

Determination of the Molecular Packing in the Crystal of Coumarin by Means of Potential-Energy Calculations

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Coumarin (*o*-coumaric acid lactone, $C_9H_6O_2$) forms orthorhombic crystals, space group $Pca2_1$, $Z=4$, $a=15.466$ (12), $b=5.676$ (6), $c=7.917$ (6) Å. The structure was solved by potential-energy calculations coupled with the minimum residual analysis. Three-dimensional X-ray data were measured with an off-line Siemens automatic single-crystal diffractometer by the ω -scan technique. The refinement was carried out by least-squares methods and the final R is 0.048. The carbon and oxygen atoms of coumarin lie in the same plane, the greatest deviation being 0.015 Å. The crystal packing is characterized mainly by van der Waals and dipole-dipole interactions. However, the dipole-dipole contribution to the total potential energy does not seem to determine the molecular packing.

Introduction

Van der Waals, hydrogen bonding, coulombic and ion-dipole semi-empirical potentials have been verified in known crystal structures and employed to solve the phase problem (Dosi, Giglio, Pavel & Quagliata, 1973; Coiro, Giglio, Lucano & Puliti, 1973, and references quoted therein). Another energy term, which may be important in the stabilization of the crystal lattice, is that arising from the interactions among permanent electric dipoles. In order to ascertain the role that the dipole-dipole energy plays in determining the energy minimum, which corresponds to the experimental packing, the crystal of coumarin has been examined. Coumarin is a rigid molecule (Fig. 1) which possesses a large dipole moment in the range 3.8–4.9 D (Jatkar & Deshpande, 1960). Since it is probable that several nearly equal van der Waals minima exist in the packing analysis of an aromatic molecule, especially if translational degrees of freedom are present in the crystal, it is possible that it is the dipole-dipole energy that is conclusive in locating the actual minimum. On the other hand Kitaigorodskii & Mirskaya (1965) have demonstrated that the dipole-dipole contribution to the total potential energy is small.

A further point of interest concerns the determination of the hydrogen atom positions in coumarin in order to compare distances between hydrogen atoms with those deduced from n.m.r. experiments on oriented molecules in a nematic mesophase (Cappelli, Di Nola & Segre, 1974). Although X-ray analysis is not very suitable for this purpose, the accurate location of the heavier atoms may lead to rather precise coordi-

ates for the hydrogen atoms. After this work was completed we became aware of the crystal structure determination of coumarin by Miasnikova, Davydova & Simonov (1973), hereinafter referred to as MDS.

Experimental

Crystals of coumarin (Merck-Schuchardt) were grown from ethyl ether in the form of colourless rhombohedral pyramids, m.p. 68°C. They are orthorhombic and the unit-cell dimensions, as measured on a diffractometer with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å) at room temperature, are: $a=15.466$ (12), $b=5.676$ (6), $c=7.917$ (6) Å. A density of 1.41 g cm⁻³, calculated for four molecules per unit cell, agrees with the value of 1.39 (1) g cm⁻³ measured by flotation in an aqueous solution of Cd(NO₃)₂.

The space groups $Pca2_1$ or $Pcam$ were indicated by the systematic absences $h0l$ and $0kl$ with h and l odd respectively. However, the space group $Pcam$ can be discarded because it would require the molecule to lie in a mirror plane at $c=\frac{1}{2}$, resulting in a systematic decrease in the $00l$ structure factors with increasing l . An inspection of the intensities shows that this is not true. A crystal of dimensions 1.4 × 0.4 × 0.5 mm ($\mu=1.08$ cm⁻¹) was mounted on the Siemens automatic single-crystal diffractometer AED, equipped with a scintillation counter and pulse-height analyser, the c axis being nearly coincident with the polar ϕ axis of the goniostat. The crystal was sealed in a glass capillary since coumarin sublimates very readily. Intensities were recorded at room temperature with zirconium-filtered Mo $K\alpha$ radiation. The setting angles χ , ϕ and

θ were accurately measured for 14 reflexions with a very narrow counter aperture and were used for a least-squares refinement of orientation. The reflexions were recorded up to $2\theta = 58^\circ$, each reflexion being scanned twice at a rate of $2.5^\circ \text{ min}^{-1}$ over a range from -0.75 to 0.75° . The moving-crystal stationary-detector (ω -scan) technique was employed. Background counts were taken for a time equal to that of the scan.

The intensities of 750 independent reflexions greater than $3\sigma(I)$ out of a possible total of 938 were collected. Four standard reflexions, measured after every 40 reflexions, remained essentially constant throughout the run, showing only the deviations from the mean predicted by counting statistics. The data were corrected first for counting losses (Arndt & Willis, 1966) with $t = 2.5 \times 10^{-6}$ s and $K=1$ and then for background. Standard deviations were assigned according to the formula $\sigma(I) = [P + B + (pI)^2]^{1/2}$ where P is the total integrated peak count obtained in the two scans, B is the total background count, $I = P - B$ and p is the 'ignorance factor' (Corfield, Doedens & Ibers, 1967) fixed as 0.06.

Molecular packing determination

The molecular packing was determined by means of potential-energy calculations (Coiro, Giglio & Quagliata, 1972). The packing energy in the crystal depends on three rotations (ψ_1, ψ_2, ψ_3) and two translations (t_x, t_y) along the a and b axes. The rotations were performed in a right-handed orthogonal framework $Oxyz$, coinciding with the crystallographic system $Oabc$. ψ_1, ψ_2 and ψ_3 stand for clockwise rotations about Oz, Ox and Oz , provided that they are accomplished in the order given, moving the orthogonal system and keeping the molecule fixed.

The starting model of the coumarin molecule was taken to be planar with bond lengths $C-C = 1.40, C=O = 1.24, C-O = 1.37$ and $C-H = 1.08$ Å, and trigonal bond angles, except for the following: $C(2)-O(1)-C(9) = 124.50^\circ$; $O(11)-C(2)-O(1) = 120.25^\circ$; $C(3)-C(2)-O(1) = C(10)-C(9)-O(1) = 117.75^\circ$; $O(11)-C(2)-C(3) = 122.00^\circ$. The atomic coordinates in Å of the molecule at $\psi_1 = \psi_2 = \psi_3 = 0^\circ$ and $t_x = t_y = 0$ Å were generated (Gavuzzo, Pagliuca, Pavel & Quagliata, 1972) and are reported in Table 1. The coefficients of the van der Waals potentials in the generalized form:

$$V(r) = \frac{a \exp(-br)}{r^a} - cr^{-6}$$

are listed in Table 2. Angular and translational increments of 20° and 0.5 Å were given in the first run, assuming a cut-off distance of 7.5 Å. The scanning of the multi-dimensional parametric space was performed in the reduced Cheshire cell of Hirshfeld (1968) taking into account both the space group and the molecular symmetry.

The van der Waals energy was estimated by considering all the intermolecular non-bonded interac-

Table 1. Atomic fractional coordinates in the starting position

	x	y	z
O(1)	-0.0864	0.0000	0.1534
C(2)	-0.0452	0.0000	0.3066
C(3)	0.0452	0.0000	0.3066
C(4)	0.0904	0.0000	0.1533
C(5)	0.0904	0.0000	-0.1533
C(6)	0.0452	0.0000	-0.3066
C(7)	-0.0452	0.0000	-0.3066
C(8)	-0.0904	0.0000	-0.1533
C(9)	-0.0452	0.0000	0.0000
C(10)	0.0452	0.0000	0.0000
O(11)	-0.0876	0.0000	0.4395
H(3)	0.0801	0.0000	0.4248
H(4)	0.1601	0.0000	0.1533
H(5)	0.1601	0.0000	-0.1533
H(6)	0.0801	0.0000	-0.4248
H(7)	-0.0801	0.0000	-0.4248
H(8)	-0.1601	0.0000	-0.1533

Table 2. The coefficients of the van der Waals potential functions used in the packing-energy calculations

The energy is in kcal per atom pair if the interatomic distance is in Å.

Interaction	$a (\times 10^{-3})$	b	c	d
H-H	6.6	4.080	49.2	0
H-C	44.8	2.040	125.0	6
H-O	42.0	2.040	132.7	6
C-C	301.2	0.000	327.2	12
C-O	278.7	0.000	342.3	12
O-O	259.0	0.000	358.0	12

tions between 17 atoms of one molecule and the atoms of the nearest 13 molecules with multiplicity 2. The regions of minima were subsequently explored by decreasing the angular and translational increments finally to 0.5° and 0.0125 Å, by a program, written by C. Quagliata, in the following manner. Each parameter to be optimized is changed either positively or negatively by a prespecified amount. If a successful change occurs the parameter assumes the value corresponding to the lowest energy (otherwise it is left unchanged) and the same procedure is then repeated for the other parameters. The new set of parameters is again tested as indicated above and another set is determined. This process continues until the energy improvement for an entire cycle is less than a prespecified amount E . Thereafter the increments and E are halved and the same process applied anew. This analysis is continued until it fails to decrease the energy more than an amount fixed at the beginning of the program. As an option the minimum search may be interrupted if the increments of the parameters become smaller than some values previously established. Two minima noticeably deeper than the others were found with parameters:

- (I) 23.5, 108.0, 76.0° ; 5.36, 1.22 Å;
 (II) 25.5, 109.0, 83.0° ; 1.70, 1.34 Å.

Four parameters are almost the same, while t_x differs by about $a/4$. Their energy values are nearly equal, being separated by only 0.2 kcal. These two minima were tested by computing R for the 52 reflexions with $\sin \theta/\lambda \leq 0.25 \text{ \AA}^{-1}$ as a function of the five rotational and translational degrees of freedom (Damiani, Giglio, Liquori & Ripamonti, 1967). The best R values were 0.22 and 0.10 for (I) and (II) respectively and it was therefore decided to start the refinement of (II).

Refinement of the structure

The programs of Domenicano, Spagna & Vacigi (1969) were used to refine the structure and for the geometrical calculations. Atomic scattering factors for carbon and oxygen were taken from Cromer & Mann (1968) and for hydrogen from Hanson, Herman, Lea & Skillman (1964).

Refinement proceeded by isotropic and anisotropic block-diagonal least-squares methods and was carried out with only the 750 observed reflexions. The function minimized is $\sum w(|F_o| - |F_c|)^2$, w being equal to $1/\sigma^2(F_o)$. A difference synthesis showed all the hydrogen atoms at reasonable positions, on peaks between 0.20 and 0.37 $e \text{ \AA}^{-3}$. The hydrogen atoms were included in the last three cycles with the same isotropic B of the carbon atom to which each is linked. Their positional parameters were held fixed during the refinement. The refinement was considered to be complete when the parameter shifts were less than 50% of the estimated standard deviations. The final R and weighted R were 0.048 and 0.071 respectively for the observed reflexions. The final atomic coordinates and anisotropic thermal parameters are reported in Tables 3 and 4 with their standard deviations. The bond

Table 3. Final fractional coordinates with their standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.1541 (1)	0.5023 (4)	-0.1211 (4)
C(2)	0.2406 (2)	0.4576 (5)	-0.1348 (5)
C(3)	0.2726 (2)	0.2441 (6)	-0.0567 (5)
C(4)	0.2199 (2)	0.0930 (6)	0.0237 (4)
C(5)	0.0703 (2)	0.0027 (6)	0.1223 (5)
C(6)	-0.0155 (3)	0.0616 (6)	0.1283 (5)
C(7)	-0.0435 (2)	0.2639 (8)	0.0520 (5)
C(8)	0.0130 (2)	0.4140 (6)	-0.0325 (5)
C(9)	0.0994 (2)	0.3514 (5)	-0.0364 (4)
C(10)	0.1295 (2)	0.1440 (5)	0.0375 (4)
O(11)	0.2836 (2)	0.5977 (5)	-0.2123 (5)
H(3)	0.326	0.214	-0.065
H(4)	0.237	-0.044	0.084
H(5)	0.091	-0.154	0.160
H(6)	-0.046	0.016	0.217
H(7)	-0.102	0.295	0.058
H(8)	-0.011	0.534	-0.096

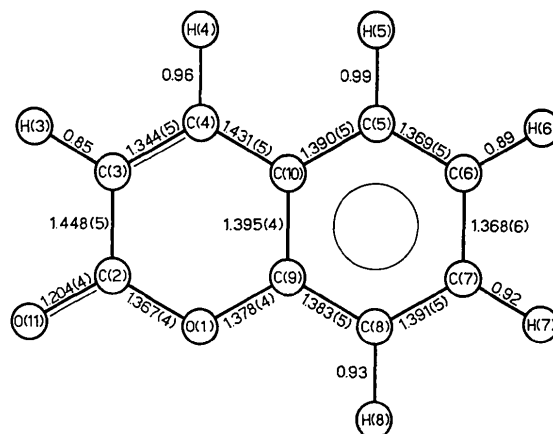


Fig. 1. Bond distances with estimated standard deviations in brackets. The estimated standard deviations of the C-H bonds are omitted.

Table 4. Final values of the thermal parameters with their standard deviations in parentheses

The form of the anisotropic temperature factor is $\exp[-10^{-4}(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)]$.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
O(1)	49 (1)	2 (4)	-1 (3)	263 (6)	108 (10)	162 (3)
C(2)	45 (1)	-30 (7)	14 (4)	322 (9)	-50 (14)	145 (4)
C(3)	39 (1)	28 (6)	6 (5)	357 (10)	-18 (15)	171 (5)
C(4)	45 (1)	36 (6)	-5 (5)	283 (8)	8 (13)	150 (5)
C(5)	51 (1)	-40 (6)	3 (5)	320 (9)	50 (15)	146 (5)
C(6)	57 (2)	-72 (8)	14 (6)	447 (15)	63 (18)	153 (5)
C(7)	41 (1)	-5 (8)	6 (5)	473 (13)	-67 (17)	171 (5)
C(8)	48 (1)	26 (7)	-18 (5)	335 (10)	18 (14)	155 (5)
C(9)	44 (1)	-16 (5)	-8 (4)	216 (7)	-9 (10)	112 (4)
C(10)	41 (1)	2 (5)	-15 (4)	215 (7)	-37 (10)	126 (4)
O(11)	55 (1)	-76 (5)	47 (6)	416 (8)	41 (14)	245 (5)
H(3)	4.0					
H(4)	3.7					
H(5)	4.1					
H(6)	4.7					
H(7)	4.6					
H(8)	4.0					

Table 5 (cont.)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
11	5	03	98	179	2	9	71	21	-84	14	0	72	66	0	14	6	22	22	-97
11	5	141	129	5	3	10	15	161		14	0	72	66	0	14	6	22	22	-97
11	6	169	89	151						14	0	72	66	0	14	6	22	22	-97
11	6	103	133	-11						14	2	37	37	65	14	2	15	16	174
11	7	82	73	-1						14	4	20	22	114	14	4	20	21	110
11	9	23	74	-11						14	4	20	21	110	14	4	20	21	110
11	1	103	117	-86	12	0	90	94	1						14	4	20	21	110
11	2	20	37	23	12	1	35	35	-100						14	4	20	21	110
11	3	101	109	-108	12	3	40	41	156						14	4	20	21	110
11	4	73	77	-90	12	6	18	18	71						14	3	27	24	100
11	5	15	30	-78	12	8	26	26	108						14	3	27	24	100
11	6	51	52	-90	12	1	35	35	-100						14	3	27	24	100
11	8	24	23	-84	12	2	36	36	90						14	4	20	21	110
					12	5	14	14	21						14	5	22	22	68
					12	8	14	12	-12						14	1	12	14	10
11	1	91	30	-152	14	3	24	25	142						14	3	24	25	142
11	2	80	73	-170	14	2	37	37	138						14	2	17	18	135
11	4	40	51	150	14	5	40	40	-167						14	5	40	40	-167
11	7	20	10	11	14	3	12	18	-133						14	3	12	18	-133
11	1	13	13	150	14	1	16	14	140						14	1	16	14	140
11	2	27	27	-90	14	2	17	17	135						14	2	17	17	135
11	4	17	17	-115	14	4	17	17	-115						14	4	17	17	-115
11	5	15	15	150	14	5	15	15	150						14	5	15	15	150
11	6	24	24	0	14	6	24	24	0						14	6	24	24	0
11	8	15	15	145	14	8	15	15	145						14	8	15	15	145
11	1	35	35	90	15	1	34	34	41						15	1	34	34	41
11	3	15	15	150	15	3	16	16	100						15	3	16	16	100
11	5	15	15	145	15	5	16	16	100						15	5	16	16	100
11	6	24	24	0	15	6	24	24	0						15	6	24	24	0
11	8	15	15	145	15	8	16	16	100						15	8	16	16	100
12	0	31	10	140	15	0	32	32	0						15	0	32	32	0
12	1	34	63	-20	15	1	18	18	100						15	1	18	18	100
12	2	71	72	-111	15	2	24	24	79						15	2	24	24	79
12	3	117	116	59	15	3	25	25	178						15	3	25	25	178
12	4	146	147	-130	15	4	26	26	152						15	4	26	26	152
12	5	112	115	32	15	5	26	26	152						15	5	26	26	152
12	6	47	47	-90	15	6	17	17	100						15	6	17	17	100
12	7	83	78	-53	15	7	16	16	105						15	7	16	16	105
12	8	63	61	-84	15	8	16	16	105						15	8	16	16	105
12	0	61	62	100	15	0	17	20	-90						15	0	17	20	-90
12	1	98	97	-89	15	1	17	17	89						15	1	17	17	89
12	2	106	106	194	15	2	18	18	100						15	2	18	18	100
12	3	93	90	-87	15	3	18	18	100						15	3	18	18	100
12	4	13	11	191	15	4	23	23	-97						15	4	23	23	-97
12	5	77	74	-120	15	5	23	23	-97						15	5	23	23	-97
12	6	64	65	-103	15	6	24	24	0						15	6	24	24	0
12	7	30	30	177	15	7	24	24	0						15	7	24	24	0
12	0	111	101	0	16	0	57	50	100						16	0	57	50	100
12	1	114	113	-100	16	1	39	43	108						16	1	39	43	108
12	2	42	42	2	16	2	43	43	108						16	2	43	43	108
12	3	93	90	-87	16	3	43	43	108						16	3	43	43	108
12	4	56	56	107	16	4	27	26	152						16	4	27	26	152
12	5	43	43	127	16	5	31	30	115						16	5	31	30	115
12	6	24	24	99	16	6	26	26	81						16	6	26	26	81
12	7	18	18	-113	16	7	26	26	81						16	7	26	26	81
12	8	16	12	-6	16	8	27	27	52						16	8	27	27	52
12	0	16	13	0	16	0	27	32	0						16	0	27	32	0
12	1	67	64	68	16	1	31	34	100						16	1	31	34	100
12	2	70	68	64	16	2	30	34	100						16	2	30	34	100
12	3	49	49	177	16	3	16	19	73						16	3	16	19	73
12	4	24	27	14	16	4	16	19	73						16	4	16	19	73
12	5	26	27	142	16	5	21	16	113						16	5	21	16	113
12	6	26	27	142	16	6	21	16	113						16	6	21	16	113

and are somewhat below normal. This shortening may be due to thermal libration. The double-bond character for C(3)–C(4) appears to be retained as for 4-hydroxycoumarin (1.34₄ and 1.35 Å respectively). Furthermore the C(2)–C(3) and C(4)–C(10) bonds, which are adjacent to the double bond, are systematically longer than 1.40 Å in both compounds. The bonds C(2)–O(1) and C(9)–O(1) are nearly equal (about 1.37

Table 6. Differences between the bond lengths and angles of this work and of MDS

The difference is calculated assigning a minus sign to the value reported by MDS.

C(2)–O(11)	-0.012 Å	C(3)–C(2)–O(11)	-0.4°
C(2)–O(1)	0.001	O(1)–C(2)–O(11)	1.1
C(9)–O(1)	-0.001	C(3)–C(2)–O(1)	-0.6
C(8)–C(9)	-0.007	C(2)–O(1)–C(9)	0.1
C(7)–C(8)	0.010	C(10)–C(9)–O(1)	0.0
C(6)–C(7)	-0.034	C(8)–C(9)–O(1)	-0.1
C(5)–C(6)	-0.008	C(8)–C(9)–C(10)	0.2
C(5)–C(10)	0.000	C(7)–C(8)–C(9)	-1.4
C(9)–C(10)	0.003	C(5)–C(6)–C(7)	-1.7
C(4)–C(10)	-0.020	C(5)–C(6)–C(10)	-0.3
C(3)–C(4)	0.007	C(6)–C(5)–C(10)	0.2
C(2)–C(3)	0.010	C(5)–C(10)–C(9)	-0.3
		C(4)–C(10)–C(5)	-0.2
		C(4)–C(10)–C(9)	0.5
		C(3)–C(4)–C(10)	-0.1
		C(2)–C(3)–C(4)	0.2

Å) except in the case of 3-bromo-4-hydroxycoumarin (1.31 and 1.43 Å) where the estimate of these bond lengths is less reliable.

The C(7)–C(8)–C(9) bond angle is smaller than 120° in all the compounds. The angles C(8)–C(9)–O(1) and C(4)–C(10)–C(5) at the junction of the two rings are respectively smaller and greater than 120° in these three molecules and cause the approach of O(1) to C(8) and the removal of C(4) from C(5). The angles around C(2) in coumarin (Fig. 2) agree with those of 4-hydroxycoumarin reported in parentheses: 125.6° (125°), 117.3° (117°) and 117.2° (117°). This geometry resembles that of a carboxylic group. The least-squares plane passing through the carbon and oxygen atoms, all considered with unit weight, is:

$$2.5363x + 2.4824y + 6.7287z - 0.9969 = 0.$$

This equation is referred to the crystal axes and x , y and z are fractional coordinates. The atomic deviations from the least-squares plane are reported in Table 7. The molecule is planar, as is 4-hydroxycouma-

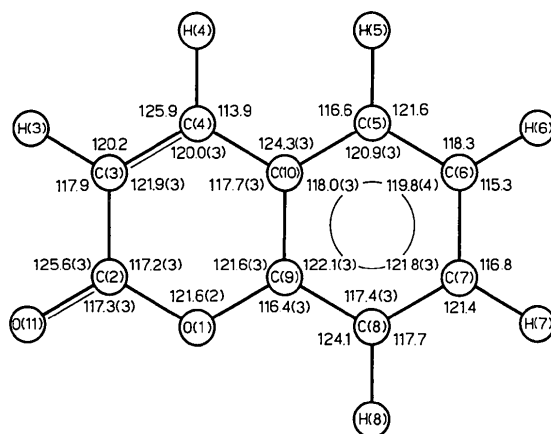


Fig. 2. Bond angles with estimated standard deviations in brackets. The estimated standard deviations of the C–C–H angles are omitted.

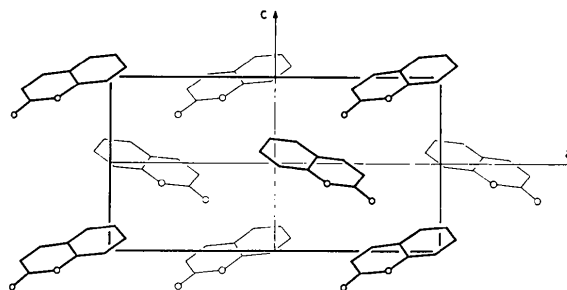


Fig. 3. View of the packing along b . The circles indicate the oxygen atoms.

rin, the greatest deviation being 0.015 Å. The molecular packing is shown in Fig. 3. All intermolecular approaches agree well with the normal van der Waals separations. The shortest distances for each type of atom-pair are: H...H=2.87, H...C=2.97, H...O=2.60, C...C=3.43, C...O=3.37, O...O=3.42 Å, using the coordinates of the hydrogen atoms found in the difference synthesis. The oxygen atom O(11) is involved in many intermolecular contacts and is probably the atom which contributes most to the stabilization of the crystal lattice by means of van der Waals interactions.

Table 7. Atomic deviations (Å) from the least-squares plane

O(1)	-0.007	C(5)	-0.012	C(9)	-0.009
C(2)	-0.007	C(6)	-0.002	C(10)	0.007
C(3)	-0.007	C(7)	0.007	O(11)	0.007
C(4)	0.015	C(8)	0.006		

There are several types of van der Waals interactions, all equally important. Nevertheless the energy minimum corresponding to the actual structure has been located with reasonable accuracy. This is a satisfactory test of the qualitative reliability of the potentials employed in the packing analysis.

Coumarin oriented in a nematic mesophase has been studied by n.m.r. (Capelli, Di Nola & Segre, 1974). The intramolecular H-H distances were determined on the basis of the dipole-dipole coupling constants, assuming the H(4)-H(5) distance to be 2.49 Å as in deuterated naphthalene (Pawley & Yeats, 1969). Since the hydrogen atoms cannot be located with sufficient accuracy by X-ray diffraction methods we have preferred to generate them on the bisectors of the C-C-C angles at the expected positions (C-H=1.08 Å) in order to verify the n.m.r. results. The n.m.r. and X-ray results (Table 8) are in good agreement.

Table 8. Comparison between n.m.r. and X-ray intramolecular H-H distances (Å)

	N.m.r.	X-ray
H(1)-H(2)	2.47	2.41
H(1)-H(3)	4.80	4.78
H(1)-H(4)	6.73	6.70
H(1)-H(5)	7.10	7.08
H(1)-H(6)	5.77	5.82
H(2)-H(3)	2.54	2.57
H(2)-H(4)	4.84	4.83
H(2)-H(5)	5.96	5.92
H(2)-H(6)	5.53	5.53
H(3)-H(4)	2.49	2.44
H(3)-H(5)	4.31	4.23
H(3)-H(6)	4.97	4.94
H(4)-H(5)	2.49	2.44
H(4)-H(6)	4.31	4.28
H(5)-H(6)	2.49	2.48

This agreement, which would be even better if the H(4)-H(5) distance were slightly decreased, shows the possibility of applying n.m.r. spectroscopy for direct resolution with high precision to structural problems concerning the determination of the coordinates of hydrogen atoms. At present, unfortunately, this analysis can only be carried out on relatively simple molecules containing at most eight hydrogen atoms not related by symmetry (Diehl & Khetrapal, 1969).

The dipole-dipole energy was calculated from

$$V(r_{ab}, \theta_a, \theta_b, \varphi) = -14.393 \mu_a \mu_b r_{ab}^{-3} (2 \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos \varphi)$$

where μ_a and μ_b represent the electric moments of two point dipoles r_{ab} apart, θ_a and θ_b are the angles formed by the vectors of magnitude μ_a and μ_b respectively with r_{ab} , and φ is the dihedral angle between the planes passing through μ_a , r_{ab} and μ_b , r_{ab} . V is in kcal if μ_a and μ_b are in Debye units and r_{ab} in Å.

The induced effects, which are generally less important, were neglected. A dipole moment of 4.5 D was assigned to the coumarin molecule and the corresponding vector was oriented in the molecular plane on a straight line passing approximately through the centroid of the C(2)-O(1) ring and intersecting the C(2)-O(1) bond in such a way as to make an angle of about 15° with the axis of the carbonyl group (Le Fèvre & Le Fèvre, 1937; Jatkar & Deshpande, 1960). In additional calculations the direction of the molecular dipole moment was varied over a large range. In fact the dipole-dipole energy did not reach the best value near the actual packing. Moreover this energy is strongly dependent on the orientation and on the application point of the dipole moment vector.

Therefore we were not able to narrow the range of energy values relative to the experimental structure. However it is clear that the dipole-dipole energy term is unnecessary to establish the molecular packing, as for 5 α -androstan-3,17-dione (Coiro, Giglio, Lucano & Puliti, 1973).

If this hypothesis is supported by other evidence the tedious computation of this energy term, not always feasible because many molecular dipole moments and their directions have been not determined, can be neglected.

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The Crystal and Molecular Structure of 2,3-*exo*-Ferrocene-4,4-dimethylbicyclo[3,2,1]octa-2,6-diene, a Product of the Reaction of Cyclopentadiene with the 2-Ferrocenyl-2-propyl Cation

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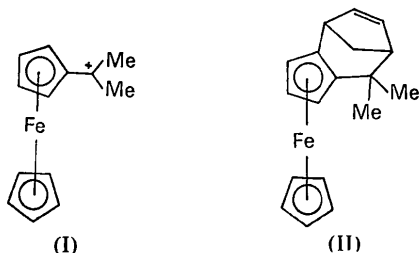
(Received 3 December 1973; accepted 2 January 1974)

(π -C₅H₅)Fe(π -C₁₃H₁₅) crystallizes in space group $P2_1/c$, $a = 10.733$, $b = 8.122$, $c = 16.873$ Å, $\beta = 110.95^\circ$, with four formula units in the unit cell. The crystals are reflexion twins about the (001) face and the structure was determined with X-ray data from one half of the twin and refined by the least-squares method to $R = 0.091$ for 842 independent reflexions. The substituted cyclopentadienyl moiety had the predicted tricyclic configuration formed with a bridging ethylene group. The cyclopentadienyl rings are in the eclipsed conformation and inclined at an angle of 7° .

Introduction

Turbitt & Watts (1974) reported that the ferrocenyl carbonium ion (I) reacts stereospecifically with cyclopentadiene to give a single product for which the structure (II) was proposed from ¹H n.m.r. evidence.

The crystal structure of this product has been determined in order to confirm the proposed structure and to establish its stereochemical features. The results have been reported in a preliminary communication (Cameron, Maguire, Turbitt & Watts 1973).



Experimental

The crystals were prepared by Turbitt & Watts (1974).

Crystal data

C₁₈H₂₀Fe, M.W. 519.14, $F(000) = 616$.

Monoclinic: $a = 10.733 \pm 0.003$, $b = 8.122 \pm 0.001$, $c = 16.873 \pm 0.005$ Å, $\beta = 110.95 \pm 0.01^\circ$.

$D_m = 1.414$, $D_c = 1.412$ g cm⁻³, Mo $K\alpha$ $\lambda = 0.7107$ Å, $\mu = 10.15$ cm⁻¹.

Systematic extinctions $h0l$: $l = 2n + 1$, $0k0$: $k = 2n + 1$; space group $P2_1/c(C_{2h}^2, \text{No. } 14)$.

The crystals are thin orange plates and all appear to be reflexion twins about the (001) face which is parallel to the face of the plates. It was not possible to bisect any crystal and retain a single crystal large enough for X-ray intensity measurements. A twinned crystal was mounted about the unique axis and the intensities of 924 independent reflexions (with $I > 2\sigma$)