The Crystal and Molecular Structure of the Enol Form of 1-Phenyl-1,3-butanedione (Benzoylacetone) by Neutron Diffraction

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The crystal structure of the enol form of 1-phenyl-1,3-butanedione, $C_{10}H_{10}O_2$, has been determined from three-dimensional, neutron-diffraction data. The structure was refined by full-matrix least-squares methods to an R of 0·098 (0·046 for reflexions with $I \geq 2·3\sigma_I$) and wR of 0·049 (0·042) for 1184 reflexions. The short, intramolecular $O \cdots O$ contact is 2·489 (5) Å. The hydrogen bond is slightly asymmetric but, because of large thermal motion, the asymmetry is of doubtful significance. From the bond lengths in the enol ring, it would appear that the structure is either an average of the two possible *cis* enol tautomers or a resonance hybrid. The structure is compared with a previous X-ray analysis.

Introduction

1,3-Diketones or β-diketones, (I), enolize to *cis* enols, (II) and (III).
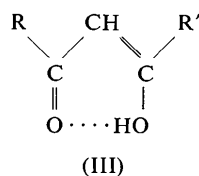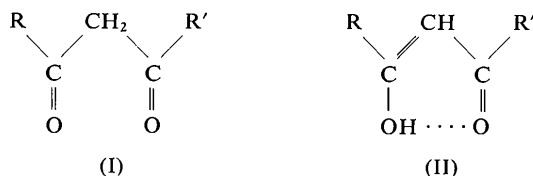
(R = CH₃, R' = C₆H₅ for this study)

Single-crystal diffraction studies show that tautomers (II) and (III) form a very short, intramolecular hydrogen bond with an $O \cdots O$ contact of $\sim 2·4$–2·5 Å (Engebretson & Rundle, 1964; Williams, Dumke & Rundle, 1962; Williams, 1966; Semmingsen, 1972; Hollander, Templeton & Zalkin, 1973; Jones, 1976*a, b, c*). This bond is probably asymmetric for unique (II) or (III), symmetric for equal contributions of (II) and (III). In some of the structures, R=R' and the bond is usually symmetric. By varying the substituents in the 1,3-positions, it might be possible to produce either (II) or (III) and hence study short, asymmetric hydrogen bonds which are free of the normal ionic interactions observed in, say, carboxylic acids and their salts.

Semmingsen (1972) studied benzoylacetone by X-ray diffraction and observed an asymmetric bond. For a variety of reasons, he excluded many reflexions. Since this compound seemed a good choice to study asymmetric hydrogen bonding, we decided to pursue the problem using neutron diffraction.

Experimental and data collection

Benzoylacetone was recrystallized from an ethanol solution. X-ray diffraction photographs of a small crystal from the batch indicated that the cell dimensions and space group were as given by Semmingsen (1972), *viz.* $a = 8·244$, $b = 5·596$, $c = 19·793$ Å and $\beta = 111·77°$; space group $P2_1/c$. The crystal selected for data collection was a plate of volume 16·7 mm³. It was mounted so that the b^* axis was slightly off-set from the φ axis of the diffractometer.

Neutron-diffraction data were collected, at room temperature, on the Australian Institute of Nuclear Science and Engineering four-circle diffractometer, 2TAN A, at the Australian Atomic Energy Commission Research Reactor, HIFAR. Intensities were measured by a θ–2θ step-scan technique (Elcombe, Cox, Pryor & Moore, 1971), each step being 0·01° in 2θ. The scan range was 2° in 2θ and the neutron wavelength was 0·983 Å. A hemisphere of data was collected, representing two equivalent sets, up to 2θ 65°. Beyond this angle, the number of reflexions above the general background was very small. Every 20 reflexions, the standard reflexion 004 was measured. Its intensity showed no systematic trends during the period of the data collection.

Each intensity was corrected for background and absorption. The absorption coefficient was 1·83 (9) cm⁻¹ (measured by transmission through a crystal) and the variation in transmission coefficients was 0·619 to 0·818. For each reflexion, the variance, σ_I^2, was determined from $\sigma_I^2 = \sigma_C^2 + \sigma_A^2 + (0·03I)^2$ where σ_C^2 is due to counting statistics, σ_A^2 is due to absorption errors (Elcombe *et al.*, 1971) and 0·03 represents the average deviation in the intensity of the standard reflexion of 3%. The intensities of equivalent reflexions were averaged and if the variance from the averaging procedure exceeded $\sigma_A^2 + \sigma_C^2$, the former was substituted for this sum in determining σ_I^2. If the intensity of a reflexion was negative, it was set to a small positive quantity but its variance was unchanged. The average in-

tensities were reduced to F_o and σ_{F_o}. The total number of unique reflexions was 1184.

Structure refinement

Structure factors were calculated with the C and O positional parameters of Semmingsen (1972). R^* was 0·32 for reflexions with $I \geq 2 \cdot 3\sigma_I$. A Fourier synthesis showed all H atoms except those bound to the methyl C atom. These appeared to be rotating or disordered. Refinement of the known atomic positions with isotropic thermal parameters caused R to fall to 0·16. Unit weight was assigned to each reflexion and the function minimized was $\sum w(|F_o| - k|F_c|)^2$. A difference Fourier synthesis showed an almost continuous ring of negative density about the methyl C atom. Six 'peak' positions were apparent. These 'peaks' were located so that each H atom could be described as two half-atoms located $\sim 0\cdot 9$ Å apart. In subsequent full-matrix, least-squares refinement with all recorded data (Moore, 1972), the half-occupancy H atoms were given isotropic temperature factors, all other atoms aniso-tropic. The weight for each reflexion was $w = \sigma_{F_o}^{-2}$. It was evident that the data were affected by extinction and, in final cycles, an isotropic extinction parameter was refined (Coppens & Hamilton, 1970). At convergence, R was 0·098 (0·046 for reflexions with $I \geq 2 \cdot 3\sigma_I$) and $wR\dagger$ was 0·049 (0·042). The error-of-fit was 1·28. The extinction coefficient was $0\cdot 88\ (5) \times 10^{-4}$ which corresponds to a mosaic spread of 6·7'' or a mean particle size of radius $0\cdot 86 \times 10^{-4}$ cm. The reflexion with the most severe extinction was 20$\bar{4}$, the extinction factor being 0·48. There was no dependence of $w\Delta^2$ on F_o or $(\sin \theta)/\lambda$. The final difference Fourier

* $R = \sum ||F_o| - k|F_c||/\sum |F_o|$.
† $wR = \sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2$.

Results

Final atomic coordinates and thermal parameters are shown in Table 1. Interatomic distances and angles, including errors due to the variance–covariance matrix and cell dimension errors, are listed in Table 2. Least-squares planes through selected atomic groupings are tabulated in Table 3. A diagram of the molecule is shown in Fig. 1.*

The thermal parameters of the non-hydrogen atoms were fitted to a rigid-body motion model (Schomaker & Trueblood, 1968). The results are in Table 4. Differences between the observed and calculated U_{ij} are ~ 1–3σ. The major axes of rotation and trans-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31633 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
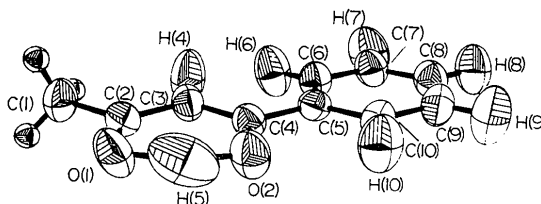

Fig. 1. A diagram of the molecule showing the numbering system. All atoms, except the methyl H atoms, are represented as 50%-probability thermal ellipsoids. The methyl H atoms are arbitrary spheres at the mid-point of the two half-atom positions.

Table 1. *Final fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

In this table, and all subsequent tables, estimated standard deviations in the least significant digit(s) are shown in parentheses. The form of the anisotropic temperature factor is $\exp\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	−2539 (4)	3205 (9)	−399 (2)	64 (2)	88 (3)	61 (2)	−6 (2)	0 (2)	−16 (2)
O(2)	−115 (4)	1413 (7)	639 (2)	73 (2)	61 (2)	62 (2)	6 (2)	4 (2)	−15 (2)
C(1)	−3680 (4)	7025 (7)	−339 (2)	60 (2)	73 (2)	71 (2)	16 (2)	13 (2)	18 (2)
C(2)	−2453 (3)	5037 (8)	−1 (1)	45 (1)	64 (2)	57 (2)	−7 (1)	14 (1)	9 (2)
C(3)	−1230 (3)	5174 (6)	719 (1)	50 (1)	57 (2)	46 (2)	2 (1)	10 (1)	2 (2)
C(4)	−89 (3)	3274 (5)	1020 (1)	44 (1)	46 (2)	46 (1)	−2 (1)	13 (1)	−4 (1)
C(5)	1215 (3)	3328 (4)	1775 (1)	42 (1)	40 (1)	48 (1)	0 (1)	18 (1)	−2 (1)
C(6)	1262 (3)	5158 (5)	2256 (1)	54 (2)	50 (2)	51 (2)	6 (2)	15 (1)	−4 (1)
C(7)	2492 (3)	5145 (6)	2963 (1)	54 (2)	65 (2)	52 (2)	0 (2)	11 (1)	−7 (2)
C(8)	3695 (3)	3299 (6)	3189 (1)	54 (2)	74 (2)	47 (2)	−0 (2)	11 (1)	4 (2)
C(9)	3659 (4)	1463 (6)	2715 (2)	59 (2)	66 (2)	58 (2)	14 (2)	17 (1)	13 (2)
C(10)	2419 (3)	1456 (6)	2009 (1)	57 (2)	51 (2)	53 (2)	7 (2)	20 (1)	7 (2)
H(4)	−1200 (9)	6772 (14)	1017 (4)	101 (4)	73 (5)	77 (4)	37 (4)	5 (3)	0 (4)
H(5)	−1263 (12)	1881 (16)	43 (5)	123 (6)	102 (6)	142 (7)	−31 (6)	56 (6)	−62 (6)
H(6)	329 (8)	6593 (13)	2088 (3)	76 (4)	85 (5)	83 (4)	25 (4)	8 (3)	−21 (4)
H(7)	2503 (8)	6545 (15)	3331 (4)	93 (4)	106 (6)	74 (4)	8 (4)	7 (3)	−34 (4)
H(8)	4676 (8)	3284 (14)	3734 (3)	80 (4)	111 (5)	59 (4)	13 (4)	−1 (3)	10 (4)
H(9)	4606 (9)	10 (14)	2888 (4)	105 (5)	93 (5)	90 (4)	37 (5)	14 (4)	13 (4)
H(10)	2373 (8)	28 (13)	1635 (4)	95 (4)	77 (4)	80 (4)	27 (4)	25 (3)	−11 (4)

Table 1 (cont.)

	x	y	z	U
H(11)	−3040 (20)	8467 (33)	−487 (9)	97 (4)
H(12)	−3532 (21)	7504 (32)	−841 (9)	100 (4)
H(21)	−3380 (23)	8706 (35)	49 (10)	114 (5)
H(22)	−4260 (21)	7709 (32)	53 (9)	100 (4)
H(31)	−4974 (21)	6512 (30)	−468 (9)	95 (4)
H(32)	−4733 (22)	6422 (30)	−789 (9)	96 (4)

lation are nearly coincident. When the rigid-body motion is subtracted from the H atoms, the residual motion is large. A 'riding motion' correction (Busing & Levy, 1964) was applied to bond lengths which involved H.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Distances marked with an asterisk have been corrected for 'riding motion'. Distances in the columns marked *a* have been corrected for rigid-body motion.

INTERATOMIC DISTANCES

C(2)-O(1)	1.279(5)	1.288^a	C(3)-H(4)	1.067(8)	1.076*
	1.305*			1.116*	
C(4)-O(2)	1.282(4)	1.310	O(1)-H(5)	1.319(12)	1.322
	1.309*		O(2)-H(5)	1.235(11)	1.238
O(1)...O(2)	2.485(5)	2.489	C(6)-H(6)	1.075(7)	1.083
C(1)-C(2)	1.486(4)	1.491		1.119*	
	1.504*		C(7)-H(7)	1.067(8)	1.082
C(2)-C(3)	1.409(4)	1.412		1.118*	
C(3)-C(4)	1.398(4)	1.405	C(8)-H(8)	1.082(6)	1.088
C(4)-C(5)	1.482(4)	1.485		1.123*	
C(5)-C(6)	1.389(4)	1.397	C(9)-H(9)	1.091(8)	1.093
C(6)-C(7)	1.392(4)	1.394		1.140*	
C(7)-C(8)	1.386(4)	1.389	C(10)-H(10)	1.080(8)	1.090
C(8)-C(9)	1.384(4)	1.393		1.124*	
C(9)-C(10)	1.393(4)	1.394	C(1)-H(11)	1.063(18)	
C(10)-C(5)	1.398(4)	1.404	C(1)-H(12)	1.079(17)	
			C(1)-H(21)	1.180(21)	
			C(1)-H(22)	1.119(17)	
			C(1)-H(31)	1.041(16)	
			C(1)-H(32)	1.043(17)	

INTERATOMIC ANGLES

C(1)-C(2)-C(3)	121.8(3)		C(2)-C(3)-H(4)	117.8(4)
C(1)-C(2)-O(1)	116.7(3)		C(4)-C(3)-H(4)	121.8(4)
C(3)-C(2)-O(1)	121.4(3)		C(2)-O(1)-H(5)	101.1(4)
C(2)-C(3)-C(4)	120.4(3)		C(4)-O(2)-H(5)	103.3(4)
C(3)-C(4)-C(5)	122.5(2)		O(1)-H(5)-O(2)	153.2(7)
C(3)-C(4)-O(2)	120.3(2)		C(5)-C(6)-H(6)	120.3(4)
C(5)-C(4)-O(2)	117.2(3)		C(7)-C(6)-H(6)	119.0(4)
C(4)-C(5)-C(6)	122.1(2)		C(6)-C(7)-H(7)	120.0(4)
C(4)-C(5)-C(10)	118.6(2)		C(8)-C(7)-H(7)	120.3(4)
C(6)-C(5)-C(10)	119.3(2)		C(7)-C(8)-H(8)	120.5(5)
C(5)-C(6)-C(7)	120.7(3)		C(9)-C(8)-H(8)	119.3(5)
C(6)-C(7)-C(8)	119.7(3)		C(6)-C(9)-H(9)	120.5(4)
C(7)-C(8)-C(9)	120.2(2)		C(10)-C(9)-H(9)	119.1(5)
C(8)-C(9)-C(10)	120.4(3)		C(9)-C(10)-H(10)	121.0(4)
C(5)-C(10)-C(9)	119.8(3)		C(5)-C(10)-H(10)	119.2(4)

Table 3. *Equations of planes through selected atomic groupings of the form* $lX + mY + nZ + D = 0$

l, *m* and *n* are the direction cosines of the plane normal relative to orthogonal axes *X*, *Y* and *Z*, in Å, along *a*, *b* and *c**. *D* is the distance of the plane from the origin in Å. Deviations (Å), of relevant atoms, from the planes are shown in square brackets.

Plane (1): C(2), C(3), C(4), O(1), O(2)
  $0.8481X + 0.4172Y − 0.3267Z = 0.537$
  [C(2) −0.001, C(3) 0.006, C(4) −0.008, O(1) −0.002, O(2) 0.005, C(1) 0.019, C(5) −0.006, H(4) 0.035, H(5) 0.040]

Plane (2): C(5), C(6), C(7), C(8), C(9), C(10)
  $0.8027X + 0.5106Y − 0.3078Z = 0.298$
  [C(5) 0.004, C(6) 0.002, C(7) −0.005, C(8) 0.003, C(9) 0.002, C(10) −0.006, H(6) −0.012, H(7) −0.022, H(8) 0.019, H(9) 0.014, H(10) −0.012]

Angle between the planes: (1)–(2) 6.0°

Table 4. *Rigid-body tensors derived from the* U_{ij} *values of the non-hydrogen atoms*

$T(\times 10^4)$	443 (24)	−24 (20)	−25 (16)
(Å^2)		416 (21)	−1 (15)
			487 (15)
$L(\times 10^4)$	53 (5)	−13 (3)	48 (8)
(rad^2)		21 (3)	−28 (4)
			111 (15)
$S(\times 10^4)$	11 (12)	16 (5)	−14 (6)
(rad Å)	−13 (3)	−3 (13)	17 (5)
	29 (8)	18 (10)	−8*

R.m.s. amplitudes (Å) along principal axes of **T**
0.223   0.211   0.200
R.m.s. amplitudes (°) along principal axes of **L**
6.9   3.0   2.1
R.m.s. $\Delta U_{ij} = 0.004$ (5)

* Fixed at this value so that Trace **S** = 0.

Discussion

Comparison with X-ray analysis

A half-normal probability plot (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972), comparing our coordinates with Semmingsen's (1972), denoted S, has zero intercept and a slope of 2.2. This indicates that the pooled estimated standard deviations are too small by this factor. Individual differences as high as 6σ were observed. Comparison of bond lengths, corrected for thermal motion, also shows significant differences. S did find significant differences in the two C–C and two C–O bond lengths in the enol ring but was not convinced the differences were real because of large thermal motion. This study shows there are no differences in these bond lengths, suggesting an equal contribution of (II) and (III) to the structure. For equal contributions, one may have expected large thermal motion along the C–O bonds and H(5) to be disordered. Neither effect could be detected but could have been masked by the overall large thermal motion. If these effects have not been masked, the structure can be described as a true resonance hybrid of the two *cis* enol tautomers with complete electron delocalization. This is probably the better description. In the phenyl ring, each of our C–C bond lengths is greater than the corresponding value of S, our average C–C distance being 1.395 Å, S's 1.387 Å *cf.* 1.397 Å for benzene (Stoicheff, 1954; Langseth & Stoicheff, 1956). The molecule is not planar, the dihedral angle between the phenyl and enol rings being 6°.

The hydrogen bond

The hydrogen bond is asymmetric. O(1)–H(5), 1.322 (12) Å, is larger than O(2)–H(5), 1.238 (11) Å. In solution studies, it has been shown that the direction of enolization is towards the phenyl ring because of the stability of the cinnamoyl system, C_6H_5-C=C-C=O (Lowe & Ferguson, 1965). The O···O contact is 2.489 (5) Å, consistent with the distance found in other β-diketones. When, for the enol H atom, the contributions from the rigid-body model were subtracted

from the thermal parameters derived from the least-squares refinement (Sequeira, Berkebile & Hamilton, 1967; Schlemper, Hamilton & La Placa, 1971), the resultant U values were non-positive definite. The values obtained suggest the residual motion is approximately isotropic with r.m.s. amplitude of vibration of ~ 0.2–0.3 Å. This is much greater than the difference in O–H bond lengths. Inspection of the shorter non-bonded contacts of O(1) and O(2) in Table 5 shows that the distance between O(2) atoms, related by a centre of symmetry at the origin, is only 3·047 Å. Such asymmetry of environment of the O atoms might contribute to the asymmetry of the hydrogen bond. Thus H(5) could best be described as vibrating in a large potential well which is slightly asymmetric.

Table 5. *Shorter non-bonded contacts* (Å) *to* O(1) *and* O(2)

O(1)···C(3)	2·345	O(2)···C(3)	2·325
C(1)	2·356	C(5)	2·362
C(4)	2·786	C(10)	2·742
C(8^{i})	3·424	C(2)	2·761
C(4^{ii})	3·473	O(2^{iii})	3·047
C(3^{ii})	3·512	C(2^{ii})	3·466
O(2^{iii})	3·530	C(1^{ii})	3·505
C(1^{iv})	3·597	O(1^{iii})	3·530
C(5^{ii})	3·817	C(3^{iv})	3·629
O(2^{ii})	3·854	C(6)	3·657
		C(1^{iv})	3·767

Symmetry code
Superscript

None	$x,$	$y,$	z	(i)	$-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$
(ii)	$-x,$	$1-y,$	$-z$	(iii)	$-x, \quad -y, \quad -z$
(iv)	$x,$	$-1+y,$	z		

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