The Crystal Structure of *p*-Bromophenacyl Isamate

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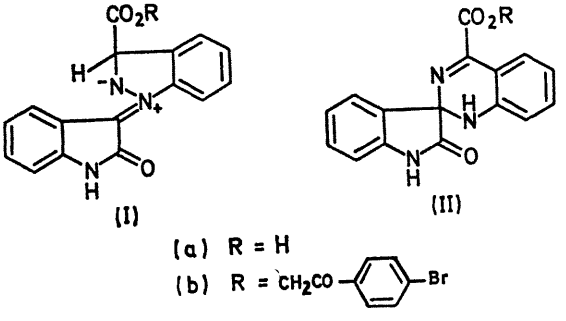
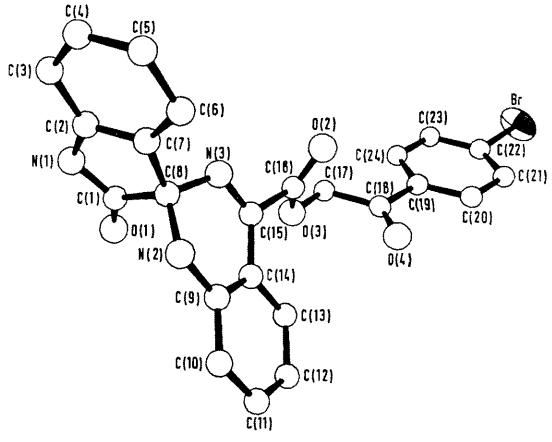
Summary The crystal structure of *p*-bromophenacyl isamate, determined by single-crystal *X*-ray diffraction analysis, is in agreement with a 1,2-dihydroquinazoline structure for isamic acid.

Two significantly different structures (Ia)[1] and (IIa),[2] have recently been suggested for isamic acid, which was originally prepared by Laurent[3] more than a century ago. The crystal structure of the *p*-bromophenacyl ester of isamic acid was undertaken in order to resolve this controversy.



Pale yellow crystals of *p*-bromophenacyl isamate, recrystallized from a tetrahydrofuran–methanol–water mixture, were kindly supplied by Dr. G. F. Field. The blade-shaped crystals are triclinic with reduced cell[4] parameters $a = 5{\cdot}488(1)$, $b = 8{\cdot}591(2)$, $c = 22{\cdot}079(8)$ Å, $\alpha = 99{\cdot}56(2)°$, $\beta = 90{\cdot}15(2)°$, $\gamma = 95{\cdot}57(2)°$; $D_m = 1{\cdot}59_5$ g cm^{-3} (flotation in CCl_4), $D_c = 1{\cdot}595$ g cm^{-3} for $C_{24}H_{16}N_3O_4Br$ with $Z = 2$. The centrosymmetric space group $P\bar{1}$ was confirmed by the structure analysis; 2288 reflections (1120 unobservably weak) were measured on a Hilger–Watts Y290 four-circle diffractometer with Ni-filtered Cu-K_α radiation. Absorption corrections were applied ($\mu = 33{\cdot}7$ cm^{-1}). The structure was solved by Patterson and Fourier methods. Refinement was by full-matrix least-squares with anisotropic thermal parameters for the bromine atom and isotropic thermal parameters for the carbon, nitrogen, and oxygen atoms; hydrogen atoms were not included. The discrepancy index is $R = 7{\cdot}7\%$. The molecular structure is shown in the Figure. The individual C–N bond-lengths are: N(1)–C(1), 1·37; N(1)–C(2), 1·39; N(2)–C(8), 1·47; N(2)–C(9), 1·40; N(3)–C(8), 1·49; N(3)–C(15), 1·29 Å; the estimated standard deviation for a C–N bond-length is 0·02 Å. C–N–C bond angles about N(1), N(2), and N(3) are 112°, 119°, and 117°, respectively.



FIGURE

The structure determined for the isamic acid ester (IIb) is in complete agreement with that suggested by Field[2] for isamic acid, (IIa). No rearrangement seems to have occurred in the formation of the *p*-bromophenacyl ester, which was prepared by a standard method,[5] since its u.v. spectrum with maxima at 420 (ϵ 1,400) and 245 nm (38,000) is very similar to that of isamic acid [λ_{max} 417 (1400) and 234 nm (35,000)].[1]

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[1] P. de Mayo and J. J. Ryan, *Chem. Comm.*, 1967, 88; *Canad. J. Chem.*, 1967, **45**, 2177.
[2] G. F. Field, *Chem. Comm.*, 1969, 886.
[3] A. Laurent, *J. prakt. Chem.*, 1842, **25**, 456; 1845, **35**, 108.
[4] L. V. Azaroff and M. J. Buerger, "The Powder Method in *X*-ray Crystallography," McGraw–Hill, 1958, pp. 124—145.
[5] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edn., Wiley, 1948, p. 157.