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The Crystal and Molecular Structure of 1,6:8,13-Pentane-1,5-diylidene[14]annulene

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$C_{19}H_{18}$ crystallizes in the monoclinic space group Cc with $a=18{\cdot}197$ (2), $b=6{\cdot}623$ (1), $c=11{\cdot}681$ (2) Å, $\beta=109{\cdot}80$ (1)°, $Z=4$, $D_c=1{\cdot}24$, $D_m=1{\cdot}20$ g cm^{-3}. The structure was solved by the Patterson method and the minimum residual technique. With 1184 counter-measured observed reflexions the structure was refined to an R of 0·039 ($wR=0{\cdot}045$). In the crystal the molecular symmetry is near to m; in the annulene ring the bond lengths show small but systematic deviations from the aromatic value. Simple Hückel molecular orbital calculations are in qualitative agreement with the experimental results. Owing to the strain imposed by the bridges, the pentane chain is not planar.

Introduction

This work is part of a study of the structures of bridged annulenes (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972; Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972; Gramaccioli, Mimun, Mugnoli & Simonetta, 1973; Gramaccioli & Simonetta, 1971; Bianchi, Morosi, Mugnoli & Simonetta, 1973; Mugnoli & Simonetta, 1974). It has been noted (Gramaccioli, Mimun, Mugnoli & Simonetta, 1973) that the strain imposed by the bridges on an annulene ring results in a more or less marked division (with respect to the aromatic value) into shorter and longer bond distances along the annulene perimeter. Therefore it seemed worth while to study the effect of a pentane chain connecting the C(1)–C(15)–C(6) and C(8)–C(16)–C(13) bridges.

The crystal structure of 1,6:8,13-pentane-1,5-diylidene[14]annulene is presented in this paper.

Experimental

Crystals were kindly provided by Professor E. Vogel. Preliminary film data showed that the crystals are monoclinic, space group Cc or $C2/c$ (hkl, only for $h+k=2n$; $h0l$, only for $l=2n$). Lattice constants were obtained from a least-squares fit of 12 reflexions (plus their equivalents) centred with Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å) on a Syntex $P\bar{1}$ four-circle diffractometer equipped with graphite monochromator. The density was measured by flotation in a dilute Thoulet (K_2HgI_4) solution. The crystallographic data are given in the abstract.

Intensities were collected on a crystal of dimensions $0{\cdot}29\times0{\cdot}13\times0{\cdot}18$ mm with the θ–2θ scan technique, scan width $2{\cdot}1°+\alpha_1\alpha_2$ separation, variable scan speed between 1 and 12° min^{-1}, and dead time for coincidence correction $2{\cdot}1\times10^{-6}$ s. The background was counted for half the total scanning time on each side of the reflexion. Two standard reflexions were measured periodically; these showed no significant change during data collection. In the range of measurements ($2\theta_{\max}=140°$) 1233 reflexions were measured, of which 1184 had intensity above background. The variance $\sigma^2(I_{\rm rel})$ was calculated as $[S+B+(0{\cdot}03\ S)^2]v^2$, with S=scan count, B=total background count and v=scan speed. Lorentz and polarization factors were applied; absorption effects were neglected ($\mu=5{\cdot}3$ cm^{-1} for Cu $K\alpha$ radiation). The $N(z)$ test and the statistics on the normalized structure factors were in agreement with the acentric distribution, whence space group Cc was assumed. This was later confirmed by the structure solution.

The structure was solved by determining the orientation and then the position of a molecular model in the unit cell. The first step was accomplished by means of an automated interpretation of the sharpened Patterson map calculated around the origin (Filippini & Gramaccioli, 1969; modified for the monoclinic system by R.B.). An incomplete molecular model (16 out of 19 C atoms) was constructed leaving out the three central atoms of the pentane chain, on the basis of the molecular geometry of 1,6:8,13-butane-1,4-diylidene-[14]annulene (Gramaccioli *et al.*, 1972). By assuming the orientation corresponding to the highest peak in the Patterson sum function, the position of the oriented model along the non-polar y axis was then found by the minimum residual technique; a difference map showed the positions of the three remaining C atoms.

Refinement on all observed reflexions was accomplished by a full-matrix least-squares process, minimizing $\sum w(|F_o|-|F_c|)^2$ with weights $w=1/\sigma^2(F)$. The program used was a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors for C were obtained from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). Initially C atoms were treated as isotropic; in a later stage the corresponding thermal parameters were converted to their anisotropic equivalents, and refinement was continued including the contributions of the H atoms located in calculated positions. During the last cycles, the coordinates and the isotropic thermal parameters of the H atoms were allowed to vary. When all the shifts were less than 0·11σ the refinement was considered complete; the final values for the residuals converged to $R=0·039$ for the 1184 observed reflexions and to $R=0·045$ for all 1233 measured data ($R_w=0·045$), with a goodness of fit $[\sum w(\Delta F)^2/(n-p)]^{1/2}=1·74$.* A final difference map showed no significant features, the electron density values being between $\pm0·27$ e Å^{-3}.

The final atomic parameters are given in Tables 1 and 2. The numbering of atoms is shown on the thermal ellipsoids plot (Johnson, 1965) of Fig. 1.

The standard deviations for the coordinates derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle correspond to positional uncertainties of the order of 0·005 Å for the C and of 0·045 Å for the H atoms. The corresponding standard deviations in the bond distances involving only C atoms are around 0·007 Å, in the bond angles 0·4°, and in the torsion angles 0·7° (calculated according to Huber, 1961); in the C–H bonds they are about 0·05 Å and in the angles involving H atoms they are between 1·8 and 3·6° (for H–C–H angles).

Results

To test the rigidity of the molecule the interpretation of thermal parameters in terms of rigid-body motion was attempted. Accordingly, the tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were derived from a least-squares treatment with a Fortran IV program written by G. Filippini. In these calculations, equal weights were assigned to all thermal factors; the results are shown in Table 3. The agreement between observed and calculated values of B_{ij} for each C atom is good, the differences exceeding 3σ only for 11 cases over a

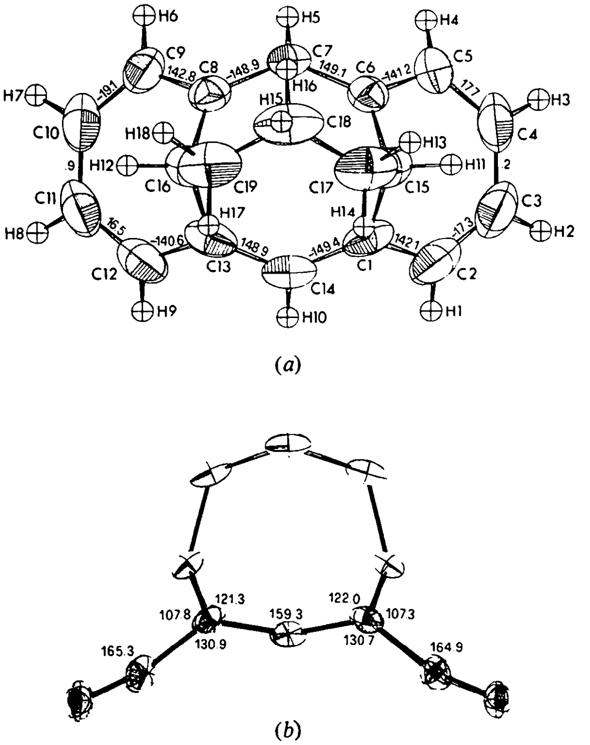

Fig. 1. Temperature ellipsoids. Carbon atoms are drawn at probabilities 0·50 and 0·20 in (*a*) and (*b*), respectively. Hydrogen atoms, treated as isotropic, are on an arbitrary scale. (*a*) Numbering of atoms and torsion angles around the annulene ring. Values for torsion angles C(15)–C(17)–C(18)–C(19) and C(17)–C(18)–C(19)–C(16) are 70·7 and −67·8°, respectively. (*b*) Side view of the molecule and dihedral angles between least-squares planes. The dihedral angle between planes C(15), C(16), C(17), C(19) and C(17), C(18), C(19) is 122·5°.

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30844 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *The carbon atom parameters and their standard deviations*

All the values in this table have been multiplied by 10^4. Thermal factors are of the form $\exp[-(B_{11}h^2+2B_{12}hk+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	758 (0)	2690 (5)	−56 (0)	47 (1)	192 (8)	78 (3)	45 (3)	20 (1)	9 (3)
C(2)	1386 (3)	2908 (7)	−518 (5)	47 (2)	375 (12)	108 (4)	56 (4)	26 (2)	−16 (6)
C(3)	1937 (3)	4387 (9)	−182 (5)	32 (1)	509 (17)	147 (5)	34 (4)	26 (2)	−22 (7)
C(4)	1903 (3)	6239 (8)	417 (5)	23 (1)	452 (14)	134 (4)	−14 (3)	10 (2)	−14 (6)
C(5)	1314 (3)	6941 (6)	791 (4)	27 (1)	294 (10)	96 (3)	−2 (3)	3 (1)	−24 (4)
C(6)	713 (3)	5743 (4)	942 (4)	30 (1)	211 (7)	58 (2)	5 (2)	5 (1)	−26 (3)
C(7)	−36 (3)	6558 (4)	592 (4)	35 (1)	151 (6)	64 (2)	9 (2)	16 (1)	−13 (3)
C(8)	−762 (3)	5618 (4)	141 (4)	33 (1)	197 (7)	78 (3)	−1 (2)	26 (1)	−24 (3)
C(9)	−1390 (3)	6699 (6)	−679 (4)	30 (1)	273 (9)	110 (3)	18 (3)	24 (2)	0 (5)
C(10)	−1960 (3)	5870 (8)	−1658 (5)	26 (1)	441 (13)	121 (4)	1 (3)	14 (2)	1 (6)
C(11)	−1945 (3)	4038 (8)	−2251 (5)	31 (1)	465 (15)	110 (4)	−38 (4)	8 (2)	−40 (6)
C(12)	−1350 (3)	2636 (7)	−1968 (5)	48 (2)	319 (10)	108 (4)	−52 (4)	28 (2)	−68 (5)
C(13)	−709 (3)	2533 (5)	−831 (4)	51 (1)	172 (7)	81 (3)	−31 (3)	29 (2)	−22 (3)
C(14)	30 (3)	2076 (4)	−846 (4)	56 (1)	158 (7)	73 (3)	7 (3)	31 (2)	−10 (3)
C(15)	941 (3)	3554 (5)	1204 (4)	39 (1)	241 (8)	71 (3)	30 (3)	7 (1)	1 (4)
C(16)	−931 (3)	3397 (5)	204 (4)	41 (1)	225 (8)	91 (3)	−24 (2)	34 (2)	−14 (4)
C(17)	735 (3)	2386 (6)	2190 (4)	72 (2)	237 (10)	74 (3)	37 (3)	14 (2)	27 (4)
C(18)	5 (4)	2923 (6)	2428 (4)	90 (3)	222 (8)	79 (3)	19 (4)	47 (2)	13 (4)
C(19)	−720 (3)	2321 (6)	1437 (4)	74 (2)	243 (10)	110 (4)	−9 (3)	60 (3)	16 (5)

total of 114, and in most cases being of the order of 1σ. On the whole, this can be taken as proof of essential rigid-body motion of the molecule. The mean square rotational displacements about the principal axes of the tensor **L** amount to 20, 14 and 10 (°)^2.

Bond distances (uncorrected and corrected for rigid-body motion) and angles are collected in Tables 4 and 5, respectively. Torsion angles are reported in Fig. 1(*a*). The corrections for distances have been derived under the rigid-body assumption from the tensor **L**, accord-

Table 2. *Parameters for the hydrogen atoms*

	x	*y*	*z*	10*B* (Å^2)
H(1)	0·136 (3)	0·208 (7)	−0·111 (4)	69 (10)
H(2)	0·235 (3)	0·440 (7)	−0·053 (4)	86 (12)
H(3)	0·229 (2)	0·709 (6)	0·046 (4)	59 (9)
H(4)	0·122 (2)	0·831 (7)	0·078 (4)	73 (11)
H(5)	−0·007 (2)	0·797 (4)	0·040 (2)	32 (5)
H(6)	−0·140 (2)	0·815 (6)	−0·059 (3)	54 (8)
H(7)	−0·239 (3)	0·674 (6)	−0·204 (4)	66 (9)
H(8)	−0·234 (3)	0·387 (6)	−0·303 (4)	69 (9)
H(9)	−0·133 (2)	0·181 (6)	−0·255 (4)	57 (9)
H(10)	0·002 (2)	0·155 (5)	−0·160 (3)	40 (6)
H(11)	0·152 (2)	0·366 (4)	0·155 (3)	33 (5)
H(12)	−0·150 (2)	0·329 (6)	−0·003 (3)	53 (8)
H(13)	0·114 (3)	0·261 (7)	0·296 (5)	82 (12)
H(14)	0·074 (2)	0·094 (6)	0·197 (4)	58 (8)
H(15)	−0·006 (2)	0·221 (7)	0·317 (4)	77 (11)
H(16)	−0·003 (2)	0·429 (6)	0·258 (3)	55 (8)
H(17)	−0·071 (2)	0·074 (7)	0·129 (4)	67 (9)
H(18)	−0·116 (3)	0·262 (7)	0·175 (4)	74 (10)

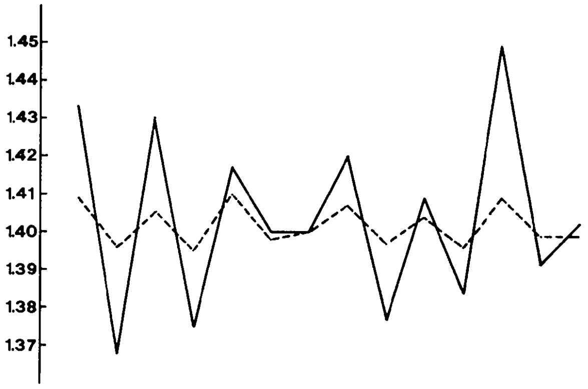

Fig. 2. Experimental (solid line) and calculated (dashed line) bond lengths (Å) for bonds C(1)–C(2) to C(14)–C(1) in the annulene ring.

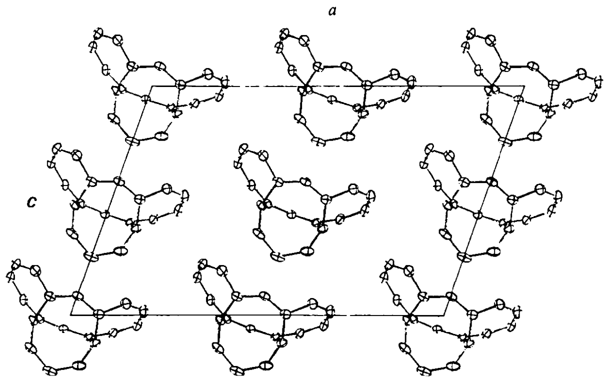

Fig. 3. Packing of molecules as seen along the *y* axis.

Table 3. *Rigid-body tensors*

The tensors are referred to a Cartesian coordinate system defined by unit vectors **a**, **b**, **a** × **b**. All values have been multiplied by 10^4.

T (Å^2)	1295 (26)	66 (11)	233 (22)
('unreduced')		320 (14)	−46 (14)
			716 (30)
L (rad^2)	33 (4)	−3 (2)	−8 (2)
		44 (2)	2 (2)
			59 (2)
S (Å rad)	−50 (7)	3 (4)	−110 (10)
	45 (5)	10 (3)	15 (5)
	229 (7)	8 (2)	40 (7)

Table 4. *Bond distances* (Å)

	Observed	Corrected*	Calculated
C(1)—C(2)	1·426	1·433	1·409
C(2)—C(3)	1·361	1·368	1·396
C(3)—C(4)	1·424	1·430	1·405
C(4)—C(5)	1·369	1·375	1·395
C(5)—C(6)	1·410	1·417	1·410
C(6)—C(7)	1·393	1·400	1·398
C(7)—C(8)	1·393	1·400	1·400
C(8)—C(9)	1·413	1·420	1·407
C(9)—C(10)	1·371	1·377	1·397
C(10)-C(11)	1·402	1·409	1·404
C(11)-C(12)	1·378	1·384	1·396
C(12)-C(13)	1·443	1·449	1·409
C(13)-C(14)	1·384	1·391	1·399
C(14)-C(1)	1·395	1·402	1·399
C(1)—C(15)	1·508	1·513	
C(6)—C(15)	1·510	1·517	
C(8)—C(16)	1·509	1·516	
C(13)-C(16)	1·511	1·517	
C(15)-C(17)	1·536	1·543	
C(17)-C(18)	1·490	1·498	
C(18)-C(19)	1·485	1·492	
C(19)-C(16)	1·534	1·541	

* After rigid-body correction

Table 5. *Bond angles*

C(1)—C(2)—C(3)	124·8	C(14)-C(1)—C(15)	127·0
C(2)—C(3)—C(4)	127·7	C(2)—C(1)—C(15)	113·0
C(3)—C(4)—C(5)	128·2	C(5)—C(6)—C(15)	113·2
C(4)—C(5)—C(6)	125·0	C(7)—C(6)—C(15)	127·3
C(5)—C(6)—C(7)	118·0	C(7)—C(8)—C(16)	126·9
C(6)—C(7)—C(8)	130·3	C(9)—C(8)—C(16)	113·3
C(7)—C(8)—C(9)	118·4	C(12)-C(13)-C(16)	111·5
C(8)—C(9)—C(10)	124·9	C(14)-C(13)-C(16)	128·1
C(9)—C(10)-C(11)	128·5	C(6)—C(15)-C(17)	121·0
C(10)-C(11)-C(12)	127·6	C(1)—C(15)-C(17)	120·8
C(11)-C(12)-C(13)	125·2	C(15)-C(17)-C(18)	118·7
C(12)-C(13)-C(14)	119·0	C(17)-C(18)-C(19)	113·8
C(13)-C(14)-C(1)	129·6	C(18)-C(19)-C(16)	118·7
C(14)-C(1)—C(2)	118·9	C(8)—C(16)-C(19)	120·6
C(1)—C(15)-C(6)	102·2	C(13)-C(16)-C(19)	121·7
C(8)—C(16)-C(13)	102·5		

ing to Schomaker & Trueblood (1968). Corrections for bond and torsion angles (less than 0·1°) were neglected.

Hückel molecular orbital (HMO) calculations were used to calculate bond orders in the annulene perimeter. Starting bond distances were put all equal to 1·40 Å, whereas the effect of the misalignment between adjacent p_z orbitals was taken care of by means of experimental torsion angles. In the calculations, the same procedure and parameters were used as described in a previous paper (Gramaccioli *et al.*, 1973). Bond lengths as obtained at convergence are reported in the last column of Table 4.

In Fig. 1(*a*), signs for the torsion angles are given following the convention of Klyne & Prelog (1960). The mean planes, calculated according to Schomaker, Waser, Marsh & Bergman (1959), are described in Table 6; values for dihedral angles between adjacent least-squares planes in the annulene ring are shown in Fig. 1(*b*).

Table 6. *Some least-squares planes through groups of atoms*

The coefficients q_i are the direction cosines relative to the crystallographic axes *a*, *b* and *c*, multiplied by 10^4. The distance of the defining atoms from the mean plane involving four atoms is always less than 0·013 Å, with the exception of the C(15), C(16), C(17), C(19) plane (0·017 Å).

Plane	q_1	q_2	q_3	D
C(2), C(3), C(4), C(5)	−1278	4457	−7903	1·013 Å
C(1), C(2), C(5), C(6)	−3705	3717	−6753	0·195
C(1), C(6), C(15)	9762	2152	−3045	1·751
C(1), C(6), C(7), C(14)	4422	5024	−8488	1·560
C(7), C(8), C(13), C(14)	1053	4842	−8529	1·510
C(8), C(13), C(16)	−7693	1443	−3250	1·550
C(8), C(9), C(12), C(13)	8080	4057	−6757	0·285
C(9), C(10), C(11), C(12)	6364	4634	−7958	1·076
C(3), C(4), C(10), C(11)	2798	5031	−8641	2·629
C(2), C(5), C(9), C(12)	2816	5006	−8656	2·185
C(1), C(6), C(8), C(13)	2779	5035	−8639	1·336
C(15), C(16), C(17), C(19)	−1916	8671	4975	2·403
C(17), C(18), C(19)	1398	8856	−4640	0·399

C–H distances are in the range 0·87–0·97 Å and 0·93–1·06 Å for H atoms bonded to the annulene ring and to the pentane chain, respectively.

Discussion

The geometry of the molecule is described in Tables 4 to 6 and in Fig. 1. On the whole, the observed geometry fits *m* symmetry; the highest differences between *m*-symmetry related bond distances, angles, and absolute values of torsion angles are 0·02 Å, 1·8°, and 4·5°, respectively.

The strain imposed by the bridges is reflected in a quite remarkable deviation of the annulene ring from planarity, as shown in Fig. 1(*b*); with reference to the C(2), C(5), C(9), C(12) mean plane, deviations as high as 0·87 Å are found for perimeter C atoms. The corresponding highest deviation in 1,6:8,13-butane-1,4-diylidene[14]annulene (hereinafter BUT; Gramaccioli *et al.*, 1972) is 0·75 Å, and in 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene (hereinafter ANTI; Gramaccioli *et al.*, 1973), 0·69 Å. However, bond lengths along the annulene ring in the present compound deviate only slightly, though systematically (in the sense that in the ring approximately *mm*2 symmetry is observed) from the aromatic value. Similar behaviour has been noticed in BUT, the sample standard deviation in bond lengths and the maximum misalignment angle $\varphi_{\max}$ between adjacent p_z orbitals being 0·025 and 35° respectively in BUT, *vs.* 0·022 and 39° respectively in the present compound [for details, see Gramaccioli *et al.* (1973)].

In other words, deviations from the aromatic value in bond distances around the ring, although significant, are not very high owing to the sufficiently low value of the φ angles. This does not happen in ANTI, where the high value in $\varphi_{\max}$ (74°) causes a complete division into long and short bond distances (averages: 1·47 and 1·35 Å, respectively) corresponding to a system of localized single and double bonds.

As a test of the connexion between φ angles and splitting of bond lengths in the ring, we performed for the present compound the same semi-empirical calculations as for ANTI; the results are shown in Table 4 (last column) and in Fig. 2. The matching between observed and calculated bond distances is not so good as in ANTI; however a qualitative agreement is found, the observed longer and shorter distances being calculated as longer and shorter with respect to the aromatic bond length. On the whole, deviations of observed bond distances from the aromatic value along the annulene ring are small enough to suggest an aromatic behaviour of the substance.

The non-bonded distance between the summit of the bridges is 3·21 Å, *i.e.* much shorter than the distance of 5·08 Å between the terminal C atoms of n-pentane itself (Mathisen, Norman & Pedersen, 1967), for which the conformation of the C atom skeleton in the crystal is anti-periplanar (torsion angles 178°). In the present compound the shortening of the pentane chain is accomplished by a shortening and a rotation of the two central bonds, giving rise to torsion angles of 69° (mean of absolute values) and to a dihedral angle (out-of-plane bending angle) of 122·5°. This situation approximately corresponds to the next energy favoured synclinal (*gauche*) conformation.

The packing of the molecules in the crystal is shown in Fig. 3. The range of intermolecular distances is normal. There is only one contact shorter than the sum of van der Waals radii (C 1·7, CH_2 2·0, H 1·2 Å; Pauling, 1960), *i.e.* between C(4) in x,y,z and H(13) in $x,1-y,-\frac{1}{2}+z$ (2·84 Å).

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Topochemical Studies. IV. The Crystal and Molecular Structure of 4-Methylumbelliferone

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The structure of the title compound has been determined from visually estimated Cu $K\alpha$ data. The crystals are orthorhombic, space group $P2_12_12_1$, $Z=4$, with $a=11{\cdot}90$ (1), $b=13{\cdot}17$ (1), $c=5{\cdot}243$ (5) Å. The structure was solved by the symbolic addition procedure, and refined by the block-diagonal least-squares method to a final R value of 0·067 for 862 non-zero reflexions. The molecule is nearly planar. The bond lengths and angles in the benzene ring show some variations due to fusion of a pyrone ring. The C(3)–C(4) and C(2)–O(11) bonds in the pyrone ring are distinctly double-bond in character. The molecules are linked together by an O–H···O=C hydrogen bond (2·719 Å) nearly parallel to the *ac* plane to form infinite ribbons along the *b* axis. The perpendicular distance between stacked molecules is 3·33 Å.

Introduction

Not only does coumarin itself photodimerize in both polar and non-polar solvents (Hammond, Stout & Lamola, 1964; Krauch, Farid & Schenck, 1966), but also its derivatives undergo photocycloaddition with themselves or with pyrimidine bases of DNA (Song, Harter, Moore & Herndon, 1971). The photochemical reactivity of coumarin derivatives may primarily be related to the C(3)–C(4) bond in conjunction with the carbonyl group at C(2) in the pyrone ring. It is also of interest that a group of natural carcinogens, 'aflatoxin', contain the moiety 5-methoxy-7-hydroxycoumarin (Wogan & Newberne, 1967) and that a group of skin-photosensitizers, 'psoralen', consists of furocoumarin (Musajo & Rodighiero, 1970). It is of physiological interest that close chemical similarity between coumarin and vitamin K is apparent (Kralt & Claassen, 1972).

As part of a programme of topochemical studies of two-fused-ring aromatic compounds to obtain ther stucture–reactivity relationship in the solid state, we have determined the crystal structure of 7-hydroxy-4-methylcoumarin, which is of particular interest in view of its usefulness in enzyme determination (Wald & Feuer, 1971) and in the field of dye lasers owing to its wide tunability (Dienes, Shank & Trozzolo, 1970).

Experimental

Crystals were obtained, from ethanol solution by slow evaporation, as thin plates elongated along the *c* axis. Crystallographic data are listed in Table 1. The intensity data were collected on equi-inclination Weissenberg photographs for the layers *hk*0 to *hk*4 and 0*kl* by using specimens of dimensions 0·5 × 0·5 × 1·3 and 0·3 × 0·4 × 0·4 mm, respectively. In total, 878 reflexions (79 % in the Cu $K\alpha$ sphere) were observed as non-zero