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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 $a=11\cdot90$ (1), $b=13\cdot17$ (1), $c=5\cdot243$ (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 $0\cdot067$ 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 $hk0$ to $hk4$ and $0kl$ by using specimens of dimensions $0\cdot5 \times 0\cdot5 \times 1\cdot3$ and $0\cdot3 \times 0\cdot4 \times 0\cdot4$ mm, respectively. In total, 878 reflexions (79 % in the Cu $K\alpha$ sphere) were observed as non-zero

reflexions. The intensities were estimated visually and corrected for Lorentz, polarization and spot shape, but not for absorption effects.

Table 1. *Crystallographic data*

4-Methylumbelliferone (7-hydroxy-4-methyl-2H-1-benzo-pyran-2-one)

$C_{10}H_8O_3$ M.W.   176·17   m.p.   193 °C
Orthorhombic, $a = 11·90(1)$, $b = 13·17(1)$, $c = 5·243(5)$ Å,
$V = 821·1$ Å^3
$D_m = 1·43$ g cm^{-3} (by flotation in aqueous KI solution)
$D_x = 1·425$ g cm^{-3} $Z = 4$ $F(000) = 368$
$\mu = 9·1$ cm^{-1} for Cu $K\alpha$ ($\lambda = 1·5418$ Å)
Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd
Space group: $P2_12_12_1$

Structure determination

The structure was solved by means of the symbolic addition procedure (Karle & Karle, 1966). The statistics of the normalized structure factors show values intermediate between those expected for centrosymmetric and non-centrosymmetric space groups as shown in Table 2. The starting set of phases was chosen as shown in Table 3. By giving the symbols to the last

three phases in Table 3, the phases of 50 reflexions out of 97 with $|E| > 1·60$ were assigned, on the basis of the Σ_2 relationships. The phases of 186 reflexions with $|E| > 1·20$ were then determined by the tangent formula. An E map revealed all the non-hydrogen atoms, the structure giving a conventional R value of 0·22 for an overall isotropic thermal parameter $B = 2·86$ Å^2.

Refinement

Three cycles of diagonal least-squares refinement with the c axis data reduced the R value to 0·11. A difference Fourier map at this stage showed all the hydrogen atoms. Excluding the four reflexions (210, 201, 211 and 311) which were considered to suffer from extinction, refinements by the block-diagonal least-squares method were carried out by using the weighting scheme: $w = 1·0$ for $0 < |F_o| \leq F_{max}(= 7·5)$, $w = (F_{max}/|F_o|)^2$ for $|F_o| > F_{max}$. The final R value was 0·067 for 862 non-zero reflexions from the c axis data.*

Table 2. *Statistics of the E's*

	This structure	Theoretical values Centric	Acentric
$\langle |E| \rangle$	0·82	0·80	0·89
$\langle |E|^2 \rangle$	1·00	1·00	1·00
$\langle ||E|^2 - 1| \rangle$	0·89	0·97	0·74
Reflexions with $|E| > 3$	0·41 %	0·27 %	0·01 %
$|E| > 2$	4·3	4·6	1·8
$|E| > 1$	30·6	31·7	36·8

Table 3. *Starting set of phases*

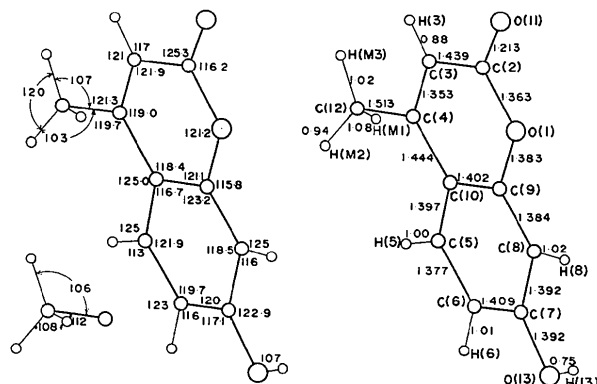| h	k	l	$|E|$	Phases	
1	12	0	4·49	−90°	
11	7	0	2·64	−90	Origin
5	0	1	1·96	−90	
0	3	5	2·83	90	Enantiomorph
12	8	0	2·35	180	from Σ_1
8	1	0	2·51	a	finally 180°
1	11	1	3·30	b	−125
3	12	1	3·00	c	−146

Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are 0·006 Å and 0·4° for non-hydrogen atoms and 0·05 Å and 4° for hydrogen atoms, respectively.

Table 4. *The final positional and thermal parameters* ($\times 10^4$) *with standard deviations in parentheses*

The anisotropic coefficients have the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	4197 (2)	2746 (2)	−819 (6)	52 (2)	30 (1)	225 (12)	7 (2)	64 (8)	14 (6)
O(11)	3949 (2)	4326 (2)	−1986 (6)	68 (2)	34 (1)	356 (14)	3 (3)	57 (9)	60 (7)
O(13)	4773 (2)	−723 (2)	1285 (6)	57 (2)	30 (1)	328 (14)	15 (3)	27 (8)	13 (7)
C(2)	3675 (3)	3659 (2)	−514 (8)	48 (2)	30 (2)	246 (18)	−4 (3)	−1 (11)	10 (9)
C(3)	2827 (3)	3750 (2)	1430 (9)	46 (2)	28 (2)	303 (19)	12 (3)	26 (11)	−28 (9)
C(4)	2567 (3)	2971 (3)	3003 (8)	35 (2)	36 (2)	217 (16)	−10 (3)	−6 (9)	−16 (9)
C(5)	2998 (3)	1164 (3)	4251 (8)	44 (2)	38 (2)	193 (17)	−9 (4)	28 (10)	−3 (9)
C(6)	3557 (3)	267 (3)	3805 (8)	56 (2)	33 (2)	213 (18)	−13 (3)	−3 (11)	16 (9)
C(7)	4307 (3)	193 (2)	1731 (8)	38 (2)	31 (2)	240 (17)	−3 (3)	−22 (9)	−10 (9)
C(8)	4518 (3)	1039 (3)	215 (8)	41 (2)	34 (2)	208 (17)	−3 (3)	41 (10)	−29 (9)
C(9)	3954 (3)	1933 (2)	757 (7)	39 (2)	29 (2)	173 (16)	−9 (3)	−5 (9)	−2 (8)
C(10)	3160 (3)	2020 (2)	2721 (8)	36 (2)	31 (2)	170 (16)	−6 (3)	10 (8)	−20 (8)
C(12)	1651 (3)	3068 (3)	4989 (9)	45 (2)	39 (2)	312 (20)	4 (4)	66 (11)	−34 (10)

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out on an NEAC 2200-700

computer at the Computation Centre of Osaka University and an NEAC 2200-500 computer at the Okayama University Computer Centre. The main programs used were *SIGM*, *TANG*, *HBLS-5* and *DAPH* (Ashida, 1973), and *RSDLS-3* (Sakurai, 1967).

Results and discussion

The final atomic parameters are given in Tables 4 and 5. Bond lengths and angles are shown in Fig. 1, and projections of the crystal structure viewed along the *b* and *c* axes together with some intermolecular contacts in Fig. 2.

Table 5. *The final parameters of the hydrogen atoms*

$\langle\sigma(x)\rangle=0.004$, $\langle\sigma(y)\rangle=0.003$, $\langle\sigma(z)\rangle=0.010$, $\langle\sigma(B)\rangle=0.94$ Å².

	x	y	z	B (Å²)
H(3)	0·250	0·435	0·159	0·05
H(M1)	0·197	0·293	0·688	1·54
H(M2)	0·116	0·254	0·455	2·39
H(M3)	0·139	0·380	0·494	1·61
H(5)	0·247	0·113	0·574	1·85
H(6)	0·339	−0·038	0·476	2·67
H(8)	0·500	0·092	−0·137	0·12
H(13)	0·515	−0·067	0·014	1·40

Molecular structure

Equations of best planes for non-hydrogen atoms in the benzene ring, the pyrone ring and the whole molecule are

$$-0.739X - 0.287Y - 0.610Z + 4.428 = 0 \quad (I)$$
$$-0.707X - 0.301Y - 0.639Z + 4.355 = 0 \quad (II)$$
$$-0.716X - 0.287Y - 0.636Z + 4.326 = 0 \quad (III)$$

respectively, where X, Y and Z refer to the crystallographic axes in Å. The deviations of the atoms from the above planes are given in Table 6. The molecule is nearly planar and lies near the (211) plane. There is a slight folding of the pyrone ring about the C(2)–C(10) axis whereas the folding occurs about the O(1)–C(4) axis in xanthotoxin (Stemple & Watson, 1972). The hydroxyl O(13) atom is forced above the benzene ring by 0·096 Å to form the hydrogen bond O(13)–H(13)··· O(11^{vi}) (2·719 Å).

The bond lengths and angles in the benzene ring show some variations due to fusion of a pyrone ring. The C(5)–C(6) and C(8)–C(9) bonds are rather shorter than the others, as expected from tautomerism (Yakatan, Juneau & Schulman, 1972), but the geometry of the pyrone ring is no indication of tautomerism. The methyl group angles are tetrahedral within experimental error, and the H(M3) atom lies near the pyrone ring while the H(M2) and H(M1) atoms are displaced equidistantly above and below the ring, respectively. The stabilization of the structure by 4-methyl substitution has been pointed out as playing a role in the structure–activity relationship in the induction of drug-metabolizing enzymes (Wald & Feuer, 1971).
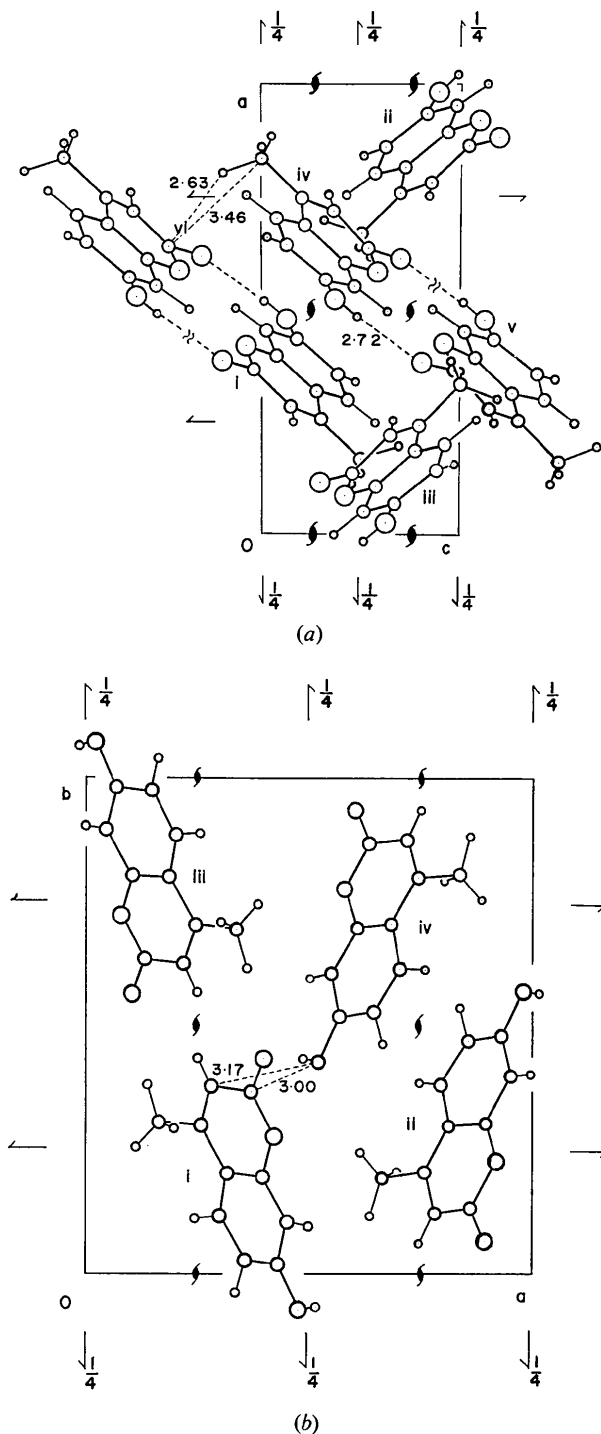

(a)

(b)

Fig. 2. Projections of the crystal structure; (*a*) viewed along the *b* axis, (*b*) viewed along the *c* axis. Symmetry code: i x,y,z; ii $\frac{1}{2}+x,\frac{1}{2}-y,1-z$; iii $\frac{1}{2}-x,1-y,\frac{1}{2}+z$; iv $1-x,\frac{1}{2}+y,\frac{1}{2}-z$; v $x,y,1+z$; vi $1-x,-\frac{1}{2}+y,-\frac{1}{2}-z$.

Table 6. *Deviation of the atoms from the planes* (I), (II) *and* (III) (Å)

Asterisks indicate the atoms used to define the least-squares planes.

	Distance from (I)	Distance from (II)	Distance from (III)
O(1)	−0·034	0·009*	−0·013*
C(2)	−0·018	−0·017*	−0·016*
C(3)	0·072	0·008*	0·024*
C(4)	0·091	0·009*	0·015*
C(5)	−0·004*	−0·053	−0·085*
C(6)	−0·015*	−0·018	−0·074*
C(7)	0·018*	0·077	0·008*
C(8)	−0·002*	0·071	0·014*
C(9)	−0·017*	0·008*	−0·024*
C(10)	0·020*	−0·017*	−0·036*
O(11)	−0·039	−0·019	−0·010*
C(12)	0·225	0·075	0·096*
O(13)	0·096	0·198	0·106*
H(3)	0·080	−0·010	0·021
H(M1)	−0·605	−0·769	−0·751
H(M2)	0·999	0·848	0·863
H(M3)	0·196	0·022	0·061
H(5)	−0·007	−0·099	−0·122
H(6)	0·069	0·058	−0·007
H(8)	0·123	0·241	0·174
H(13)	0·111	0·244	0·147

Angles between planes

Angle with (I)	2·64°	2·00°
Angle with (II)		1·11

The geometries of the pyrone ring in some coumarins are compared in Table 7, where the theoretical bond lengths by the simple HMO method are included. In order to convert the π-bond order (p) to bond length (r), the relations

$$r(\text{C–C}) = 1\cdot517 - 0\cdot18p \quad \text{(Coulson \& Golebiewski, 1961)},$$

and

$$r(\text{C–O}) = 1\cdot410 - 0\cdot18p \quad \text{(Nishimoto \& Forster, 1966)}$$

are used. It should be noted that the C(3)–C(4) and C(2)–O(11) bonds are shorter than the expected values and are distinctly double bond in character. This is in accordance with the reactivity of photocycloaddition of skin-sensitizing coumarins (Moore, Mantulin & Song, 1973). The O(11)–C(2)–O(1) angle is generally smaller than the O(11)–C(2)–C(3) angles in the coumarins in Table 7, because of the steric effect of the substituent at C(3). The only exception is found in dicoumarol (Bravic, Gaultier & Hauw, 1968) in which intramolecular hydrogen bonds are formed.

Crystal structure

As seen from Fig. 2, the molecules are linked together by a hydrogen bond nearly parallel to the *ac* plane to form infinite ribbons along the *b* axis, packed by stacking in a *c*-translation sequence in one direction and in an *a*-diad screw-axis sequence in the other direc-

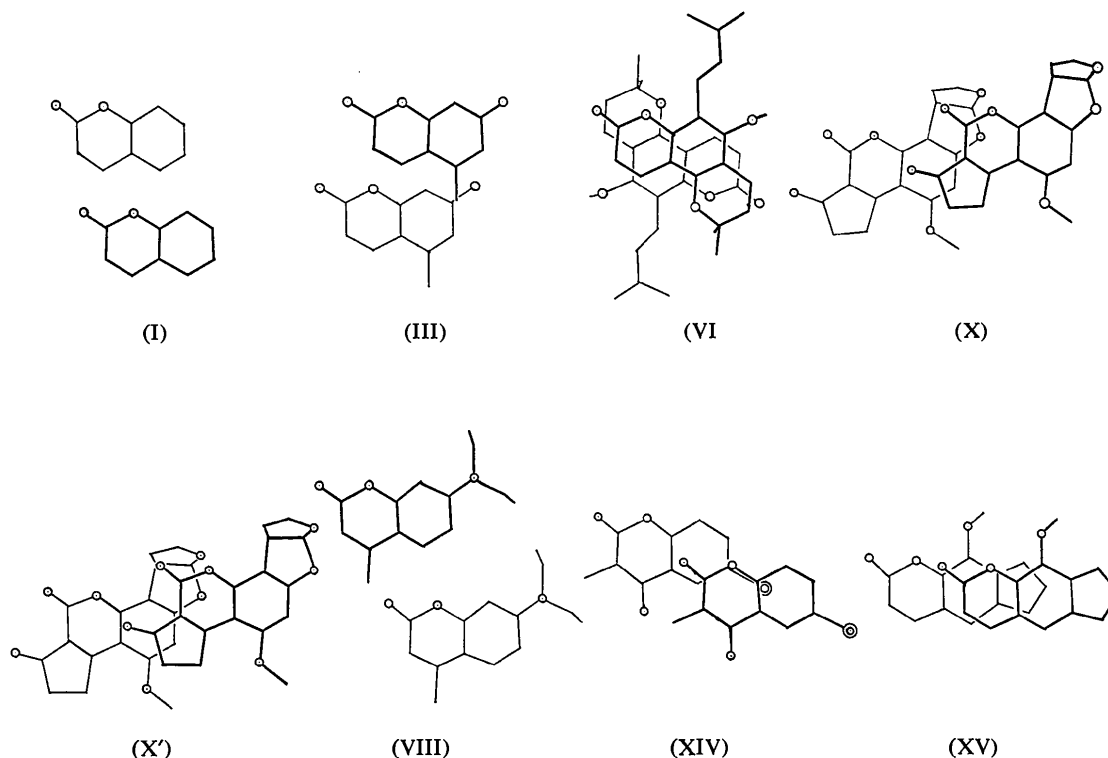(I)　　　　　(III)　　　　　(VI　　　　　(X)

(X′)　　　　　(VIII)　　　　　(XIV)　　　　　(XV)

Fig. 3. The stacking of coumarin planes. See Table 7 for compounds and references.

tion. Dipole–dipole interaction is predominant in the **a** direction. The perpendicular distance between stacked molecules is shorter than those found in the substituted coumarins listed in Table 8, owing to their slight overlap, as shown in Fig. 3. Those of coumarin itself and amyrolin (Kato, 1970) are also short because there is little superposition of molecular planes. The direction of molecular stacking corresponds to that of the shortest cell dimension, as seen in Table 8, except in the compound (IV) which has a bulky substituent. Such a short stacking spacing has been observed in 10-methylisoalloxazine (3·34 Å; Wang & Fritchie, 1973), in proflavine dichloride dihydrate (3·35 Å; Obendorf, Carrell & Glusker, 1974) and in many pyrimidine derivatives (3·3 to 3·35 Å; Bugg, Thomas, Sundaralingam & Rao, 1971).

Assuming the volume increments 20·6 Å^3 for C=O, 6·0 Å^3 for hetero O, and 12·4 Å^3 for O–H groups, the

Table 7. *Molecular geometry of the pyrone ring in some coumarins*

Theoretical values are shown in parentheses.

Compound	C(2)–O(11)	C(3)–C(4)	O(11)–C(2)–O(1)	O(11)–C(2)–C(3)	O(11)···X(3)	
(I)	1·216 Å	1·337 Å	116·2°	126·0°	2·69 Å	X=H
	1·204	1·344	117·3	125·6	2·56	
	(1·230)	(1·352)				
(II)	1·210	1·320	116·0	127·1	2·57	X=H
(III)	1·213	1·353	116·2	125·3	2·55	X=H
	(1·291)	(1·377)				
(IV)	1·23	1·37	114·4	125·4	2·92	X=C
(V)	1·21	1·36	115·7	125·3		
(VI)	1·212	1·346	115·9	126·3	2·63	X=H
(VII)	1·26	1·41	117	122		
(VIII)	1·231	1·306	123	121		
	1·217	1·315	118	122		
(IX)	1·20	1·35	117	125		
(X)	1·195	1·363	116·4	128·9	3·07	X=C
(X')	1·206	1·362	115·5	129·5	3·09	X=C
(XI)	1·197	1·377	115·8	128·9	3·08	X=C
(XII)	1·186	1·371	114·7	126·6		
(XIII)	1·271	1·323	114·3	127·7	2·73	X=H
(XIV)	1·22	1·38	116·0	124·5	2·94	X=C
(XV)	1·198	1·338	116·3	125·9	2·62	X=H

(I) Orthorhombic coumarin (Myasnikova, Davydova & Simonov, 1973; Gavuzzo, Mazza & Giglio, 1974; Song & Gordon, 1970). (II) Amyrolin (Kato, 1970). (III) 7-Hydroxy-4-methylcoumarin (this work). (IV) 3-(1-Phenylpropyl)-4-hydroxycoumarin (Bravic, Gaultier & Hauw, 1971). (V) (α-Phenyl β-acetyl)-3-ethyl-4-hydroxycoumarin (Bravic, Gaultier & Hauw, 1973). (VI) Avicennin (Lai & Marsh, 1974). (VII) 3-Bromo-4-hydroxycoumarin monohydrate (Gaultier & Hauw, 1965). (VIII) Dicoumarol (Bravic, Gaultier & Hauw, 1968). (IX) 4-Hydroxycoumarin monohydrate (Gaultier & Hauw, 1966). (X) Aflatoxin b₁, orthorhombic and monoclinic (X') forms (van Soest & Peerdeman, 1970a). (XI) Aflatoxin b₂ (van Soest & Peerdeman, 1970b). (XII) Aflatoxin b₁ chloroform complex (van Soest & Peerdeman, 1970c). (XIII) 7-Diethylamino-4-methylcoumarin (Messager & Delugeard, 1974). (XIV) 3,3′-Methylenebis-(6-bromo-4-hydroxycoumarin) (Alcock & Hough, 1972). (XV) 8-Methoxy-3′,2′;6,7-furocoumarin (Stemple & Watson, 1972).

Table 8. *Stacking mode of coumarin planes*

See Table 7 for compounds and references.

Compound	Space group	Z	a (Å)	b (Å)	c (Å)	β (°)	Interplanar spacing (Å)	Direction of stacking
(I)	Pca2₁	4	15·500	5·664	7·915		2·84	b
			15·416	5·676	7·917		2·84	
(II)	P2₁/c	4	8·428	11·112	12·328	103·14	3·08	a
(III)	P2₁2₁2₁	4	11·90	13·17	5·243		3·33	c
(IV)	P2₁/n	4	11·407	18·003	7·171	95·5	3·40	a
(V)	P2₁/c	4	8·957	10·915	18·465	108·2	3·4	a
(VI)	P1̄	2	11·209	10·196	9·634	α= 82·76	3·40	c
						β=109·43		
						γ=123·61		
(VII)	P2₁/n	4	7·11	13·73	10·14	92·5	3·42	a
(VIII)	P2₁/c	4	8·47	12·15	11·71	99·0	3·43	a
							3·61	a
(IX)	P2₁2₁2₁	4	10·11	12·18	6·95		3·44	c
(X')	P2₁	2	7·93	6·21	14·04	95·8	3·44	b
(X)	P2₁2₁2₁	4	7·84	6·36	28·35		3·46	b
(XI)	P2₁2₁2₁	4	6·927	10·146	20·171		3·46	a
(XII)	P2₁2₁2₁	4	6·16	8·04	36·25		3·48	a
(XIII)	P2₁	2	9·82	6·99	9·28	91·85	3·51	b
(XIV)	P4₁2₁2	4	5·496	5·496	54·49		3·52	b
(XV)	Pna2₁	4	12·911	15·804	4·882		3·58	c

packing coefficient of Kitaigorodskii (1961) amounts to 0·730, as compared with 0·714 for α-naphthol, 0·740 for 2,6-dimethylnaphthalene, and 0·753 for 1,4-naphthoquinone. The intermolecular distances of closest neighbours are: $H(M1)\cdots C(2^v)$ 2·63 Å, $C(12)\cdots C(2^v)$ 3·46 Å, $C(2)\cdots O(13^{iv})$ 3·00 Å, and $C(3)\cdots O(13^{iv})$ 3·17 Å. The relatively high melting point and density of this compound seem to result from the hydrogen bond and the dipole–dipole interactions.

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