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Acta Cryst. (1995). **C51**, 2196–2198

Archangelin

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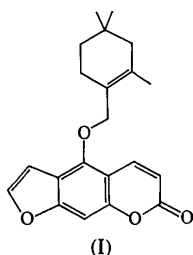
(Received 15 February 1995; accepted 21 April 1995)

Abstract

In the title compound, 4-[(2,4,4-trimethyl-1-cyclohexen-1-yl)methoxy]-7*H*-furo[3,2-*g*][1]benzopyran-7-one, C₂₁H₂₂O₄, the furocoumarin system is planar. The cyclohexene ring adopts a half-chair conformation and makes a dihedral angle of 130.3 (1)° with the fused ring system. Molecules are held together in the crystal by C—H···O hydrogen bonds.

Comment

This paper presents the results of a structural study of archangelin, (I), a furocoumarin isolated from the roots of *Angelica archangelica* L. (Thappa, 1989), and is part of a systematic study of coumarin derivatives isolated from plants of the *Umbelliferae* family.



An *ORTEPII* (Johnson, 1976) drawing of the title molecule with the atomic numbering scheme is shown in Fig. 1. The rings of the furocoumarin moiety are coplanar, as in other furocoumarin derivatives (Bideau, Bravic & Desvergne, 1979; Bravic & Bideau, 1978; Dall'Acqua, Benetollo & Bombieri, 1981). The deviations of atoms from the least-squares plane of the three rings range from -0.029 (4) to 0.027 (4) Å, indicating a reasonably planar system. The cyclohexene ring shows a half-chair conformation with the twofold axis bisecting the C16—C17 and C19—C20 bonds, and an asymmetry parameter ΔC_2 (C16—C17) of 4.0° (Duax & Norton, 1975). The observed variations in bond lengths and angles in the phenyl ring have also been reported for various coumarin derivatives and may be attributed to the fusion of the pyrone and furan rings (Shimizu, Kashino & Haisa, 1975). The mean value of the four C—O bonds in the two heterocyclic rings is 1.376 (4) Å, which is in agreement with the normal C_{sp^2} —O distance (1.369 Å; Allen *et al.*, 1987). The C5—C11 and C6—C7 bond distances of 1.424 (4) and 1.442 (3) Å, respectively, are consistent with the values of 1.427 (3) and 1.448 (4) Å found in furocoumarin (Borowiak & Wolska, 1989).

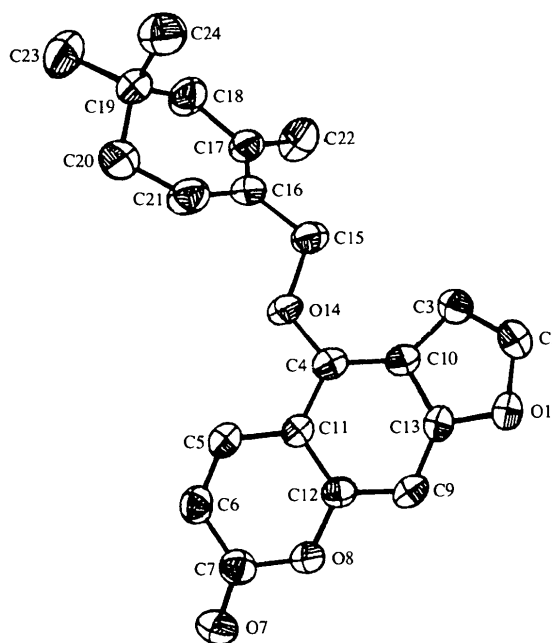


Fig. 1. *ORTEPII* (Johnson, 1976) view of the title compound with displacement ellipsoids plotted at the 50% probability level. H atoms have been omitted for clarity.

The intra- and intermolecular C—H···O hydrogen bonds which contribute to the stabilization of the molecular and crystal structure are summarized in Table 2.

Experimental

The sun-dried and pulverized roots of *Angelica archangelica* L. were exhaustively extracted with petrol (b.p. 333–353 K) in a Soxhlet apparatus. Chromatographic separation of the concentrated extract over deactivated alumina followed by elution with the same solvent furnished archangelin, which was crystallized from methanol (m.p. 405 K).

Crystal data

$C_{21}H_{22}O_4$
 $M_r = 338.4$
 Monoclinic
 $P2_1/n$
 $a = 6.732(2) \text{ \AA}$
 $b = 24.375(4) \text{ \AA}$
 $c = 12.027(3) \text{ \AA}$
 $\beta = 115.10(2)^\circ$
 $V = 1787.2 \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.258 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 none
 2944 measured reflections
 2695 independent reflections
 1938 observed reflections
 $[F > 4\sigma(F)]$

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.154$
 $S = 0.679$
 2695 reflections
 315 parameters
 All H-atom parameters
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.1588P)^2 + 2.79P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25
 reflections
 $\theta = 8.1\text{--}13.8^\circ$
 $\mu = 0.080 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Rectangular prism
 $0.35 \times 0.20 \times 0.17 \text{ mm}$
 Transparent

$R_{int} = 0.017$
 $\theta_{max} = 25^\circ$
 $h = -7 \rightarrow 0$
 $k = -28 \rightarrow 0$
 $l = -12 \rightarrow 14$
 2 standard reflections
 monitored every 100
 reflections
 intensity decay: 2%

$(\Delta/\sigma)_{max} = 0.496$
 (for U_{iso} of H232)
 $\Delta\rho_{max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.16 \text{ e \AA}^{-3}$
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992),
 Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	0.0077 (4)	0.5739 (1)	0.2230 (2)	0.0522 (11)
C2	-0.0628 (6)	0.5319 (2)	0.1381 (3)	0.0535 (16)
C3	-0.0135 (6)	0.4829 (2)	0.1899 (3)	0.0481 (14)
C4	0.1951 (5)	0.4600 (1)	0.4280 (3)	0.0384 (11)
C5	0.3842 (5)	0.4584 (1)	0.6567 (3)	0.0416 (14)
C6	0.4721 (5)	0.4851 (1)	0.7636 (3)	0.0478 (14)
C7	0.4778 (5)	0.5442 (1)	0.7684 (3)	0.0469 (14)
O7	0.5592 (5)	0.5723 (1)	0.8590 (2)	0.0668 (13)
O8	0.3819 (3)	0.5714 (1)	0.6579 (2)	0.0444 (10)
C9	0.1997 (5)	0.5771 (1)	0.4439 (3)	0.0439 (16)
C10	0.0989 (5)	0.4915 (1)	0.3207 (3)	0.0387 (12)
C11	0.2891 (5)	0.4871 (1)	0.5429 (3)	0.0363 (12)
C12	0.2889 (5)	0.5444 (1)	0.5465 (3)	0.0372 (11)

C13	0.1060 (5)	0.5487 (1)	0.3348 (3)	0.0408 (13)
O14	0.2112 (4)	0.4047 (1)	0.4357 (2)	0.0514 (10)
C15	0.1113 (6)	0.3712 (1)	0.3268 (3)	0.0474 (15)
C16	0.1533 (5)	0.3125 (1)	0.3660 (3)	0.0436 (13)
C17	0.2497 (6)	0.2776 (1)	0.3193 (3)	0.0471 (14)
C18	0.2742 (9)	0.2173 (2)	0.3536 (4)	0.063 (2)
C19	0.1444 (6)	0.1965 (1)	0.4213 (3)	0.0518 (15)
C20	0.1604 (8)	0.2389 (2)	0.5174 (4)	0.0664 (19)
C21	0.0698 (8)	0.2949 (2)	0.4584 (4)	0.060 (2)
C22	0.3453 (10)	0.2918 (2)	0.2305 (5)	0.070 (2)
C23	0.2439 (10)	0.1418 (2)	0.4850 (5)	0.083 (3)
C24	-0.0942 (8)	0.1869 (2)	0.3310 (5)	0.080 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—C2	1.380 (5)	C7—O8	1.376 (4)
O1—C13	1.367 (4)	O8—C12	1.381 (4)
C2—C3	1.323 (6)	C10—C13	1.403 (3)
C4—C11	1.416 (4)	C16—C17	1.330 (5)
C5—C6	1.335 (4)		
C6—C7—O8	116.7 (2)	C12—C9—C13	114.4 (2)
C6—C7—O7	126.8 (3)	O8—C12—C9	116.1 (2)
O7—C7—O8	116.5 (2)	C9—C13—C10	126.4 (3)
C17—C16—C21—C20	15.5 (6)	C17—C18—C19—C20	-42.3 (5)
C21—C16—C17—C18	2.1 (6)	C18—C19—C20—C21	59.2 (5)
C16—C17—C18—C19	12.3 (6)	C19—C20—C21—C16	-47.0 (5)
D—H...A	H...A	D...A	D—H...A
C5—H5...O14	2.43 (3)	2.740 (4)	101 (3)
C21—H212...O14	2.51 (4)	2.892 (6)	101 (2)
C2—H2...O7 ⁱ	2.51 (3)	3.386 (4)	158 (3)

Symmetry code: (i) $x - 1, y, z - 1$.

Data were corrected for Lorentz and polarization effects. All H atoms were located from a difference Fourier map and their positions and isotropic displacement parameters were refined. All calculations were performed on a PC/AT computer.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors are thankful to the Head, RSIC, IIT, Madras, for use of the data collection facility. One of us (KNG) is thankful to the University Grants Commission, New Delhi, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 2198–2200

Bis[4-(dimethylamino)phenyl](*N*-methylcarbamoyl)amine, C₁₈H₂₄N₄O

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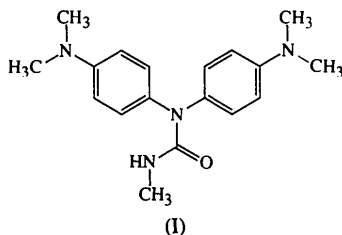
(Received 5 January 1995; accepted 10 May 1995)

Abstract

The two phenyl rings in the title compound, *N,N*-bis[4-(dimethylamino)phenyl]-*N'*-methylurea, are almost perpendicular to one another, with dihedral angles of 79.9 (4) and 89.2 (4)° for the two crystallographically independent molecules in the asymmetric unit.

Comment

In the presence of peroxidase and hydrogen peroxide, the title compound, (I), is converted into 4,4'-bis(dimethylamino)diphenylamine (Bindshedler's green leuco base) (Cheng, Ueno & Imamura, 1982; Tichý & Petter, 1984) and a blue colour is developed. Therefore, the molecule can be applicable clinically as a functional dye used to measure the activity of monoamine oxidase



in blood. Effective conversion is essential for the sensitivity and accuracy of the clinical diagnosis. The structure analysis of the title compound was undertaken in order to discover the structure–function relationships.

The two crystallographically independent molecules in the asymmetric unit have similar conformations. The molecules as a whole have propeller forms as opposed to the butterfly form observed in a similar functional dye (MCDP; Fujii, Hirayama & Miike, 1993). The angles at the hinge N atoms total 359.3 (9) and 359.8 (9)°, indicating a very planar structure at the N atom. The N–C(=O) distances of 1.400 (4) and 1.383 (4) Å in the independent molecules are significantly longer than the corresponding distances in the *N*-methylcarbamoyl group, indicating that this group may be a good leaving group due to the bond difference. The sum of the bond angles around atoms N4 and N4' indicates that the terminal dimethylamino groups are very planar even though they are not coplanar with the phenyl rings to which they are attached. The conjugated system in the molecule can be schematically represented by formula (II) below.

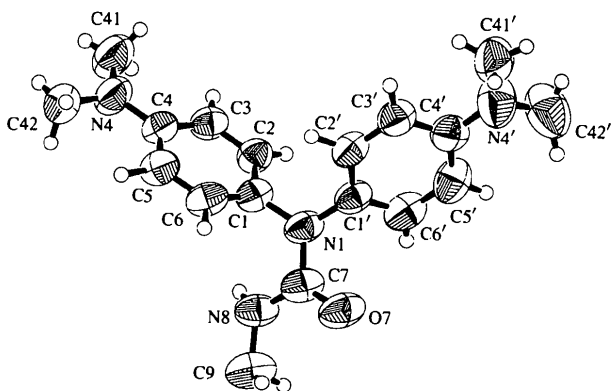
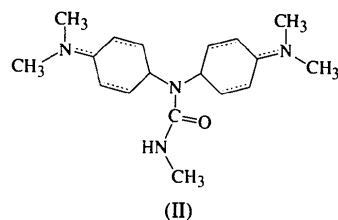


Fig. 1. ORTEPII drawing (Johnson, 1976) of molecule A, showing heavy atoms with 50% probability ellipsoids and H atoms as circles of arbitrary radii.

Experimental

The crystals were grown from an ethanol solution at 281 (2) K. A crystal sealed in a glass capillary filled with nitrogen gas was used for the diffraction experiments.

Crystal data

C₁₈H₂₄N₄O
M_r = 312.41

Cu Kα radiation
λ = 1.54184 Å