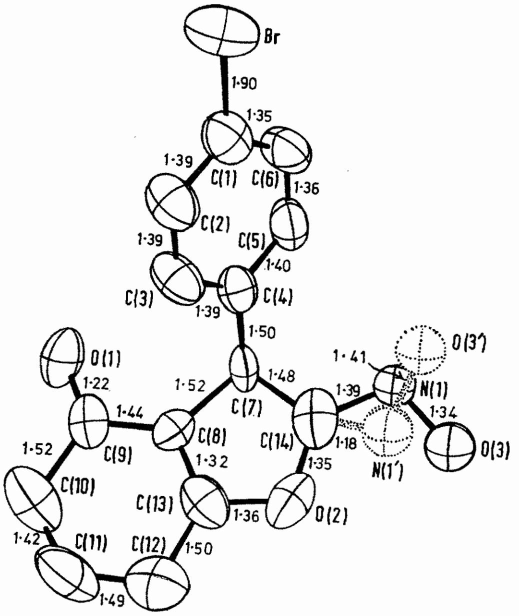


FIGURE. *E.s.d. for* C–Br 0·01 Å *and for all other bonds* 0·03 Å. *Hydrogen atoms omitted.* N(1), O(3) 2/3 *occupancy*; N(1′),O(3′) 1/3 *occupancy*.

Fractional crystallization of (V) from methanol and ethanol gave *syn*- and *anti*-forms (pure by n.m.r. assay) of 3-(4-bromophenyl)-2-hydroxyimino-6,7-dihydro-4(5*H*)-benzofuranone, $C_{14}H_{12}BrNO_3$ (VA), m.p. 200—205°, decomp., (less-soluble, hexagonal plates) and (VB), m.p. 179—181°, decomp., (more soluble, long rectangular prisms). Both forms showed ν_{max} (KBr) 3300 cm^{-1} (OH) and bands at 1720w and 1740s cm^{-1} due to C=C–C=O and C=N groups, but differed noticeably in certain absorption characteristics below 1400 cm^{-1}. U.v. spectra (ethanol) were similar: for (VA) λ_{max} 219 (ϵ 14,500) and 267 nm (12,500); for (VB) λ_{max} 222 (ϵ 15,500) and 269 nm (12,000). N.m.r. spectra [$(CD_3)_2SO$, 1%, 30°] of both forms revealed differences; for (VA) and (VB), respectively, the following peaks were observed (τ): $-0{\cdot}46$, $-0{\cdot}32$ (1, OH); 2·72, 2·68 and 2·38, 2·37 (A_2B_2 multiplet, *J* 8 Hz, 4 aryl protons); 4·99, 4·88 [C-3 methine proton apparent triplets due to coupling ($J \sim 2$ Hz) with the C-7 methylene group]; 7·24, 7·27 (C-5 methylene multiplet); 7·75, 7·77 (C-6, C-7 ethylene multiplet.)

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