

Structure of 7-Methyl-4-(*p*-tolylloxymethyl)coumarin

BY KRISHNAGIRI T. VASUDEVAN AND PUTTARAJA

Department of Physics, Jnana Bharathi Campus, Bangalore University, Bangalore-560 056, India

AND MANOHAR V. KULKARNI

Department of Chemistry, Central College, Banaglore-560 001, India

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Abstract. C₁₈H₁₆O₃, *M_r* = 280.32, triclinic, *P* $\bar{1}$, *a* = 7.757 (1), *b* = 9.907 (2), *c* = 11.053 (2) Å, α = 65.94 (2), β = 85.65 (2), γ = 74.13 (2)°, *V* = 745.43 Å³, *Z* = 2, *D_x* = 1.247, *D_m* = 1.24 (5) Mg m⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.5418 Å, μ = 0.72 mm⁻¹, *F*(000) = 296, *T* = 300 K, final *R* = 0.052 for 2734 observed reflections. The coumarin moiety is planar and makes a dihedral angle of 5.7° with the mean plane of the *p*-tolylloxymethyl group. The molecules are packed in parallel layers head-to-tail along the (012) plane and are held by van der Waals interactions.

Introduction. The coumarin nucleus has been a seat of diverse biological properties through its innumerable derivatives. In the coumarin molecule the 4 and 7 positions are of vital importance because many 4-substituted coumarins have shown excellent vasodilatory, CNS-stimulating, antimicrobial and enzyme-inhibiting properties. 4-(Phenoxymethyl)coumarins have been reported as possible antibacterials (Kulkarni, Pujar & Patil, 1983). The title compound was synthesized by the reaction of 7-methyl-4-bromomethylcoumarin with *p*-cresol. The spectral analysis agreed with the proposed structure. Further, it has been found that some 7- and 4,7-substituted coumarins give rise to interesting crystal structures in terms of their reactivity (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985) and the nature of their packing (Ramasubbu, Guru Row, Venkatesan, Ramamurthy & Rao, 1982). In view of this, the crystal structure analysis of the title compound was undertaken.

Experimental. Colourless transparent crystal of size 0.6 × 0.5 × 0.5 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, ω -2 θ scan, variable scan rate, lattice parameters from least-squares refinement of 25 centred reflections, density measurement by flotation. Cu *K* α intensity data collected in the range 18.5 ≤ 2 θ ≤ 120°, two standard reflections 777 and 169 monitored at intervals showed no

significant variation, a total of 3300 reflections collected of which 3132 reflections were unique and 2860 reflections with *I* ≥ 3 σ (*I*) were considered observed, *h* -9 to 9, *k* -10 to 12, *l* 0 to 13, data corrected for Lorentz-polarization effects, no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All the hydrogen atoms except the methyl hydrogens were located from the difference Fourier maps with methyl hydrogens fixed from geometrical considerations. Full-matrix least-squares refinement of non-hydrogen atoms with anisotropic thermal parameters and hydrogens with isotropic thermal parameters, using *SHELX*76 (Sheldrick, 1976), final *R* = 0.052 and *wR* = 0.071, $w = K[\sigma^2(F) + |g|F^2]^{-1}$, *K* = 3.6089, *g* = 0.0012, σ 's based on counting statistics, the refinement was terminated when the shift/e.s.d. for non-hydrogen atoms was less than 0.15, the minimum and maximum residual electron densities in the final difference Fourier map were -0.21 and 0.24 e Å⁻³ respectively. Final positional parameters for non-hydrogen atoms with *U_{eq}* values are given in Table 1.* Atomic scattering factors for C, O and H were those incorporated in *SHELX*76.

Discussion. A perspective view of the molecule with bond lengths and angles is shown in Fig. 1 and an *ORTEP* (Johnson, 1965) plot of the molecule with 50% probability thermal ellipsoids is shown in Fig. 2. The coumarin moiety is planar except for the atom C(2) which has a deviation of 0.014 (2) Å from the mean plane. The *p*-tolylloxymethyl group at C(4) is almost planar and makes a dihedral angle of 5.7° with the mean plane of the coumarin ring.

* 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 52976 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

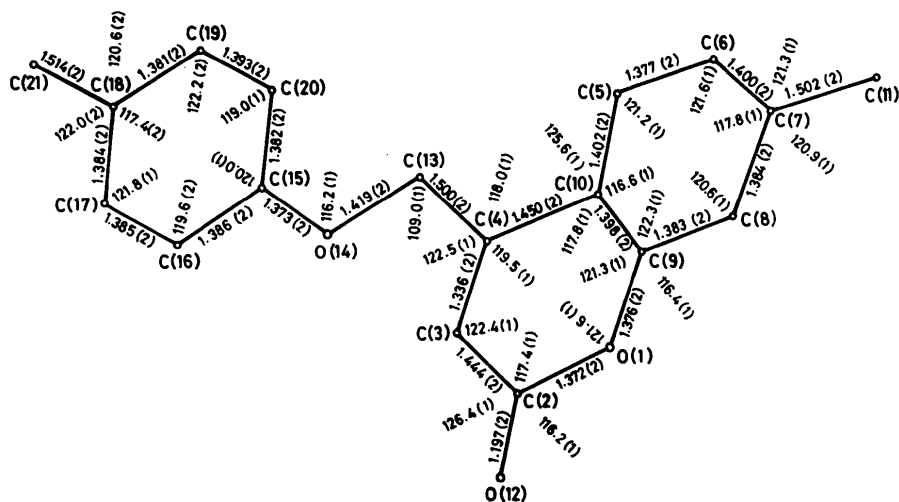


Fig. 1. A perspective view of the molecule with bond lengths (Å) and angles (°).

Table 1. Positional parameters of non-hydrogen atoms ($\times 10^4$) and U_{eq} ($\text{Å}^2 \times 10^4$), with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} *
O(1)	2448 (1)	5023 (1)	-1760 (1)	565 (4)
O(12)	4783 (1)	3153 (1)	9271 (1)	804 (5)
O(14)	-86 (1)	754 (1)	1165 (1)	553 (3)
C(2)	3183 (2)	3544 (2)	-879 (2)	565 (5)
C(3)	1966 (2)	2621 (2)	-216 (1)	509 (5)
C(4)	195 (2)	3144 (2)	-465 (1)	447 (4)
C(5)	-2381 (2)	5397 (2)	-1775 (1)	526 (5)
C(6)	-2963 (2)	6895 (2)	-2678 (2)	585 (5)
C(7)	-1760 (2)	7778 (2)	-3288 (1)	551 (5)
C(8)	47 (3)	7095 (2)	-2955 (1)	536 (5)
C(9)	629 (2)	5594 (2)	-2041 (1)	470 (4)
C(10)	-555 (2)	4698 (2)	-1422 (1)	447 (4)
C(11)	-2404 (3)	9412 (2)	-4268 (2)	725 (6)
C(13)	-1073 (2)	2187 (1)	217 (1)	474 (4)
C(15)	-1062 (2)	-257 (2)	1888 (1)	498 (4)
C(16)	-85 (3)	-1641 (2)	2826 (2)	620 (6)
C(17)	9048 (3)	-2742 (2)	3590 (2)	733 (7)
C(18)	2781 (3)	2502 (2)	-3442 (2)	717 (7)
C(19)	-3719 (2)	-1121 (2)	2490 (2)	666 (7)
C(20)	-2891 (2)	17 (2)	1717 (2)	582 (5)
C(21)	-3731 (5)	-3712 (4)	4258 (3)	1037 (12)

* The temperature factor is of the form: $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_j$.

Variations in the bond lengths and angles in the phenyl ring, which are due to the fusion of the pyrone ring, have been reported in various coumarin derivatives (Shimizu, Kashino & Haisa, 1975). The observed C(5)—C(6) bond length [1.377 (2) Å] is shorter than the normal aromatic C—C bond and is in agreement with the reported values. In the pyrone ring the C(3)—C(4) bond length has been found to be 1.336 (2) Å. Comparison of this bond length with other coumarin derivatives indicates that this bond length varies from 1.30 to 1.41 Å depending on the groups attached at C(3) or C(4) (Shimizu *et al.*, 1975). The bond angle C(4)—C(10)—C(5) = 125.6 (1)° is larger than O(1)—C(9)—C(8) = 116.4 (1)° and may be attributed to non-bonded repulsive interaction between the hydrogens attached to C(5) and C(13). Since there is no periplanar atom

attached to O(1) such repulsive interaction will be less and consequently the angle at C(9) is less than 120° (Ramasubbu, 1982). The bond lengths O(1)—C(2) and O(1)—C(9) are equal. The observed $\text{H}_2\text{C}(sp^3)\text{—O}$ bond length is 1.419 (2) Å and there is a residual bond contraction of 0.055 Å in the $\text{H}_2\text{C}(sp^3)\text{—O}$ bond which cannot be accounted for in terms of the hybridization changes of carbon but might be due to electron delocalization (Lide, 1962; Ferguson, 1969). Variations in bond lengths have been explained in terms of electron delocalization in the structure of a lactone oxime (Jones & Chaney, 1972) and an oxazolone peptide (Nair & Vijayan, 1980). The C—CH₃ bonds have an average value of 1.508 (2) Å.

The molecular packing viewed down *c* is shown in Fig. 3. The molecules are packed in parallel layers head-to-tail along the (012) plane. There is a close spatial proximity between the ether oxygen and the C(3)—H of the coumarin [C(3)⋯O(14) = 2.688, H(3)⋯O(14) = 2.459 Å and C(3)—H(3)⋯O(14) =

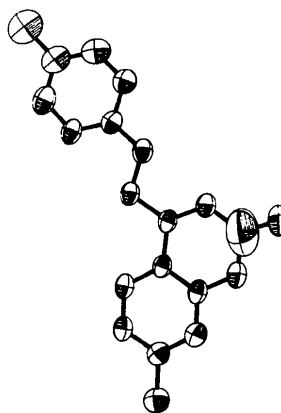


Fig. 2. ORTEP plot of the molecule with 50% probability thermal ellipsoids.

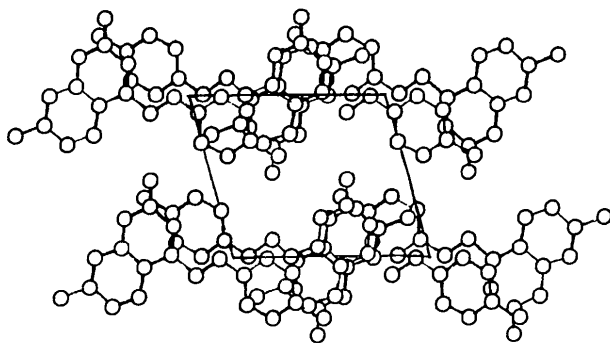


Fig. 3. Molecular packing viewed down *c*.

91–61°]. This type of intramolecular interaction is quite likely between the C(3)—H and ether oxygen, and is favoured sterically in the formation of a stable five-membered ring. There are no abnormal intermolecular contacts and the structure is stabilized by van der Waals interactions.

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Structure of Ethyl 1-(2-Cyanoethyl)-5-methoxy-3-methylindole-2-carboxylate

BY T. N. CHANDRAKANTHA AND PUTTARAJA

Department of Physics, Jnana Bharathi Campus, Bangalore University, Bangalore-560 056, India

AND M. NETHAJI

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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Abstract. $C_{16}H_{18}N_2O_3$, $M_r = 286.34$, triclinic, $P\bar{1}$, $a = 9.120$ (5), $b = 11.954$ (2), $c = 14.877$ (2) Å, $\alpha = 105.65$ (1), $\beta = 102.16$ (2), $\gamma = 78.84$ (2)°, $Z = 4$, $V = 1510.5$ Å³, $D_x = 1.259$, $D_m = 1.25$ (5) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.05$ mm⁻¹, $F(000) = 608$, $T = 300$ K, final $R = 0.065$ for 2459 observed reflections. There are two independent molecules per asymmetric unit. The indole ring system is planar. The ethyl carboxylate group makes an angle of 13.7 (6)° with the mean plane of the indole rings in molecule *A* and 18.5 (6)° in molecule *B*. The cyanoethyl group is inclined at an angle of 89° to the mean plane of the indole rings in both molecules.

Introduction. Indole derivatives exhibit important pharmacological properties, such as being a CNS depressant, and have muscle relaxant properties (Harris & Uhle, 1960; Wei & Stanley, 1970; Reynolds & Carson, 1970; Houlihah, 1973; White & Black, 1976; Ho, Haegman & Prisco, 1986). Reduction of the title compound in the presence of lithium aluminium hydride and cyclization of the resulting amino compound yields a novel compound, 9-methoxy-11-methyl-1,2,3,4-tetrahydro-1*H*-1,4-diazepino[1,2-*a*]indole which exhibits a marked tranquilizing property (Archer & Sternbach, 1968). The crystallographic study of the title compound was