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The Structures of Two 2-Acyl-1,3-indandiones

BY JAMES D. KORP AND IVAN BERNAL

Chemistry Department, University of Houston, Houston, TX 77004, USA

AND THOMAS L. LEMKE

Department of Medicinal Chemistry, University of Houston, Houston, TX 77004, USA

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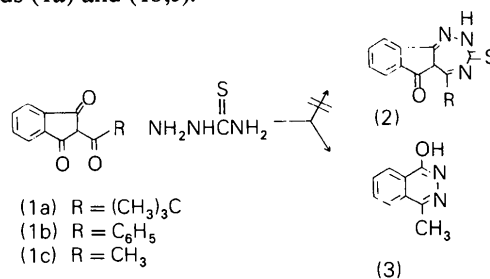
Abstract

Crystals of 2-pivaloyl-1,3-indandione are monoclinic, space group $P2_1/m$, with two molecules positioned on mirror planes in a cell with dimensions $a = 8.411$ (3), $b = 6.897$ (6), $c = 10.522$ (4) Å, $\beta = 105.22$ (3)°; while crystals of 2-acetyl-1,3-indandione are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions $a = 5.305$ (3), $b = 7.314$ (2), $c = 23.214$ (10) Å, $\beta = 94.94$ (4)°. Both structures were solved *via* *MULTAN*, and each refined to a conventional R value of 0.038. Both compounds are in the enol form in the solid state, with the enolic H external to the indan system. Considerable steric strain is noted in the pivaloyl derivative due to the bulk of the *tert*-butyl group, and yet this compound is found to have a higher degree of delocalization (stronger internal hydrogen bonding) than the acetyl derivative. NMR and IR spectral analyses, as well as chemical-reactivity studies, support this conclusion derived from the single-crystal X-ray results. The indan portions of both molecules are essentially planar.

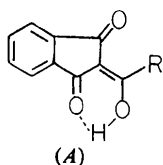
Introduction

The reaction of 2-acyl-1,3-indandiones with hydrazine leading to substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones

has been extensively studied by Mosher & Meier (1970), Mosher, El-Zimaity & Lipp (1971), Mosher & Banks (1971), Mosher, Serridge & Lipp (1972) and Braun & Mosher (1958, 1959). Since the cyclization of β -ketoesters with thiosemicarbazides leads to triazepinones (Losse, Hessler & Barth, 1958) an attempt was made to prepare new and unique tricyclic heterocycles starting from 2-acyl-1,3-indandiones (1). When 2-pivaloyl-1,3-indandione (1a) was treated with thiosemicarbazide in aqueous sodium carbonate, the expected product (2) did not form; instead, 1-hydroxy-4-methylphthalazine (3) was recovered (Lemke & Parker, 1976). However, when the same reaction was attempted with 2-benzoyl-1,3-indandione (1b) or with 2-acetyl-1,3-indandione (1c), none of the *retro*-Claisen condensation product (3) formed. These results suggest important differences in molecular structure for compounds (1a) and (1b,c).



Work by Forsén, Merényi & Nilsson (1964) suggests that 2-acyl-1,3-indandiones exist exclusively in the enol form (A), and this has been partially confirmed by the single-crystal X-ray diffraction study of Csöregi & Norrestam (1976). Thus, in an attempt to find a clear explanation for differences in reactivity, the single-crystal X-ray diffraction study of (1c) was undertaken. When the results were compared with those of (1a) previously reported by Csöregi & Norrestam (1976), some inexplicable differences were noted in the internal hydrogen-bonding parameters. In an effort to clear up these discrepancies, and since it was felt that a comparison between the two crystal structures would be more meaningful if the data were collected on the same diffractometer and refined similarly, a re-investigation of 2-pivaloyl-1,3-indandione was undertaken. The current results show that the original choice of space group may have been in error, and that refinements of our two data sets do, indeed, yield more meaningful comparisons as far as the hydrogen bonding is concerned. This is particularly clear when one takes into account the spectral results and chemical reactivities.



Experimental

Analyses

All ^1H NMR spectra were recorded on a Varian EM 360 spectrometer in CDCl_3 , while IR spectra were obtained for the compounds on a Perkin-Elmer 283 as KBr pellets. Single crystals of the methyl and *tert*-butyl derivatives were obtained by sublimation and by evaporation from alcohol, respectively.

Crystals of both were bright-yellow flat plates, approximately $0.75 \times 0.50 \times 0.20$ mm. Data collections were similar, except where noted below. An Enraf-Nonius CAD-4 automatic diffractometer was used with $\text{Mo } K\alpha$ radiation which was monochromatized by a dense graphite crystal, assumed for all purposes to be ideally imperfect. Lattice constants and orientation matrices were obtained from least-squares fits of 25 automatically centered reflections representing all parity groups, well distributed over reciprocal space. Final cell constants, as well as other pertinent data, are given in Table 1. The Laue symmetry in both cases was determined to be $2/m$ and, from the systematic absences noted, the space groups were determined to be $P2_1/n$ for the methyl derivative, and $P2_1$ or $P2_1/m$ for the *tert*-butyl.

Table 1. Summary of data collection and processing parameters; $|E|$ statistics; significance test on R_w

	<i>tert</i> -Butyl derivative $\text{C}_{14}\text{H}_{14}\text{O}_3$	Methyl derivative $\text{C}_{11}\text{H}_{10}\text{O}_3$
Space group	$P2_1/m$	$P2_1/n$
Cell constants: <i>a</i>	8.411 (3) Å	5.305 (3) Å
<i>b</i>	6.897 (6)	7.314 (2)
<i>c</i>	10.522 (4)	23.214 (10)
β	105.22 (3)°	94.94 (4)°
<i>V</i>	589.0 Å ³	897.4 Å ³
<i>Z</i>	2	4
M_r	230.27	188.18
Density (calc.)	1.30 Mg m ⁻³	1.39 Mg m ⁻³
Absorption coefficient	0.053 mm ⁻¹	0.061 mm ⁻¹
Data-collection range	$5^\circ \leq 2\theta \leq 55^\circ$	$4^\circ \leq 2\theta \leq 50^\circ$
Scan width, $\Delta\theta^\circ$	$1.10 + 0.35 \tan \theta$	$1.10 + 0.35 \tan \theta$
Maximum scan time	300 s	300 s
Scan-speed range	0.4 to 3.4° min ⁻¹	0.4 to 3.4° min ⁻¹
Total data collected	1455	1589
Data with $ I > 3\sigma(I)^*$	1020	766
Total variables	134	157
$R = \sum F_o - F_c / \sum F_o $	0.038	0.038
$R_w = \{ \sum w(F_o - F_c)^2 / \sum w F_o ^2 \}^{1/2}$	0.033	0.032
Weights, <i>w</i>	$\sigma(F)^{-2}$	$\sigma(F)^{-2}$
Goodness of fit	1.55	1.71

$|E|$ Statistics

	Theoretical		Experimental	
	Centro-symmetric	Noncentro-symmetric	<i>tert</i> -Butyl derivative	Methyl derivative
$\langle E ^2 \rangle$	1.00	1.00	1.00	1.00
$\langle E ^2 - 1 \rangle$	0.97	0.74	0.96	1.05
$\langle E \rangle$	0.80	0.89	0.80	0.75

Significance test on R_w for *tert*-butyl derivative

Space group	$P2_1/m$	$P2_1$
Parameters varied	134	209
Number of reflections	1020	1020
<i>R</i>	0.038	0.034
R_w	0.033	0.029

$$\mathcal{A} = R_w(P2_1/m) / R_w(P2_1) = 1.14.$$

$$\mathcal{A}_{75, 811, 0.005} \text{ (Hamilton, 1965)} \approx 1.07.$$

* Standard deviations in the intensities were estimated from the expression $\sigma^2(I) = I_{\text{TOT}} + 2\sum I_{\text{BG}}$, where I_{TOT} is the total intensity of the peak and I_{BG} is the total counts for background at each end of the peak.

Intensities were measured using the θ - 2θ scan technique, with the scan rates depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours of exposure time as a check of electronic reliability and crystal stability, and showed no unusual trends during the course of the data collections. In each case, a unique quarter of the reciprocal sphere was collected, according to the limits listed in Table 1. In reducing the data, Lorentz and polarization factors were applied but no correction was made for absorption. An acceptance criterion of $I > 3\sigma(I)$ was employed in determining the reflections to be used in least-squares refinement.

Both structures were solved using *MULTAN* (Germain, Main & Woolfson, 1971) despite the fact that previously published atomic coordinates for the *tert*-butyl compound were available. The normalized structure factor ($|E|$) statistics are shown in Table 1, giving strong indications that both structures are centrosymmetric. The usual sequence of isotropic and

Table 2. 2-Pivaloyl-1,3-indandione: atomic coordinates ($\times 10^4$, for H $\times 10^3$)

	x	y	z
C(1)	-2288 (3)	2500	718 (2)
O(1)	-3770 (2)	2500	251 (1)
C(2)	-1311 (2)	2500	2109 (2)
C(3)	416 (3)	2500	2105 (2)
O(3)	1606 (2)	2500	3107 (1)
C(4)	1893 (3)	2500	217 (2)
C(5)	1614 (3)	2500	-1132 (2)
C(6)	41 (3)	2500	-1953 (3)
C(7)	-1330 (3)	2500	-1446 (2)
C(8)	-1055 (2)	2500	-96 (2)
C(9)	529 (2)	2500	731 (2)
C(10)	-1741 (3)	2500	3287 (2)
O(10)	-532 (2)	2500	4391 (1)
C(11)	-3445 (3)	2500	3497 (2)
C(12)	-3391 (4)	2500	4967 (3)
C(13)	-4346 (2)	655 (3)	2867 (2)
H(4)	304 (3)	250	81 (2)
H(5)	249 (2)	250	-155 (2)
H(6)	-17 (3)	250	-291 (3)
H(7)	-247 (2)	250	-206 (2)
H(10)	67 (4)	250	409 (3)
H(12A)	-458 (3)	250	509 (2)
H(12B)	-279 (2)	133 (2)	542 (1)
H(13A)	-369 (2)	-60 (3)	333 (2)
H(13B)	-545 (2)	68 (2)	300 (1)
H(13C)	-444 (2)	62 (2)	185 (1)

Table 3. 2-Acetyl-1,3-indandione: atomic coordinates ($\times 10^4$, for H $\times 10^3$)

	x	y	z
C(1)	-857 (6)	4923 (5)	6444 (2)
O(1)	-2562 (4)	5707 (4)	6659 (1)
C(2)	556 (6)	5533 (5)	5952 (1)
C(3)	2441 (6)	4152 (5)	5862 (1)
O(3)	3991 (4)	4197 (4)	5493 (1)
C(4)	3518 (8)	1092 (6)	6372 (2)
C(5)	2922 (8)	-104 (6)	6803 (2)
C(6)	954 (8)	349 (7)	7139 (2)
C(7)	-379 (8)	1933 (7)	7055 (2)
C(8)	230 (6)	3133 (5)	6622 (1)
C(9)	2199 (6)	2676 (5)	6289 (1)
C(10)	205 (7)	7006 (5)	5610 (2)
O(10)	1664 (5)	7307 (4)	5170 (1)
C(11)	-1752 (9)	8412 (7)	5665 (2)
H(4)	474 (5)	89 (4)	616 (1)
H(5)	377 (5)	-137 (4)	686 (1)
H(6)	59 (5)	-50 (4)	742 (1)
H(7)	-178 (6)	235 (4)	724 (1)
H(10)	288 (8)	602 (6)	523 (2)
H(11A)	-264 (6)	793 (5)	602 (1)
H(11B)	-118 (6)	974 (4)	556 (2)
H(11C)	-264 (6)	859 (6)	532 (2)

anisotropic refinement was followed, after which H atoms were located in difference density maps. All parameters were allowed to vary in the methyl refinement, but several restrictions were necessary in the *tert*-butyl least squares for space group $P2_1/m$, chosen because of the centric statistics. After all shift/e.s.d.

ratios were less than 0.1, the refinements converged to the agreement factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions (Cromer & Mann, 1968); for H, those of Stewart, Davidson & Simpson (1965) were used. All calculations were made with the *SHELX* 76 series of programs (Sheldrick, 1976). No unusually high correlations were noted in either refinement. Final positional parameters are listed in Tables 2 and 3, and bond lengths, angles, and least-squares planes are given in Tables 4-6, based on these positions. The numbering schemes are shown in the stereoviews of Figs. 1 and 2. Unlabeled H atoms have numbers corresponding to the atoms to which they are bonded.

In order to determine whether $P2_1/m$ was indeed the proper space group for the *tert*-butyl derivative, the refinement in space group $P2_1$ was also carried out. The

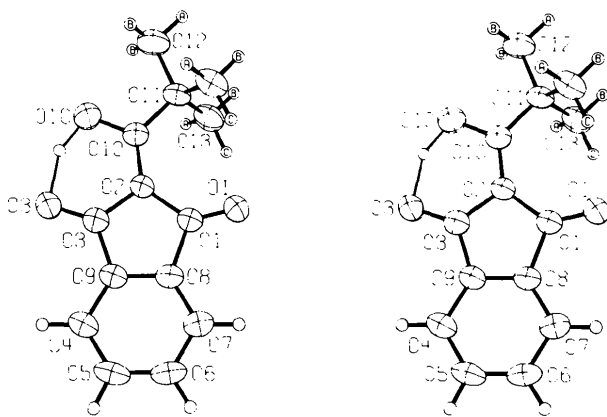


Fig. 1. Stereographic view of the atom-labeling scheme for 2-pivaloyl-1,3-indandione. The thermal ellipsoids are 50% equiprobability envelopes. H atoms are shown as spheres of arbitrary diameter, with numbers corresponding to the atoms to which they are attached.

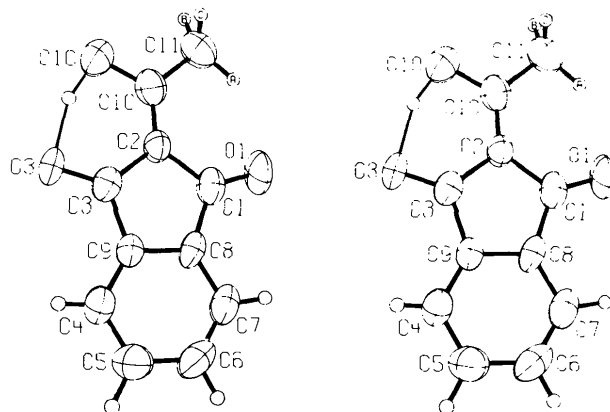


Fig. 2. Stereographic view of the atom-labeling scheme for 2-acetyl-1,3-indandione. The thermal ellipsoids are 50% equiprobability envelopes. H atoms are shown as spheres of arbitrary diameter, with numbers corresponding to the atoms to which they are attached.

Table 4. Bond lengths (Å)

	<i>tert</i> -Butyl derivative	Methyl derivative		<i>tert</i> -Butyl derivative	Methyl derivative
C(1)—O(1)	1.214 (2)	1.214 (3)	C(10)—C(11)	1.506 (3)	1.475 (5)
C(1)—C(2)	1.479 (4)	1.488 (4)	C(11)—C(12)	1.536 (3)	—
C(1)—C(8)	1.508 (3)	1.475 (4)	C(11)—C(13)	1.539 (2)	—
C(2)—C(3)	1.453 (3)	1.448 (4)	C(4)—H(4)	1.00 (2)	0.86 (2)
C(2)—C(10)	1.379 (3)	1.342 (4)	C(5)—H(5)	0.95 (2)	1.04 (3)
C(3)—O(3)	1.249 (2)	1.239 (3)	C(6)—H(6)	0.98 (3)	0.94 (3)
C(3)—C(9)	1.474 (3)	1.479 (4)	C(7)—H(7)	1.00 (2)	0.94 (3)
C(4)—C(5)	1.377 (3)	1.386 (5)	O(10)—H(10)	1.14 (3)	1.14 (5)
C(4)—C(9)	1.391 (3)	1.358 (4)	O(3)—H(10)	1.45 (3)	1.56 (5)
C(5)—C(6)	1.377 (3)	1.396 (5)	C(12)—H(12A)	1.04 (2)	—
C(6)—C(7)	1.391 (3)	1.363 (5)	C(12)—H(12B)	1.00 (2)	—
C(7)—C(8)	1.379 (3)	1.394 (4)	C(13)—H(13A)	1.07 (2)	Me _e 1.05 (3)
C(8)—C(9)	1.387 (3)	1.393 (4)	C(13)—H(13B)	0.98 (2)	Me _e 1.05 (3)
C(10)—O(10)	1.327 (2)	1.352 (4)	C(13)—H(13C)	1.05 (1)	Me _e 0.91 (3)

Table 5. Bond angles (°)

	<i>tert</i> -Butyl derivative	Methyl derivative		<i>tert</i> -Butyl derivative	Methyl derivative
C(2)—C(1)—C(8)	106.0 (2)	105.7 (3)	C(9)—C(8)—C(1)	109.5 (2)	110.6 (3)
O(1)—C(1)—C(2)	130.2 (2)	128.1 (4)	C(8)—C(9)—C(3)	108.5 (2)	108.0 (3)
O(1)—C(1)—C(8)	123.8 (2)	126.2 (3)	C(8)—C(9)—C(4)	120.7 (2)	121.8 (4)
C(1)—C(2)—C(3)	107.0 (2)	107.5 (3)	C(3)—C(9)—C(4)	130.8 (2)	130.2 (3)
C(1)—C(2)—C(10)	133.0 (2)	129.9 (3)	C(2)—C(10)—O(10)	117.7 (2)	121.2 (3)
C(3)—C(2)—C(10)	120.0 (2)	122.6 (3)	C(2)—C(10)—C(11)	128.0 (2)	124.9 (4)
C(2)—C(3)—C(9)	108.9 (2)	108.2 (3)	O(10)—C(10)—C(11)	114.3 (2)	113.9 (4)
C(2)—C(3)—O(3)	125.3 (2)	126.0 (3)	C(10)—C(11)—C(12)	111.7 (2)	—
C(9)—C(3)—O(3)	125.8 (2)	125.8 (3)	C(10)—C(11)—C(13)	108.5 (1)	—
C(9)—C(4)—C(5)	117.8 (2)	119.6 (4)	C(12)—C(11)—C(13)	108.3 (1)	—
C(4)—C(5)—C(6)	121.5 (2)	118.8 (4)	C(12)—C(11)—C(13')	111.5 (2)	—
C(5)—C(6)—C(7)	121.1 (2)	121.8 (4)			
C(6)—C(7)—C(8)	117.6 (2)	119.2 (4)	C(3)—O(3)—H(10)	98 (1)	93 (2)
C(7)—C(8)—C(9)	121.3 (2)	118.8 (4)	C(10)—O(10)—H(10)	107 (1)	98 (2)
C(7)—C(8)—C(1)	129.1 (2)	130.7 (3)	O(10)—H(10)—O(3)	153 (1)	160 (2)

Table 6. Least-squares planes and atomic deviations for the methyl derivative

Plane A: all nine carbons of the indan group

$$0.599x + 0.466y + 0.651z = 10.313$$

C(1)	0.014 Å	C(7)	-0.005 Å
C(2)	-0.010	C(8)	-0.003
C(3)	-0.004	C(9)	0.007
C(4)	0.003	*C(10)	-0.093
C(5)	0.002	*O(10)	-0.136
C(6)	-0.005	*C(11)	-0.161

Average e.s.d. = 0.003 Å.

Plane B: all fourteen non-hydrogen atoms

$$0.601x + 0.480y + 0.639z = 10.157$$

C(1)	0.042 Å	C(6)	-0.044 Å
O(1)	0.065	C(7)	-0.026
C(2)	0.039	C(8)	0.002
C(3)	0.034	C(9)	0.017
O(3)	0.044	C(10)	-0.019
C(4)	-0.005	O(10)	-0.045
C(5)	-0.031	C(11)	-0.075

Average e.s.d. = 0.004 Å.

* Additional atoms not defining the plane.

y coordinates of all atoms previously fixed on the mirror plane at $\frac{1}{4}$ were moved to 0.30 to avoid any pseudosymmetry in the noncentrosymmetric refinement; all other atoms were shifted a like amount. With 209 variables [*y* of C(1) fixed at 0.30 to define the origin] the refinement now converged at $R = 0.034$ and $R_w = 0.029$. If the statistical test of Hamilton (1965) is applied then, mathematically, the $P2_1/m$ refinement is rejected at the 0.5% confidence level (Table 1), just as Csöregi & Norrestam (1976) reported for their results. We feel, however, that there are other factors which bear on this question, such that the weight of evidence actually supports the choice of $P2_1/m$:

(i) As shown in Table 1, the statistics of the normalized structure factors indicate a centrosymmetric structure. (We realize, however, that centric statistics can be misleading in special situations.)

(ii) In the $P2_1$ refinement, there are extremely high (~90%) correlations between several parameters (other than *y* coordinates) of the two methyl groups which are mirror relatives in $P2_1/m$. These correlations lead to unusually disparate bond lengths and e.s.d.'s for which

there is no chemically reasonable explanation. Csöregi & Norrestam (1976) simply reported these peculiar results [$C(11)-C(13) = 1.494(10)$, $C(11)-C(13') = 1.572(10)$ Å] with no comment.

(iii) After refinement in $P2_1$, the two planes comprising the indan ring, *viz* the five- and six-membered rings, are *co-planar* within one standard deviation. Further, the equation of the best plane through all 14 non-methyl C and O atoms is: $-0.005x + 1.000y + 0.000z = 2.046$, essentially *independent* of x and z !

(iv) The bond distances obtained for each of the two refinements are statistically identical, except for the methyl distances which are quite highly correlated and thus unreliable in the $P2_1$ case.

(v) Hamilton's test makes the underlying assumption of normally distributed random errors, which is probably rarely the case in actual practice, and deviations from which are accentuated at lower values of R_w such as those found both in the current study and in that of Csöregi & Norrestam. An illustration of this point is the following: if the two R_w values of the $P2_1/m$ and $P2_1$ refinements had been 0.065 and 0.061, with the same 0.004 difference as now, the $P2_1/m$ refinement would *not* be rejected by this test.

Thus, for the above reasons, we submit that $P2_1/m$ is the more reasonable choice of space group, and the following discussion is based on the results stemming from this choice for the *tert*-butyl refinement. For the readers' convenience, full details of the refinements in *both* space groups have been deposited.*

Discussion

As can be seen in Figs. 1 and 2, both the methyl and the *tert*-butyl derivatives crystallize in the enolic form, with the H associated most closely with the O external to the indandione system. The reason why this particular configuration is favored over the other two possible enol tautomeric forms is not clear. In fact, other reported structures of 2-substituted 1,3-indandiones are *all* in the keto form if there is no available proton acceptor external to the indandione group (Bravic, Gaultier & Hauw, 1974*a,b*; Bechtel, Bravic, Gaultier & Hauw, 1972; Bravic, Bechtel, Gaultier & Hauw, 1976). Several examples of 1,2,3-indantriones are known (Bolton, 1965; Christensen & Thom, 1971; Silverman, Krukonić & Yannoni, 1974), but only recently has one been reported in which tautomeric variations similar to those seen in the present study are

* Lists of structure factors and thermal parameters for both compounds and details of the alternative refinement in space group $P2_1$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34852 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

possible (McMillan, Curtin & Paul, 1978), and it is also in the external enol form.

The bond distances and angles of the indan portions of the present molecules are in very good agreement with the previously reported structures listed above, as well as with related fragments of ninhydrin (Medrud, 1969) and 2,2'-spirobi[indan]-1,1'-dione (Petersen & Danielsen, 1974). The only noticeable discrepancies occur in the bonds to the bridgehead carbon, C(2), and in the keto groups. Bonds $C(1)-C(2)$ (1.479 and 1.488 Å) are significantly longer than bonds $C(2)-C(3)$ (1.453 and 1.448 Å), and bonds $C(1)-O(1)$ (1.214 and 1.214 Å) are considerably shorter than $C(3)-O(3)$ (1.249 and 1.239 Å). Both of these observations are consistent with the extended resonance system suggested for the *tert*-butyl derivative by Csöregi & Norrestam (1976), wherein O(3), C(3), C(2), C(10), O(10), and H(10) form a conjugated pseudo-six-membered ring (Fig. 3). Examples both exhibiting (McMillan, Curtin & Paul, 1978) and not exhibiting (Bolton, 1965; Silverman, Krukonić & Yannoni, 1974) this resonance are known. In the *tert*-butyl derivative, bond $C(1)-C(8)$ seems unusually long compared to other sp^2-sp^2 bonds, which may be a result of steric constraints elsewhere in the molecule since no such aberration is observed in the methyl derivative.

Other significant differences, in solid-state geometry and spectra, also indicate subtly distinct degrees of resonance in the two compounds used for this study. For the X-ray determinations, the results are shown in Fig. 3. Fig. 3(a) shows a higher degree of delocalization (stronger hydrogen bonding) for the *tert*-butyl compound, due to the lengthening (more single-bond character) of bonds $C(3)-O(3)$ and $C(2)-C(10)$, and concomitant shortening (more double-bond character) of bonds $C(10)-O(10)$ and $O(3)\cdots H(10)$. In contrast, Csöregi & Norrestam (1976) reported values of 1.38 Å for $C(10)-O(10)$, 1.01 Å for $O(10)-H(10)$, and 1.62 Å for $O(3)\cdots H(10)$, all of which would indicate a *lower* degree of delocalization

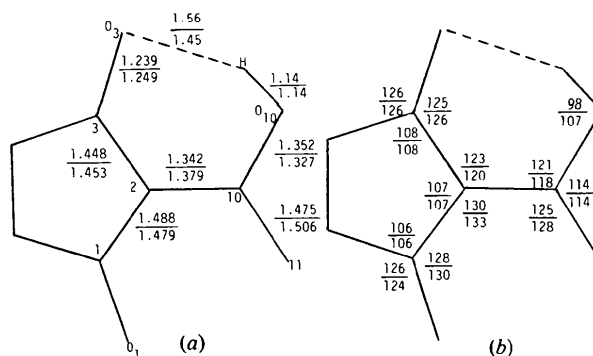


Fig. 3. (a) Bonds (Å) and (b) angles (°) involved in resonance and steric repulsion. Upper numbers are for methyl derivative, lower numbers for *tert*-butyl.

for the *tert*-butyl compound (weaker hydrogen bonding). Since arguments could be made as to the effects of different methods of collecting and refining the X-ray data, we report here the NMR and IR spectral results, which substantiate our models for the *tert*-butyl and methyl compounds.

NMR spectral studies demonstrated significant differences in the location of the exchangeable proton for compounds (1a)–(1c): the exchangeable proton in (1a) appears at 16δ ($w_{\frac{1}{2}}$ 10 Hz), while for (1b) and (1c) the protons appear at 14.9δ ($w_{\frac{1}{2}}$ 4Hz) and 13.2δ ($w_{\frac{1}{2}}$ 4Hz), respectively. This is interpreted to mean that the *tert*-butyl has a stronger H bond than either the phenyl or methyl compounds (Forsén *et al.*, 1964). The peak half-width ($w_{\frac{1}{2}}$) may also be used as a measure of the strength of H bonding: the $w_{\frac{1}{2}}$ is solvent dependent, but in each case the $w_{\frac{1}{2}}$ for (1a) is larger than that for (1b) or (1c). The IR data also show differences between the various derivatives; *i.e.*, the *tert*-butyl 'carbonyl' bands are found at 1700, 1640, and 1570 cm^{-1} , while the methyl derivative's 'carbonyl' bands appear at 1705, 1660, 1630, and 1590 cm^{-1} . The phenyl compound is complicated by additional aromatic absorption, but does appear similar to (1c). In agreement with Forsén *et al.* (1964), the 1700 cm^{-1} band is assigned to the non-bonded carbonyl, while the 1630–1660 cm^{-1} band corresponds to the 'chelated carbonyl'. The 1590–1570 cm^{-1} region has been assigned to the enolic double bond which, when shifted to lower frequency as with the *tert*-butyl derivative, may suggest a greater amount of extended resonance in this derivative. It is interesting to note that our NMR and IR data agree quite closely with the NMR–IR correlation graph generated by Forsén *et al.* for enolic protons–chelated carbonyls.

Chemical-reactivity studies of the three compounds (1a)–(1c) have been carried out, and attempts to relate the X-ray, NMR and IR data to the reactivity differences observed for the *tert*-butyl derivative *versus* the methyl derivative require that subtle structural differences be analyzed. Easily seen in space-filling models, and in the X-ray results, is the fact that the *tert*-butyl derivative is under considerable strain due to the presence of the bulky *tert*-butyl group. This is evidenced by the longer distances for bonds C(2)–C(10) and C(10)–C(11) for the *tert*-butyl derivative (Table 4), and in the larger angles O(1)–C(1)–C(2), C(1)–C(2)–C(10), and C(2)–C(10)–C(11), with necessary compressions at O(1)–C(1)–C(8), C(3)–C(2)–C(10), and C(2)–C(10)–O(10) (Table 5). Such steric repulsion is certainly expected when one reviews the results of Christensen & Thom (1971) for the dimethyl- λ^4 -sulfanylidene derivative, in which similar interference with the keto O atoms is observed despite the longer C–S bond and the smaller methyl bulk. The *tert*-butyl group itself is little affected, showing only the expected shortening of the bond to the sp^2 -hybridized C(10) – a characteristic also noted in quite different skeletal

systems (Hegarty, McCormack, Hathaway & Hulett, 1977).

The strain in the five-membered ring is relieved when (1a) undergoes the *retro*-Claisen reaction and may be a very significant factor in allowing (1a) to proceed to (3). As pointed out by Forsén *et al.* (1964), an inverse relationship exists between the strength of H bonding and acidity. Thus, compounds that are more highly enolized (*i.e.* with stronger H bonding) should be weak acids. 1,8-Decalindione is completely enolic and a very weak acid ($\text{p}K_a = 11$), hydro-1,2-indandione is 80% enolic ($\text{p}K_a = 8.64$), and bicyclo[3.3.0]octane-2,8-dione is little enolized (1.4%) and reasonably acidic ($\text{p}K_a = 7.04$). Compounds (1a) – (1c) are completely enolic but display subtle $\text{p}K_a$ differences, as seen by the chemical shift of the enolic proton, the *tert*-butyl derivative being least acidic because of strong H bonding ($\delta = 16$ p.p.m.) and the methyl analog most acidic ($\delta = 13.2$ p.p.m.). If the 2-acyl-1,3-indandiones (1) are converted to salts, this would be expected to inhibit the *retro*-Claisen reaction which is initiated by base attack on a ring carbonyl C (the details of this chemistry will be reported elsewhere: Lemke, Parker & Martin, 1979). Therefore, the more acidic methyl compound (1c) would be predicted to be less reactive than the *tert*-butyl compound (1a), which is found to be the case experimentally.

Since the strong steric repulsions in the *tert*-butyl derivative could be relieved if an external keto configuration were adopted [*i.e.* with the proton attached to an sp^3 -hybridized C(2)], then it must be assumed that the driving force towards a planar, enolic extended resonance system is more than adequate compensation for the steric problems engendered. Obviously, the *tert*-butyl derivative's skeleton is perfectly planar, due to mathematical constraints of the crystallographic model. As can be seen in Table 6, the methyl derivative is also quite planar, with the acetyl atoms bent slightly out of the plane of the indan group. Perhaps this minor distortion leads to the observed differences in resonance, hydrogen-bonding strength, and chemical reactivity between the two molecules, since the resonance stability gained from π – π orbital overlap would be expected to be smaller for the methyl derivative.

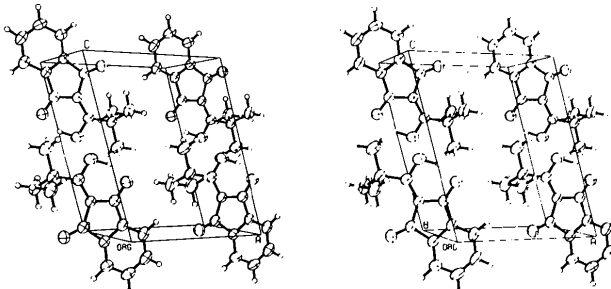


Fig. 4. Stereographic packing diagram for 2-pivaloyl-1,3-indandione, as viewed along the *b* axis.

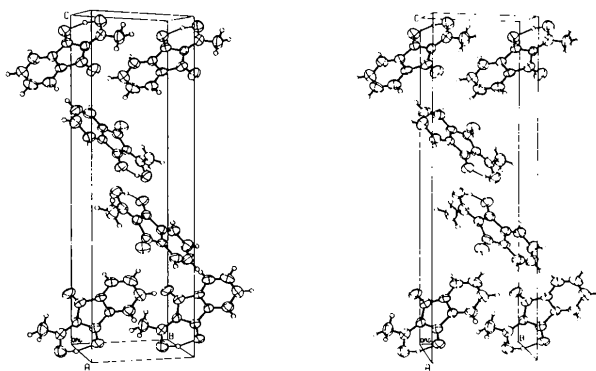


Fig. 5. Stereographic packing diagram for 2-acetyl-1,3-indandione, as viewed into the *a* axis.

Figs. 4 and 5 are stereographic packing diagrams of the two unit cells. As can be seen, the *tert*-butyl derivative packs in parallel planes of molecules stacked along *b* related by an inversion center, giving opposite senses of direction to adjacent planes. The methyl derivative packing is more complicated, with irregularly offset strings of molecules forming herringbone patterns. Pairs of molecules oppose each other through the enolic O atoms across centers of symmetry at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

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