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Structure of 3-(Bromoacetyl)coumarin

BY KRISHNAGIRI T. VASUDEVAN AND PUTTARAJA

Department of Physics, Bangalore University, Bangalore-560056, India

AND MANOHAR V. KULKARNI

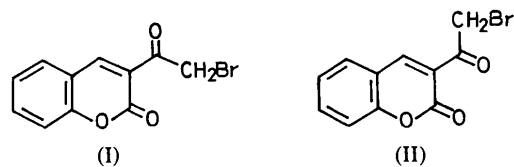
Department of Chemistry, Central College, Bangalore University, Bangalore-560001, India

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Abstract. $C_{11}H_7BrO_3$, $M_r = 267.09$, monoclinic, $P2_1/n$, $a = 21.555$ (2), $b = 4.229$ (2), $c = 10.784$ (1) Å, $\beta = 93.89$ (1)°, $V = 980.8$ Å³, $Z = 4$, $D_m = 1.79$ (5), $D_x = 1.808$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 5.2$ mm⁻¹, $F(000) = 528$, $T = 300$ K. Final R for 1692 observed reflections is 0.054. The coumarin moiety is nearly planar and makes a dihedral angle of 4.5 (8)° with the mean plane of the bromoacetyl group. The molecule adopts an *S-cis* eclipsed conformation in the solid state and the molecules are linked by weak C—H...O bonds.

Introduction. The coumarin moiety with various groups at the 3 position has given rise to many derivatives of biological and structural importance. 3-(Bromoacetyl)coumarin (Koelsch, 1950) has been a key intermediate in the synthesis of some 3-heterocyclic coumarins (Kulkarni, Patil, Biradar & Nanjappa, 1981) and many other compounds of biological relevance (Hanumanthgad, Kulkarni & Patil, 1984). A preliminary examination of its structure shows that due to free rotation about the C(3)—CO bond this molecule can give rise to two conformations. In these two conformers the carbonyl group attached to C(3) can be *S-cis* (I) or *S-trans* (II) to the C(3)—C(4) double bond of the pyrone ring.

Further, many *o*-haloketones are known to exhibit interesting conformations (Rao, 1963) which have been explained using different projection formulae when the molecule is viewed along the OC—CH₂Br axis. In order to establish the preferred conformation of the title compound in the solid state, an X-ray crystal structure analysis has been carried out.



Experimental. Colourless transparent crystals grown by slow evaporation from chloroform solution, D_m by flotation in a mixture of bromoform and acetone. Crystal of size 0.2 × 0.3 × 0.3 mm mounted on an Enraf–Nonius CAD-4 diffractometer, ω - 2θ scan, variable scan rate. Lattice parameters from least-squares refinement of 25 centred reflections; $\text{Cu } K\alpha$ intensity data collected to a maximum $2\theta = 152^\circ$ ($-26 < h < 26$, $0 < k < 5$, $0 < l < 12$); two standard reflections ($\bar{7}\bar{1}\bar{1}$ and $0\bar{1}\bar{6}$) monitored at regular intervals, intensity variation 2%. 2184 reflections of

Table 1. Positional parameters ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Br	2247.1 (3)	2639 (2)	657 (1)	64 (0)
O(1)	80 (1)	-2410 (10)	3686 (3)	53 (1)
O(2)	1061 (2)	-2927 (11)	3342 (3)	63 (1)
O(3)	865 (2)	3726 (12)	432 (4)	66 (2)
C(2)	580 (2)	-1627 (14)	3022 (4)	46 (2)
C(3)	463 (2)	576 (13)	1988 (4)	42 (2)
C(4)	-125 (2)	1552 (14)	1671 (5)	45 (2)
C(5)	-1252 (2)	1535 (16)	2055 (6)	54 (2)
C(6)	-1720 (2)	538 (16)	2769 (6)	59 (2)
C(7)	-1575 (3)	-1360 (17)	3804 (6)	59 (2)
C(8)	-972 (2)	-2349 (17)	4119 (5)	54 (2)
C(9)	-518 (2)	-1360 (13)	3378 (4)	44 (2)
C(10)	-640 (2)	565 (14)	2344 (5)	45 (2)
C(11)	979 (2)	1845 (14)	1279 (5)	47 (2)
C(12)	1632 (2)	837 (18)	1671 (6)	56 (2)

which 1735 reflections unique ($R_{int} = 0.051$) and 1692 reflections with $I \geq 3\sigma(I)$ considered observed; data corrected for Lorentz-polarization effects. Empirical absorption correction (North, Phillips & Mathews, 1968) applied and the transmission factors varied from 0.37 to 1.0. The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms were located from difference Fourier maps. Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms and isotropic for H atoms with unit weights using *SHELX76* (Sheldrick, 1976); final $R = 0.054$, $wR = 0.054$. Refinement terminated when the shift/e.s.d. for non-H atoms was 0.10; minimum and maximum residual electron densities in the final difference Fourier map were -0.75 and 0.53 e \AA^{-3} , respectively. The final positional parameters of non-H atoms with U_{eq} values are given in Table 1.*

Discussion. The molecule viewed along **b** with its bond lengths and angles is shown in Fig. 1. The structure consists of a planar bromoacetyl group connected at C(3) to a nearly planar coumarin moiety making a dihedral angle of $4.5 (8)^\circ$.

The molecules are packed in layers parallel to the **ac** plane and are held by C(8)—H \cdots O(2) and C(4)—H \cdots O(3) weak hydrogen bonds alternately [C(8) \cdots O(2) = $3.406 (7)$, H(8) \cdots O(2) = $2.49 (5)$ \AA, C(8)—H(8) \cdots O(2) = $158 (6)^\circ$, C(4) \cdots O(3) = $3.334 (6)$, H(4) \cdots O(3) = $2.48 (6)$ \AA, and C(4)—H(4) \cdots O(3) = $143 (4)^\circ$]. Molecular packing viewed down **b** is shown in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53346 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The dihedral angle between the planes of Br, C(12), C(11) and O(3), C(11), C(12) is $1.5 (8)^\circ$, and this indicates that the molecule prefers the eclipsed conformation. The enantiomeric H atoms on C(12) are almost equidistant from O(2), and bromine, with an atomic radius three times that of hydrogen, would suffer severe steric congestion and hence cannot be *gauche* or *trans* to O(3). This is revealed by its large separation from O(2) [$4.409 (5)$ \AA]. The increased bond angle Br—C(12)—C(11) = $113.0 (2)^\circ$ facilitates minimization of the dipole-dipole interaction and it can be deduced that the molecule prefers the *S-cis* eclipsed conformation in the solid state as shown by Newman structure (III).

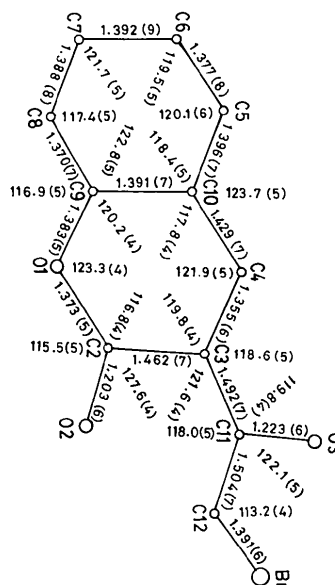
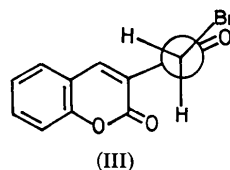


Fig. 1. A view of the molecule along **b** with bond lengths (\AA) and angles ($^\circ$).

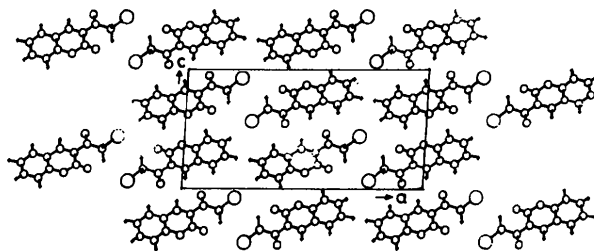


Fig. 2. Molecular packing viewed along **b**.

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Structure of the Aglycone Ethyl Ether of Jasminin

BY K. TAKAHASHI AND T. KAMIKAWA

Department of Chemistry, Faculty of Science and Technology, Kinki University, Higashi-Osaka, Osaka 577, Japan

M. ASAKA

Department of Chemistry, Faculty of General Education, Kinki University, Higashi-Osaka, Osaka 577, Japan

AND M. FUKUYO

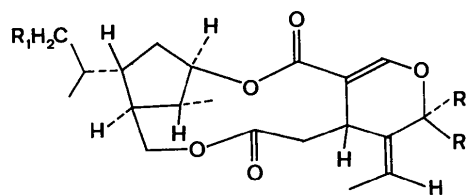
Department of Chemistry, Faculty of Science, Osaka City University, Osaka, Osaka 558, Japan

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Abstract. *rel*-(7*S*,14*S*,15*S*,17*S*)-7-Ethoxy-8-(*E*)-ethylidene-17-methyl-15-[(1*S*)-1-methyl-2-hydroxyethyl]-2,6,12-trioxatricyclo[12.2.1.0^{4,9}]heptadec-4-ene-3,11-dione, C₂₂H₃₂O₇, *M_r* = 408.49, orthorhombic, *P*₂₁₂₁, *a* = 25.773 (15), *b* = 10.540 (3), *c* = 8.087 (5) Å, *V* = 2196.8 (2) Å³, *Z* = 4, *D_x* = 1.24 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 7.14 cm⁻¹, *F*(000) = 880, *T* = 299 K, *R* = 0.043 for 2294 observed reflections. The molecular structure of the aglycone ethyl ether of jasminin is consistent with the structure of jasminin proposed from the results of chemical and spectroscopic methods.

Introduction. The structure of jasminin (1), the bitter principle of *Jasminum mesnyi* (*unnan oubai*) has been extensively studied by chemical and spectroscopic methods (Kamikawa, Inoue & Kubota, 1970; Asaka, Kamikawa & Kubota, 1974). The hydrolysis of jasminin by *p*-toluenesulfonic acid in ethanol gives the title compound, the aglycone ethyl ether (2), in which the β-D-glucose unit of jasminin is replaced with ethyl ether by *S*_N₂ substitution. The bromination of the aglycone ethyl ether gives the bromide derivative (3). Preliminary X-ray analysis of (3)

has been performed by the Patterson method (Fukuyo & Shimada, 1969). Crystallographic data for (3) are *a* = 26.54, *b* = 10.14, *c* = 8.43 Å, *P*₂₁₂₁, *R* = 0.16. The structure of jasminin has been uncertain because of the possibility of skeletal transformation by ethanolysis.



- (1): *R*₁ = OH, *R*₂ = β-D-glucoside, *R*₃ = H
 (2): *R*₁ = OH, *R*₂ = H, *R*₃ = OCH₂CH₃
 (3): *R*₁ = Br, *R*₂ = H, *R*₃ = OCH₂CH₃
 (4): *R*₁, *R*₂ = β-D-glucoside, *R*₃ = H

Recently, ¹³C NMR spectra of aglycone ethyl ether (2) and jasminin (1) were recorded (Inoue & Kuwashima, 1990). The ¹³C NMR spectrum of jasminin is similar to that of its aglycone ethyl ether: corresponding chemical shifts and peak splittings