Acta Cryst. (1976). B32, 2450

The Crystal and Molecular Structure of 2-Pivaloyl-1,3-indandione

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(*Received* 20 *January* 1976; *accepted* 1 *March* 1976)

The crystal structure of 2-pivaloyl-1,3-indandione, $C_{14}O_3H_{14}$, has been derived from three-dimensional X-ray diffractometer data. The crystal cell is monoclinic, space group $P2_1$ (or possibly $P2_1/m$); $Z=2$; with the unit cell $a=8{\cdot}409$ (3), $b=6{\cdot}889$ (3), $c=10{\cdot}512$ (3) Å and $\beta=105{\cdot}20$ (3)°. The structure was determined by direct methods. Least-squares refinement of the structural parameters gave unweighted linear R values of 0·045 for a noncentrosymmetric model ($P2_1$) and 0·051 for a centrosymmetric one ($P2_1/m$). The molecule crystallizes in an enolic form which is stabilized by an intramolecular hydrogen bond. The crystal structure is held together by van der Waals forces.

Introduction

There exist two different classes of anticoagulants, the 4-hydroxycoumarins and the 1,3-indandiones. They are competitive inhibitors of NADH and NADPH (nicotinamide–adenine–dinucleotide) in the vitamin K dependent biosynthesis or activation of special blood coagulation proteins (Ernster, Lind & Rase, 1972). These two types of inhibitors have the same effect but probably work in different ways. 2-Pivaloyl-1,3-indandione has been widely used clinically (Hanstein & Markwardt, 1971). The present investigation is part of a research programme for structural studies of anticoagulants, such as different coumarin and indandione derivatives.

Large yellow crystals of 2-pivaloyl-1,3-indandione were obtained by slow evaporation of a methanol solution of a commercially available preparation (Ferrosan AB). Guinier, de Jong–Bouman and precession photographs of the crystal suggested space group $P2_1$ or possibly $P2_1/m$ with $Z=2$. The single crystal selected for data collection had the approximate dimensions 0·30 × 0·40 × 0·30 mm. The unit-cell parameters were refined by means of least-squares fitting of approximate parameter values to data obtained from a Guinier powder photograph with potassium chloride ($a=6{\cdot}29194$ Å) as an internal standard. Three-dimensional single-crystal X-ray diffraction data were collected with a Siemens AED diffractometer and graphite monochromatized Cu $K\alpha$ radiation. All the 1240 independent reflexions with $\theta \leq 70°$ were measured, but only the 1089 reflexions with $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0{\cdot}10$ were used in the subsequent calculations. The net intensities were corrected for Lorentz, polarization and absorption effects.

Several different attempts to solve the crystal structure in space groups $P2_1$ and $P2_1/m$ by conventional direct-method procedures with two different computer program systems (Main, Woolfson & Germain, 1971; Norrestam, 1972) failed, although the E maps for the best solutions had as many as 14 chemically reasonable peaks among the 20 highest. Least-squares refinements of the derived models gave no reasonable convergence. Since several of the best E maps showed similar molecular fragments at different positions in the asymmetric unit of the cell, it was decided to use translation functions (*cf.* Karle, 1972) to determine the position of a molecular fragment found by direct methods. Fig. 1 shows a map of a $Q(x,z)$ function (Tollin, 1966) calculated for a 14-atom fragment from the 226 highest E values. As seen, this map contains several local maxima which might explain the problems with correct origin positioning encountered when direct methods were applied. However, when the highest peak at $(x,z)=(0{\cdot}44,\ 0{\cdot}03)$, marked by an asterisk in the map in Fig. 1, was used as the translation vector for the 14-atom fragment, a least-squares refinement of the positions converged smoothly. Subsequent difference electron density calculations and

Table 1. *Fractional atomic coordinates for the* O *and* C *atoms*

The estimated standard deviations are given in parentheses.

	x	y	z
O(3)	0·1224 (2)	0·25	0·5249 (2)
O(2)	0·4462 (2)	0·2550 (12)	0·9390 (2)
O(1)	0·6607 (2)	0·2550 (12)	0·8104 (2)
C(1)	0·5419 (2)	0·2493 (12)	0·7108 (2)
C(2)	0·3692 (2)	0·2466 (12)	0·7107 (2)
C(3)	0·2713 (2)	0·2464 (12)	0·5716 (2)
C(4)	0·3660 (3)	0·2485 (13)	0·3550 (2)
C(5)	0·5032 (3)	0·2492 (13)	0·3038 (2)
C(6)	0·6619 (3)	0·2413 (12)	0·3863 (3)
C(7)	0·6900 (3)	0·2472 (13)	0·5219 (2)
C(8)	0·5530 (3)	0·2507 (11)	0·5730 (2)
C(9)	0·3942 (2)	0·2479 (12)	0·4906 (2)
C(10)	0·3265 (3)	0·2467 (12)	0·8290 (2)
C(11)	0·1540 (3)	0·2436 (12)	0·8492 (2)
C(12)	0·0663 (7)	0·0661 (11)	0·7853 (7)
C(13)	0·0621 (7)	0·4340 (11)	0·7879 (6)
C(14)	0·1617 (4)	0·2420 (17)	0·9970 (3)

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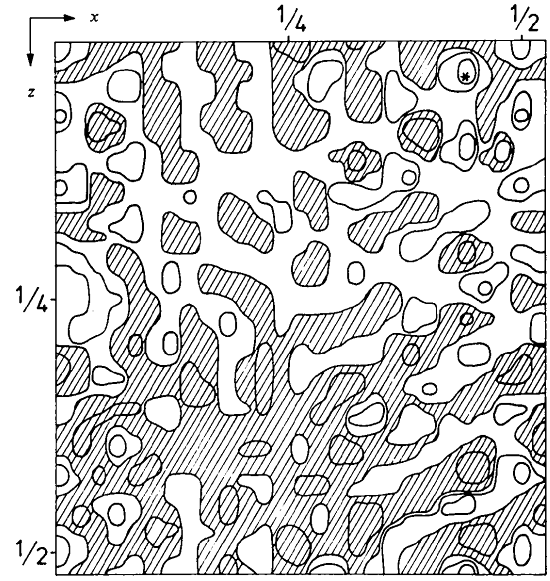
least-squares refinements revealed the positions of all the remaining atoms, including the hydrogens. Least-squares refinement of the 17 non-hydrogen atoms with anisotropic temperature factors and 14 hydrogen atoms with isotropic temperature factors yielded an R value ($R=\sum\Delta|F|/\sum|F_{\rm obs}|$) of 0·045 (1086 reflexions). In this final refinement the three strongest reflexions, all with $|F_{\rm obs}|/|F_{\rm calc}|<0{\cdot}75$, were given zero weight, since they suffered from extinction. The R value for all the 1089 reflexions used became 0·058. The scattering factors for carbon and oxygen were taken from Hanson, Herman, Lea & Skillman (1964) and for hydrogen



$Q(x,z)$

Fig. 1. $Q(x,z)$ map of 2-pivaloyl-1,3-indandione, contoured at 0, 20, 40, 60 and 80% of the maximum density. The shaded area has a density less than 40%.

Table 3. *Fractional atomic coordinates and isotropic temperature factors for* H *atoms*

The estimated standard deviations are given in parentheses.

	x	y	z	B
H(2)	0·550 (3)	0·289 (5)	0·913 (3)	3·8 (6)
H(4)	0·244 (4)	0·210 (7)	0·298 (3)	5·7 (8)
H(5)	0·490 (4)	0·281 (6)	0·202 (3)	5·0 (8)
H(6)	0·759 (3)	0·279 (5)	0·343 (2)	2·9 (5)
H(7)	0·792 (3)	0·285 (4)	0·574 (2)	2·3 (5)
H(121)	0·055 (4)	0·058 (5)	0·692 (4)	1·7 (5)
H(122)	−0·026 (5)	0·044 (6)	0·823 (4)	5·3 (9)
H(123)	0·119 (5)	−0·041 (5)	0·823 (4)	2·5 (6)
H(131)	0·044 (9)	0·452 (11)	0·668 (7)	10·9 (2·0)
H(132)	−0·071 (4)	0·509 (5)	0·785 (3)	3·1 (6)
H(133)	0·136 (9)	0·569 (12)	0·838 (8)	10·7 (1·9)
H(141)	0·044 (4)	0·222 (8)	1·005 (3)	5·2 (7)
H(142)	0·189 (7)	0·370 (9)	1·018 (5)	7·0 (1·4)
H(143)	0·233 (5)	0·135 (7)	1·050 (4)	4·6 (8)

Table 4. *Intramolecular bond distances* (Å)

The estimated standard deviations are given in parentheses.

C(1)—O(1)	1·244 (3)	O(2)—H(2)	1·01 (3)
C(1)—C(2)	1·452 (2)	C(4)—H(4)	1·08 (4)
C(1)—C(8)	1·476 (3)	C(5)—H(5)	1·07 (4)
C(2)—C(3)	1·478 (3)	C(6)—H(6)	1·07 (3)
C(2)—C(10)	1·382 (3)	C(7)—H(7)	0·93 (3)
C(3)—O(3)	1·219 (2)	C(12)–H(121)	0·96 (5)
C(3)—C(9)	1·502 (3)	C(12)–H(122)	0·97 (5)
C(4)—C(5)	1·395 (3)	C(12)–H(123)	0·90 (4)
C(4)—C(9)	1·382 (3)	C(13)–H(131)	1·24 (8)
C(5)—C(6)	1·389 (4)	C(13)–H(132)	1·12 (4)
C(6)—C(7)	1·383 (4)	C(13)–H(133)	1·16 (9)
C(7)—C(8)	1·393 (3)	C(14)–H(141)	1·03 (4)
C(8)—C(9)	1·388 (3)	C(14)–H(142)	0·92 (7)
C(10)–O(2)	1·320 (3)	C(14)–H(143)	1·02 (5)
C(10)–C(11)	1·520 (3)		
C(11)–C(12)	1·494 (10)		
C(11)–C(13)	1·572 (10)		
C(11)–C(14)	1·538 (4)		

Table 2. *Anisotropic thermal parameters* ($\times 10^4$) *for the* O *and* C *atoms*

The estimated standard deviations are given in parentheses. The temperature factor expression used is

$$\exp\left[-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})\right].$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(3)	117 (2)	348 (5)	86 (2)	10 (16)	49 (3)	80 (13)
O(2)	154 (3)	464 (7)	68 (2)	−101 (18)	74 (3)	−90 (14)
O(1)	120 (2)	403 (6)	84 (2)	−34 (17)	49 (3)	−11 (16)
C(1)	122 (3)	194 (4)	77 (2)	45 (19)	70 (4)	15 (16)
C(2)	116 (3)	180 (4)	71 (2)	−11 (19)	70 (3)	27 (14)
C(3)	125 (3)	173 (4)	73 (2)	−21 (18)	71 (4)	3 (15)
C(4)	186 (4)	212 (5)	74 (2)	39 (22)	93 (4)	−27 (16)
C(5)	240 (5)	208 (5)	84 (2)	−53 (25)	159 (5)	10 (17)
C(6)	202 (4)	186 (5)	115 (3)	56 (20)	195 (5)	−16 (16)
C(7)	141 (3)	210 (5)	105 (2)	8 (21)	126 (5)	−1 (18)
C(8)	133 (3)	157 (4)	82 (2)	−14 (19)	95 (4)	−32 (14)
C(9)	136 (3)	152 (4)	75 (2)	33 (19)	89 (4)	−1 (15)
C(10)	138 (3)	198 (4)	71 (2)	−54 (20)	77 (4)	33 (16)
C(11)	151 (3)	217 (5)	83 (2)	106 (18)	125 (4)	63 (14)
C(12)	146 (8)	218 (11)	141 (8)	−28 (14)	175 (13)	26 (15)
C(13)	189 (10)	211 (11)	109 (7)	65 (15)	110 (12)	16 (13)
C(14)	213 (5)	359 (9)	93 (3)	−60 (33)	167 (5)	−31 (24)

from Stewart, Davidson & Simpson (1965). The fractional atomic coordinates, thermal parameters, bond lengths and bond angles are listed in Tables 1–5.*

Table 5. *Intramolecular bond angles* (°)

The estimated standard deviations are given in parentheses.

O(1)—C(1)—C(2)	125·7 (2)
O(1)—C(1)—C(8)	125·6 (2)
C(2)—C(1)—C(8)	108·7 (2)
C(1)—C(2)—C(3)	107·3 (2)
C(1)—C(2)—C(10)	119·7 (2)
C(3)—C(2)—C(10)	133·0 (2)
O(3)—C(3)—C(2)	130·2 (2)
O(3)—C(3)—C(9)	123·9 (2)
C(2)—C(3)—C(9)	105·9 (2)
C(5)—C(4)—C(9)	117·5 (2)
C(4)—C(5)—C(6)	121·0 (3)
C(5)—C(6)—C(7)	121·3 (3)
C(6)—C(7)—C(8)	117·6 (3)
C(1)—C(8)—C(7)	130·5 (2)
C(1)—C(8)—C(9)	108·3 (2)
C(7)—C(8)—C(9)	121·1 (2)
C(3)—C(9)—C(4)	128·5 (2)
C(3)—C(9)—C(8)	109·8 (2)
C(4)—C(9)—C(8)	121·3 (2)
O(2)—C(10)-C(2)	118·0 (3)
O(2)—C(10)-C(11)	114·5 (2)
C(2)—C(10)-C(11)	127·5 (2)
C(10)—C(11)-C(12)	109·0 (6)
C(10)—C(11)-C(13)	108·4 (6)
C(10)—C(11)-C(14)	110·6 (2)
C(12)—C(11)-C(13)	111·5 (4)
C(12)—C(11)-C(14)	109·5 (6)
C(13)—C(11)-C(14)	107·8 (6)
C(1)—O(1)—H(2)	93 (2)
C(10)—O(2)—H(2)	107 (2)
C(5)—C(4)—H(4)	123 (2)
C(9)—C(4)—H(4)	117 (2)
C(4)—C(5)—H(5)	120 (2)
C(6)—C(5)—H(5)	118 (2)
C(5)—C(6)—H(6)	116 (2)
C(7)—C(6)—H(6)	119 (2)
C(6)—C(7)—H(7)	120 (2)
C(8)—C(7)—H(7)	120 (2)
C(11)—C(12)-H(121)	114 (3)
C(11)—C(12)-H(122)	107 (3)
C(11)—C(12)-H(123)	110 (3)
H(121)-C(12)-H(122)	122 (4)
H(121)-C(12)-H(123)	108 (4)
H(122)-C(12)-H(123)	93 (4)
C(11)—C(13)-H(131)	115 (4)
C(11)—C(13)-H(132)	105 (2)
C(11)—C(13)-H(133)	110 (4)
H(131)-C(13)-H(132)	98 (4)
H(131)-C(13)-H(133)	107 (6)
H(132)-C(13)-H(133)	123 (5)
C(11)—C(14)-H(141)	107 (2)
C(11)—C(14)-H(142)	100 (4)
C(11)—C(14)-H(143)	115 (3)
H(141)-C(14)-H(142)	107 (5)
H(141)-C(14)-H(143)	107 (4)
H(142)-C(14)-H(143)	119 (5)

Discussion

As shown in Fig. 2 the crystal structure can be described as nearly planar foursomes of molecules stacked along the *b*-axis. Each plane contains a rectangular arrangement of molecules with all their tertiary butyl groups pointing in the same direction. By virtue of the twofold screw axis, adjacent planes contain molecules with opposite orientations. The molecular packing along the *b* axis is such that the molecules become stacked upon each other with an interplanar spacing of 3·45 Å. As seen in Table 6, the shortest intermolecular distance is 3·46 Å. Thus, the molecules of the crystal structure appear to be held together by van der Waals forces. 2-Pivaloyl-1,3-indandione, which is a β-tricarbonyl compound, may exist in four possible tautomeric forms (Fig. 3). The present investigation shows that 2-pivaloyl-1,3-indandione crystallizes in an enolic form (Fig. 4) which is stabilized by a rather short intramolecular hydrogen bond [O···O distance 2·522 (3) Å] between the keto oxygen O(1) and the enolic oxygen O(2) (Table 7). The atoms C(10), O(2), C(11) and C(14) all lie within 0·055 Å from the plane through the indandione ring (*cf.* Table 8) while the atoms C(12) and C(13) are removed from the plane by 1·264 and 1·270 Å, respectively, on either side. The molecular symmetry is approximately C_{1h} (*m*).

Since the approximate mirror plane symmetry of the molecules is nearly perpendicular to the *b* axis, the crystal structure can, at least approximately, be de-

Table 6. *Intermolecular distances less than* 3·6 Å *between non-hydrogen atoms*

The estimated standard deviations are given in parentheses.

Symmetry code

Superscript			
None	x,	y,	z
(i)	$-x$,	$\frac{1}{2}+y$,	$-z$

	Unit-cell translation along axis *a* *b* *c*	
C(1)-C(5)^{i}	(1, 0, 1)	3·464 (12) Å
C(1)-C(5)^{i}	(1, −1, 1)	3·465 (12)
C(3)-C(6)^{i}	(1, 0, 1)	3·465 (12)
C(7)-C(9)^{i}	(1, −1, 1)	3·507 (12)
C(7)-C(9)^{i}	(1, 0, 1)	3·517 (12)
C(3)-C(6)^{i}	(1, −1, 1)	3·534 (12)
C(4)-C(8)^{i}	(1, −1, 1)	3·539 (11)
C(8)-C(9)^{i}	(1, 0, 1)	3·540 (11)
C(2)-C(6)^{i}	(1, 0, 1)	3·547 (11)
C(4)-C(8)^{i}	(1, 0, 1)	3·569 (11)
C(8)-C(9)^{i}	(1, −1, 1)	3·577 (11)

Table 7. *Intramolecular hydrogen bond*

O(1)···O(2)	2·522 (3) Å
O(2)—H(2)	1·01 (3)
O(1)···H(2)	1·62 (3)
∠O(1)···H(2)-O(2)	147 (3)°

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31724 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 8. *The best least-squares planes*

(*a*) The plane through the nine atoms of the indan rings satisfies the equation:

$$0\cdot0024x+1\cdot0000y-0\cdot0019z=1\cdot7060,$$

where x, y and z are in Å along **a***, **b** and **c**. The atoms indicated with asterisks were omitted from the calculation of the plane. The root mean square deviation of the atoms without asterisks from the plane is 0·0170 Å.

Atom	Deviation	Atom	Deviation
O(3)*	0·009 Å	C(7)	0·003 Å
O(2)*	0·043	C(8)	0·023
O(1)*	0·050	C(9)	0·001
C(1)	0·010	C(10)*	−0·015
C(2)	−0·012	C(11)*	−0·041
C(3)	−0·013	C(12)*	−1·264
C(4)	0·008	C(13)*	1·270
C(5)	0·017	C(14)*	−0·054
C(6)	−0·036	H(2)*	0·266

(*b*) The plane through atoms O(1), C(1), C(2), C(10), O(2) satisfies the equation:

$$-0\cdot0250x+1\cdot0000y-0\cdot196z=1\cdot4850.$$

The root mean square deviation of the atoms without asterisks from the plane is 0·0045 Å. A negative sign means that the atom lies between the plane and the origin.

Atom	Deviation
O(1)	−0·002 Å
O(2)	0·006
C(1)	−0·002
C(2)	0·007
C(10)	−0·010
H(2)*	0·215

scribed as centrosymmetric, space group $P2_1/m$, instead of $P2_1$. The possibility of such a space group was to some extent already indicated by the $|E|$ statistics. Refinement of the structural model (134 parameters) in space group $P2_1/m$ *vs* 1086 reflexions gave a linear R of 0·051, compared with 0·045 obtained for space group $P2_1$ (209 parameters). The corresponding weighted R values are 0·0605 and 0·0537 respectively [Hughes's (1941) weighting sheme with $|F_{\min}|=1\cdot6$]. A significance test (Hamilton, 1965) of the ratio (1·122) of the weighted R values indicates that the centrosymmetric space group $P2_1/m$ can be rejected at a 0·5% significance level (*cf.* Table 9). Accordingly, our discussion and description of the structure are based on $P2_1$. However, the possibility that undetected systematic errors might seriously influence the significance test cannot be completely ruled out.

Table 9. *Significance test on the crystallographic R index*

Space group	$P2_1/m$	$P2_1$
m = number of the parameters varied	134	209
n = number of reflexions	1086	1086
$R=\sum\lvert\Delta F\rvert/\sum\lvert F_{\text{obs}}\rvert$	0·0508	0·0450
$R_w=\sqrt{(\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_{\text{obs}}\rvert^2)}$	0·0605	0·0539
$S=\sqrt{[w\lvert\Delta F\rvert^2/(n-m)]}$	0·0443	0·0411

A pertinent tabular value of $\mathscr{R}$, obtained by interpolation from Hamilton (1965) (Table 1): $\mathscr{R}_{75,877,0.005}=1\cdot0594$.

The geometry found for the indandione part of the molecule agrees to some extent with that found for other indandione derivatives, *e.g.* 2-*p*-bromophenyl-1,3-indandione (Bechtel, Bravic, Gaultier & Hauw, 1972); 2-*p*-methylbenzylidene-1,3-indandione (Zalukaev, Ignatjev & Zavalishin, 1970); 2-dimethylsulphuranylidene-1,3-indandione (Christensen & Thom, 1971); and the rubidium salt of 1,3-indandione-2-sulphonic acid (Apinitis, Ancishkina & Jevins, 1971). There are no remarkable differences in bond lengths and angles for the phenyl rings among the derivatives (Table 10). In the five-membered rings the endocyclic C(sp^2)–C(sp^2) bonds, C(1)–C(8) and C(3)–C(9), agree well and are compatible with the usual value of 1·465 (5) Å (Sutton, 1965). However, the endocyclic C–C bond lengths around the atom C(2) (Fig. 2) differ significantly among the derivatives; ranging from 1·43 Å in the dimethylsulphuranilidene derivative up to 1·54 Å in the *p*-bromophenyl derivative. This bond length

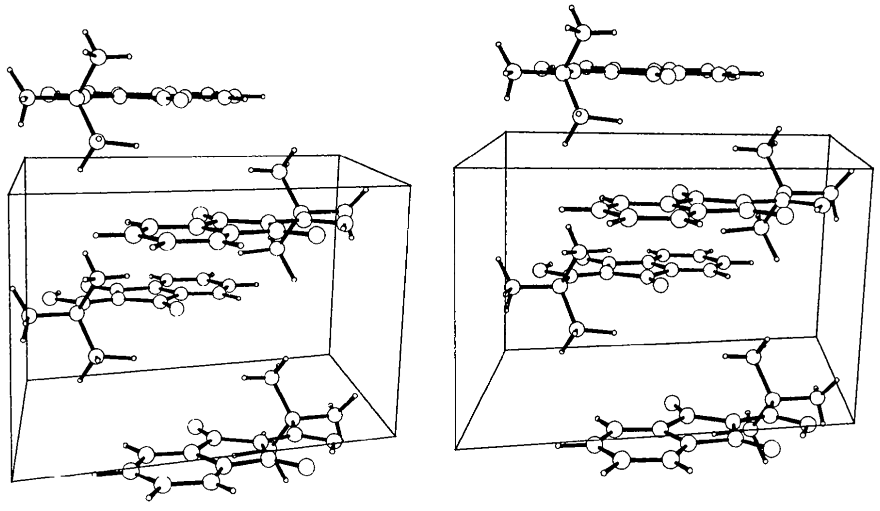

Fig. 2. Stereoscopic packing diagram of the crystal structure

variation is obviously due to the electrophilic nature of the substituents. It is also evident from the variation of the C(1)–C(2)–C(3) bond angles, which range from 111° for the dimethylsulphuranilidene derivative down to 103° for the *p*-bromophenyl derivative. The corresponding bond lengths and bond angle found in the present study are 1·452 (2) and 1·478 (3) Å, and 107·3 (2)°. The remaining bond lengths and angles within the five-membered ring all agree reasonably.

Table 10. *A comparison of bond lengths* (Å) *and angles* (°) *in indandione derivatives*

1,3-Indandione derivative studied	Mean C–C bond length in the condensed benzene ring	R.m.s. deviation of the C–C bond length from the mean C–C bond length in the condensed benzene ring	R.m.s. deviation of the bond angles from 120° in the condensed benzene ring	Mean C–O bond length in the carbonyl groups	C–C single-bond lengths in the *c*-pentene ring adjacent to the benzene ring	C–C single bond lengths in the *c*-pentene ring away from the benzene ring	R.m.s. deviation of the bond angles from 108° in the *c*-pentene ring
2-Pivaloyl-1,3-indandione	1·388 (6)	0·0048	1·5	1·231 (2)	1·476 1·502	1·452 1·478	1·3
2-*p*-Bromophenyl-1,3-indandione*	1·385 (8)	0·0077	2·1	1·207 (7)	1·488 1·495 1·487 1·462	1·536 1·539 1·529 1·540	2·6
2-*p*-Methylbenzylidene-1,3-indandione	1·39 (3)	0·028	1·6	1·23 (2)	1·45 1·45	1·51 1·49	2·7
2-Dimethylsulphuranylidene-1,3-indandione	1·384 (7)	0·0057	1·7	1·231 (2)	1·495 1·500	1·437 1·420	2·3
Rubidium salt of 1,3-indandione-2-sulphonic acid	1·39 (2)	0·014	1·5	1·21 (4)	1·44 1·44	1·53 1·55	2·5

* The crystal structure of 2-*p*-bromophenyl-1,3-indandione is built up of dimer molecules.

(*a*) This study. (*b*) Bechtel, Bravic, Gaultier & Hauw (1972). (*c*) Zalukaev, Ignatjev & Zavalishin (1970). (*d*) Christensen & Thom (1971). (*e*) Apinitis, Ancishkina & Jevins (1971).

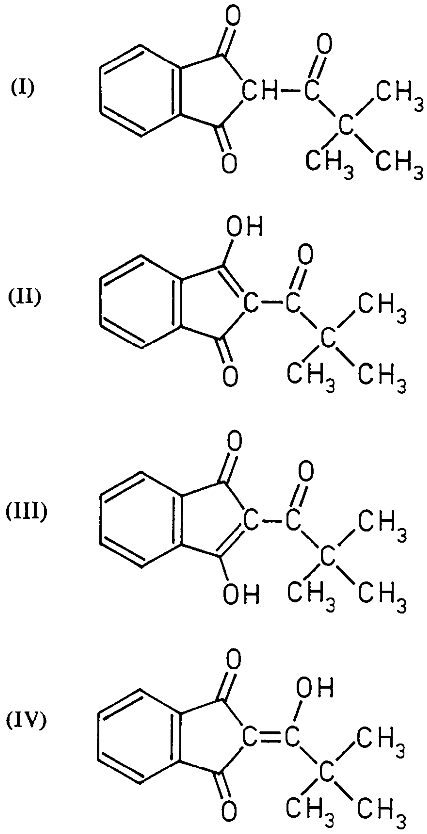

Fig. 3. Schematic drawing of 2-pivaloyl-1,3-indandione in four possible tautomeric forms.

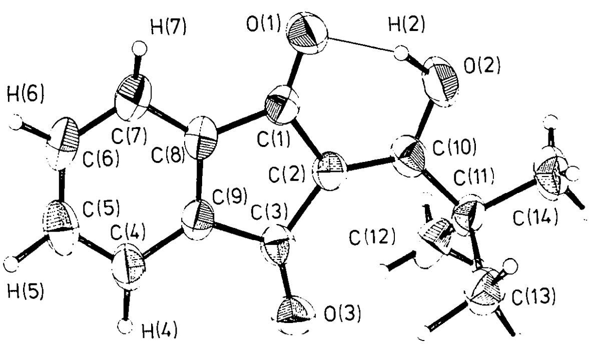

Fig. 4. The 2-pivaloyl-1,3-indandione molecule. The non-hydrogen atoms are represented by their thermal ellipsoids, while the hydrogens are drawn with constant radii.

In the pivaloyl part of the molecule the bond lengths and bond angles at C(11), the central atom of the t-butyl group, are characteristic of a tetrahedral carbon atom, as is the case for the other pivaloyl derivatives (Mellor & Nyburg, 1970; Aubry, Marraud, Protas & Neel, 1973; Bear, MacDonald & Trotter, 1973). The distance between C(10)–O(2), 1·320 (3) Å, is much longer than the common double-bond value of about 1·22 Å found in other pivaloyl derivatives. The adjacent C–C bond length between C(2)–C(10) is only 1·382 (3) Å, close to the value of 1·395 Å usually found for aromatic systems. These observations suggest that the π electrons around C(10) are delocalized over the O(2)–C(10) and C(10)–C(2) bonds. Such delocalization of π electrons could also involve the C(1) and O(1) atoms as suggested by the slight shortening of the C(2)–C(1) bond (1·45 Å) and the slight elongation of the C(1)–O(1) bond (1·24 Å) as compared to the corresponding bonds: 1·48 and 1·22 Å, at C(3) and O(3).

It is noteworthy that the atoms O(1), C(1), C(2), C(10), O(2) are coplanar within 0·010 Å and, furthermore, that O(1) and O(2) form a remarkably strong (O···O distance 2·52 Å) intramolecular hydrogen bond with an O···H–O angle of 147·(3)°. By this hydrogen bond a six-membered ring is formed in which the electrons are delocalized, at least in the non-hydrogen part of this ring. There are three quite large bond angles at C(sp^2) atoms found in the molecular structure, *viz* the two exocyclic angles of the indandione ring O(3)–C(3)–C(2) (130°) and C(3)–C(2)–C(10) (133°); and C(2)–C(10)–C(11) (128°) of the pivaloyl group. The deviation of these three angles from 120° is probably due to steric interference between the bulky t-butyl group (*cf.* Pinkus & Custard, 1970) and the indandione ring. The reason for this steric interference is the stabilization of the coplanar conformation of the atoms O(1), C(1), C(2), C(10) O(2) by the intermolecular hydrogen bond and by the resonance energy gained through π–π overlap.

The authors are indebted to Professor Peder Kierkegaard and to Mr Tor-Björn Palm for their active interest in this work. Thanks are also due to Dr Don Koenig for valuable comments on the manuscript and to Dr Sven Westman for his correction of the English.

References

APINITIS, S. K., ANCISHKINA, A. S. & JEVINS, A. F. (1971). *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **5**, 587–592.

AUBRY, A., MARRAUD, M., PROTAS, J. & NEEL, J. (1973). *C. R. Acad. Sci. Paris, Sér. C*, **275**, 1089–1092.

BEAR, C. A., MACDONALD, A. L. & TROTTER, J. (1973). *Acta Cryst.* B**29**, 2617–2619.

BECHTEL, F., BRAVIC, G., GAULTIER, J. & HAUW, C. (1972). *Cryst. Struct. Commun.* **1**, 159–162.

CHRISTENSEN, A. T. & THOM, E. (1971). *Acta Cryst.* B**27**, 581–586.

ERNSTER, L., LIND, C. & RASE, B. (1972). *Eur. J. Biochem.* **25**, 198–206.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HANSTEIN, K. O. & MARKWARDT, F. (1971). *Handb. Exp. Pharmacol.* **27**, 192–301.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.

KARLE, J. (1972). *Acta Cryst.* B**28**, 820–824.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN, a Computer Program for the Automatic Solution of Crystal Structures*, Univ. of York.

MELLOR, I. P. & NYBURG, S. C. (1970). *Acta Cryst.* B**27**, 1959–1963.

NORRESTAM, R. (1972). *Acta Cryst.* A**28**, 303–308.

PINKUS, A. G. & CUSTARD, H. C. JR (1970). *J. Phys. Chem.* **74**, 1042–1049.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.

TOLLIN, P. (1966). *Acta Cryst.* **21**, 613–614.

ZALUKAEV, L. P., IGNATJEV, N. A. & ZAVALISHIN, E. I. (1970). *Zh. Strukt. Khim.* **11**, 716–721.