

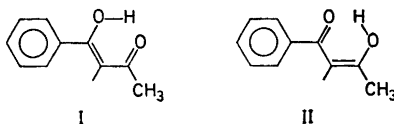
## The Crystal Structure of Benzoylacetone

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The crystal and molecular structure of benzoylacetone, 1-phenyl-1,3-butanedione, has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter techniques. The structure has been refined by least-squares methods to a weighted  $R$ -factor of 0.053 for 1090 reflections. The molecule crystallizes in space group  $P2_1/c$  of the monoclinic system. The unit cell has dimensions  $a = 8.244(7)$  Å,  $b = 5.596(5)$  Å,  $c = 19.793(4)$  Å and  $\beta = 111.77(2)^\circ$ . A rather short *intramolecular* hydrogen bond of  $2.498(2)$  Å was found. The enol ring appears to be asymmetric, with the enol hydrogen located in an asymmetric position; the two C-C and the two C-O bonds are probably of significantly different lengths. The angle between the benzene and enol ring planes is  $6.3^\circ$ .

Quite a few X-ray crystallographic studies of  $\beta$ -diketones have been undertaken.<sup>1-4</sup> It has been found that they exist in a *cis*-enol form in the crystal with a strong *intramolecular* hydrogen bond. Whether the hydrogen bond is of the symmetrical or asymmetrical type has, however, been a matter of discussion. X-Ray studies have given evidence for both; symmetrical in tetra-acetylene<sup>2</sup> and bis(*m*-bromobenzoyl)methane<sup>4</sup> and asymmetrical in dibenzoylmethane.<sup>1</sup> For an asymmetrical  $\beta$ -diketone like benzoylacetone there may be two different *cis*-enol forms, I and II where I is believed to dominate.<sup>5</sup>



In order to observe the effects of an asymmetric environment on the enol ring, the present investigation was undertaken.

### EXPERIMENTAL

The compound was purified by sublimation and suitable crystals were obtained by recrystallization from a pentane solution. Preliminary examination of Weissenberg photographs showed systematic absences for  $0k0$  reflections with  $k$  odd and  $h0l$  reflec-

tions with  $l$  odd. These extinctions determine the space group uniquely as  $P2_1/c$ . Unit cell parameters were determined by diffractometer technique varying  $2\theta$ ,  $\chi$  and  $\phi$  in conjunction with the left-right and top-bottom devices. The temperature was 18°C, the take-off-angle was 0.5°, and measurements were made with  $\text{CuK}\beta$  radiation ( $\lambda = 1.3922$  Å). The following cell dimensions were obtained:

$$\begin{aligned} a &= 8.244 \pm 0.007 \text{ \AA}, b = 5.596 \pm 0.005 \text{ \AA} \\ c &= 19.793 \pm 0.004 \text{ \AA}, \beta = 111.77 \pm 0.02^\circ \end{aligned}$$

The density of 1.26 g/cm<sup>3</sup> calculated for four molecules in the unit cell is in agreement with that of 1.24 g/cm<sup>3</sup> measured by flotation. For intensity measurements a crystal with rhombohedral cross section  $0.32 \times 0.43$  mm<sup>2</sup> and a height of 0.46 mm parallel to the  $b$  axis was used. The crystal was mounted with  $b^*$  parallel to the  $\phi$  axis, on a Picker automatic diffractometer with graphite monochromator and  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å). Intensity data were collected at 18°C using a take-off-angle of 4°. The receiving aperture was 4.0 mm wide and 5.0 mm high and positioned 22 cm from the crystal. The data were collected by the  $\omega - 2\theta$  scan technique at a scan rate of 1.0°/min. The scan angle was  $2\theta_{\alpha_1} - 0.8^\circ$  to  $2\theta_{\alpha_1} + 0.8^\circ$ . Background counts of 50 sec were taken at each end of the scan. Attenuator foils were automatically inserted in the diffracted beam when the intensity exceeded 10<sup>4</sup> counts/sec. The intensities of three medium reflections were measured for every 50 reflections throughout the experiment. No systematic variation in these standard reflections was observed. A unique data set having  $2\theta \leq 54^\circ$  was collected; a total of 1812 independent intensities were recorded. 1343 reflections had intensities greater than twice their standard deviations estimated from

$$\sigma(I) = [C_T + (0.02 C_N)^2]^{\frac{1}{2}}$$

where  $C_T$  is the total number of counts and  $C_N$  the net count (total counts minus background). The values of  $C_N$  and  $\sigma(I)$  were collected for Lorentz and polarization effects. Corrections for absorption were not made. The linear absorption coefficient of this compound is only 0.095 mm<sup>-1</sup>, and may cause maximum 2 % error in the intensities for the sample used. All calculations were performed on the CD-3300 computer at the University of Oslo. The programs used are described elsewhere.<sup>6</sup>

### STRUCTURE DETERMINATION

The phase problem was solved three-dimensionally by a computer program based on direct methods.<sup>6</sup> A total of 236 signs were determined by systematic application of the Harker-Kasper inequalities and Sayre's equation. The resulting Fourier map contained 12 peaks which clearly indicated the position of the molecule. Refinement proceeded by three dimensional full-matrix least-squares methods. The function minimized was  $\sum w(|F_o| - G|F_c|)^2$ . The weights were calculated from the standard deviations;  $w \propto Lp C_N (\sigma(I))^{-2}$  where  $Lp$  represent the Lorentz and polarization factors. The atomic scattering factors used for carbon and oxygen were those given by Hanson *et al.*<sup>7</sup> and for hydrogen those of Stewart *et al.*<sup>8</sup> Three cycles of refinement using isotropic thermal parameters, including only non hydrogen atoms, reduced the weighted  $R$ -factor ( $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}}$ ) to 23 %, ( $R = \sum (|F_o| - |F_c|) / \sum |F_o|$  to 15 %). Anisotropic thermal parameters were introduced for the carbon and oxygen atoms. Hydrogen atoms except those of the methyl group were located in a difference Fourier map and given isotropic thermal parameters. The refinement converged after three cycles with  $R_w = 0.09$  ( $R = 0.08$ ).

At this stage many low order reflections were noted to deviate from their calculated values. Corrections for secondary extinction did not reduce the  $R$ -values and were therefore not applied. The deviations mentioned above are probably due mainly to thermal diffuse scattering. Weissenberg diagrams

Table 1. Fractional atomic coordinates and anisotropic thermal vibration parameters with estimated standard deviations (multiplied by  $10^5$ ).<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
O1	-25 404	32 202	-3 993	2180	5250	344	299	54	-531
	20	29	8	29	63	45	8	19	29
O2	-1 090	14 047	6 429	2486	3492	359	774	114	-729
	20	24	8	29	47	46	6	19	25
C1	-36 682	70 595	-3 285	2080	5481	419	776	338	940
	29	45	12	42	101	73	10	28	44
C2	-24 530	50 472	-15	1454	4039	331	540	507	311
	23	39	10	38	69	60	8	24	41
C3	-12 362	51 482	7 159	1816	3230	314	-93	521	-106
	23	37	10	35	69	59	8	23	36
C4	922	33 065	10 187	1499	2783	284	-496	513	-35
	22	30	9	36	65	53	8	23	35
C5	12 150	33 247	17 726	1472	2650	268	-352	533	117
	25	29	8	33	63	59	8	23	32
C6	12 726	51 508	22 600	1702	3068	315	332	425	-95
	25	37	10	33	62	58	8	23	32
C7	24 908	51 102	29 568	1969	3822	316	-208	469	-410
	26	42	11	37	73	59	9	25	39
C8	36 810	32 851	31 829	1802	4651	273	-313	343	243
	27	39	11	35	84	59	9	24	37
C9	36 515	14 713	27 117	2049	3776	372	1245	616	574
	28	42	11	39	75	70	10	28	39
C10	24 167	14 781	20 096	2075	2815	332	470	730	105
	25	36	11	37	62	59	8	25	35

<sup>a</sup> For numbering of atoms, see Fig. 1.Table 2. Fractional atomic coordinates and isotropic thermal vibration parameters with estimated standard deviations (multiplied by  $10^4$ ) for hydrogen atoms.<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H4	-1135	6599	992	4.1
	24	37	10	0.4
H5	-1267	1830	39	8.2
	44	52	18	0.6
H6	488	6427	2103	3.9
	28	38	10	0.5
H7	2457	6362	3243	6.2
	35	54	16	0.6
H8	4524	3308	3656	5.7
	35	38	14	0.5
H9	4466	191	2856	5.4
	33	47	12	0.5
H10	2395	303	1692	4.7
	26	43	12	0.5

<sup>a</sup> For numbering of atoms, see Fig. 1.







and oxygen atoms were calculated from the temperature parameters of Table 1. Root mean square amplitudes and corresponding  $B$ -values for the atomic anisotropic thermal vibration along the principal axes together with the components of these axes along the crystal axes are given in Table 4. Bond

Table 4. The principal axes of the thermal vibration ellipsoids given by the components of a unit vector in fractional coordinates  $e_x$ ,  $e_y$ ,  $e_z$ , the corresponding r.m.s. amplitudes, and the  $B$ -values.

Atom	$e_x$	$e_y$	$e_z$	$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$B$ (Å <sup>2</sup> )
O1	.0530	.0866	-.0310	.324	8.28
	-.0656	.1477	.0027	.278	6.11
	.0998	.0511	.0446	.205	3.32
O2	.0745	.0682	.0253	.333	8.74
	.1053	-.0772	.0367	.244	4.69
	.0209	.1460	.0312	.194	2.96
C1	-.0161	.1469	.0256	.376	11.18
	.1135	.0643	.0004	.267	5.62
	.0626	-.0790	.0480	.175	2.41
C2	-.0051	.1386	.0310	.266	5.59
	.0818	-.0844	.0440	.236	4.40
	.1017	.0749	-.0079	.197	3.08
C3	.0725	.0709	-.0258	.244	4.69
	.1074	-.0711	.0372	.233	4.29
	.0169	.1478	.0302	.210	3.48
C4	.1021	.1069	.0247	.231	4.22
	.0043	.0576	.0485	.223	3.94
	.0814	.1314	.0012	.190	2.84
C5	.0256	.0964	.0453	.219	3.80
	.1098	-.0934	.0242	.217	3.72
	.0660	.1180	-.0179	.190	2.84
C6	.0531	.0704	-.0334	.248	4.86
	.0960	.0706	.0427	.223	3.94
	.0709	-.1483	.0045	.214	3.63
C7	.0224	.1275	-.0309	.265	5.56
	.1172	-.0711	.0084	.247	4.81
	.0532	.1030	.0440	.215	3.65
C8	-.0326	.1604	.0133	.280	6.20
	.0974	.0746	-.0112	.241	4.57
	.0807	-.0251	.0516	.211	3.50
C9	.0675	.1222	.0365	.280	6.20
	.0831	.0171	-.0259	.253	5.06
	.0748	-.1293	.0310	.209	3.45
C10	.1199	.0455	.0339	.254	5.10
	.0383	.0152	-.0422	.229	4.15
	.0351	-.1721	.0052	.208	3.43

distances, bond angles, short *intramolecular* contacts, and non bonded distances between molecules are presented in Table 5. The bond distances in parentheses are corrected for thermal motions. The estimated standard deviations have been calculated from the correlation matrix of the last least-squares refinement cycle without taking into account the e.s.d.'s in the cell

Table 5. Bond distances, bond angles, short intramolecular contacts, and other short contacts (equivalent position numbers as defined below in parentheses). Estimated standard deviations in bond lengths between heavy atoms is 0.003 Å and angles less than 0.2°. Distances in parentheses are corrected for anisotropic motion.

Bond distances (Å)			Bond angles (°)	
C1-C2	1.487	(1.520) <sup>a</sup>	O1-C2-C1	117.5
C2-C3	1.401	(1.405) <sup>b</sup>	O1-C2-C3	120.6
C3-C4	1.376	(1.383) <sup>b</sup>	C1-C2-C3	121.5
C4-C5	1.482	(1.487)	C2-C3-C4	121.9
C5-C6	1.394	(1.401)	C3-C4-O2	120.4
C6-C7	1.373	(1.376)	C3-C4-C5	123.9
C7-C8	1.372	(1.379)	O2-C4-C5	115.6
C8-C9	1.373	(1.380)	C4-C5-C6	121.8
C9-C10	1.385	(1.388)	C4-C5-C10	119.8
C10-C5	1.388	(1.396)	C5-C6-C7	120.5
O1-C2	1.276	(1.293) <sup>c</sup>	C5-C10-C9	120.2
O2-C4	1.294	(1.312) <sup>c</sup>	C6-C5-C10	118.4
O1-O2	2.498	(2.502) <sup>c</sup>	C6-C7-C8	120.6
O1-H5	1.40		C8-C9-C10	120.2
O2-H5	1.18		C7-C8-C9	119.9
C3-H4	0.96		O1...H5-O2	150
C6-H6	0.94		C2-O1...H5	102
C7-H7	0.91		C4-O2-H5	104
C8-H8	0.94		C2-C3-H4	119
C9-H9	0.95		C4-C3-H4	119
C10-H10	0.91		C5-C6-H6	119
			C7-C6-H6	120
			C6-C7-H7	116
			C8-C7-H7	124
			C7-C8-H8	120
			C9-C8-H8	121
			C8-C9-H9	121
			C10-C9-H9	119
			C9-C10-H10	121
			C5-C10-H10	118

<sup>a</sup> Corrected for "riding motion".

<sup>b</sup> Corrected for "rigid body motion" by assuming that the molecule except C1 is rigid.

<sup>c</sup> Corrected for "rigid body motion" by assuming the enol ring rigid. Correction in other bonds is "rigid body" corrections assuming the benzene ring+C4 rigid.

Intermolecular contacts (Å)		Intramolecular contacts (Å)	
O1...O2 (1)	3.53	O2...C5	2.35
O1...C3 (2)	3.52	O2...C10	2.73
O1...C4 (2)	3.46	O2...H10	2.40
O1...C8 (3)	3.44	C2...C4	2.43
O1...C1 (4)	3.59	C3...C5	2.52
O2...O2 (1)	3.05	C3...C6	2.99
O1...C1 (2)	3.50	C3...H6	2.68
O2...C2 (2)	3.47	C4...C6	2.51
C1...C1 (5)	3.73	C4...C10	2.48





parameters. They are approximately 0.003 Å for bonds between non hydrogen atoms, and 0.03 Å for bonds involving hydrogen atoms. The corresponding deviations in angles are 0.1° and 1°, respectively. Bond distances (uncorrected) and angles are also shown in Fig. 1. Least-squares planes were calculated for both rings. The deviations from the planes are presented in Table 6. Fig. 2 shows the packing of the molecule as viewed along the *b* axis.

Table 6. Distances from least-squares planes in Å. Plane 1 is through the enol ring, plane 2 through the benzene ring. Deviations of atoms not defining the planes in parenthesis.

Atom	1	2
O1	0.004	
O2	-0.005	
C1	-0.008	
C2	0.005	
C3	0.005	
C4	0.000	(0.001)
C5	(0.001)	-0.001
C6		-0.003
C7		0.004
C8		-0.001
C9		-0.003
C10		0.004
H4	(-0.053)	
H5	(-0.065)	
H6		(-0.028)
H7		(-0.003)
H8		(-0.017)
H9		(-0.017)
H10		(-0.010)

Plane 1 makes an angle of 6.3° with plane 2.

#### THERMAL MOTIONS

As would be expected for a structure containing no strong *intermolecular* forces, the temperature factors are generally large. Marked anisotropies are only found for the terminal atoms, *i.e.* O1, O2, and C1. The thermal vibration parameters of Table 1 were applied in a rigid-body analysis.<sup>9,10</sup> Neither the enol ring nor the whole molecule may be regarded as oscillating rigid-body. The r.m.s. discrepancies ( $\Delta u_{\text{rms}}$ ) between "observed" atomic vibration tensor components and those calculated from T.L.S. analysis<sup>9</sup> are in both cases as large as 0.006 Å<sup>2</sup>. If, however, O1, O2, and C1 are omitted, the rest of the molecule appears to be fairly rigid ( $\Delta u_{\text{rms}} = 0.0027$  Å<sup>2</sup>). Further reduction is obtained by omitting also C2 ( $\Delta u_{\text{rms}} = 0.0022$  Å<sup>2</sup>) or C2 and C3 ( $\Delta u_{\text{rms}} = 0.0017$  Å<sup>2</sup>). No better agreement was obtained by considering the benzene ring alone. The r.m.s. translation amplitudes corresponding to the discrepancy of 0.0017 Å<sup>2</sup> (for the benzene ring + C4) is 0.220, 0.208, and 0.190 Å, while the libration amplitudes are 6.2, 3.9, and 2.2°. Libration corrections<sup>10</sup> of bond distances

were made after each T.L.S. analysis. By assuming the enol ring to be rigid the increments were  $+0.017 \text{ \AA}$ , while, by assuming the whole molecule to be rigid, only  $+0.004 \text{ \AA}$ . "Riding motion" corrections<sup>11</sup> indicate that C1 is "riding" on C2, C2 on C3, and so on. The assumption that C1 rides on C2 seems reasonable. The corrected value obtained by the "riding" model for this bond is presented in Table 5.

#### DISCUSSION

The benzene ring and the enol ring are both planar within estimated limits of error. The molecule as a whole is non-planar; the plane of the benzene ring makes an angle of  $6.3^\circ$  with that of the enol ring. The largest deviations from the ring planes are  $0.008 \text{ \AA}$ , the mean value being  $0.004 \text{ \AA}$ .

After libration corrections the six C-C bonds in the benzene ring vary in length from  $1.376 \text{ \AA}$  to  $1.401 \text{ \AA}$ . The mean value of  $1.387 \text{ \AA}$  is probably significantly shorter than the value  $1.397 \text{ \AA}$ , generally accepted for benzene.<sup>12,13</sup> This may partly be due to the neglect of bonding electrons in the atomic scattering factors.<sup>14</sup> The same may be said about the average observed C-H distance of  $0.93 \text{ \AA}$ .

The intramolecular contact between H4 and H6 is  $2.1 \text{ \AA}$ . This is similar to those found in biphenyl<sup>15</sup> and dibenzoylmethane.<sup>1</sup> It is significantly shorter than  $2.4 \text{ \AA}$  which is twice the van der Waals radius for hydrogen. Owing to the systematic foreshortening of the C-H bonds the true  $\text{H4}\cdots\text{H6}$  distance is possibly somewhat less than the observed value.

The deviations of the angles C6-C5-C10, C4-C5-C6, and C3-C4-C5 from  $120^\circ$  are highly significant, and probably due to repulsions between non-bonded atoms, especially H4 and H6. The repulsive forces are also partly relieved by the rotation about the C4-C5 bond. No significant deviations of the hydrogen atoms H4 and H6 from the enol and benzene ring planes, respectively, were observed. The C4-C5 bond of  $1.487(2) \text{ \AA}$  is probably significantly shorter than the central bond in biphenyl<sup>15</sup> of  $1.497(3) \text{ \AA}$ , a fact which may be due to the reduced  $\text{H}\cdots\text{H}$  repulsion in benzoylacetone compared to biphenyl.

The short  $\text{O}\cdots\text{O}$  distance of  $2.498(2) \text{ \AA}$  agrees well with the corresponding distances of  $2.468 \text{ \AA}$  and  $2.424 \text{ \AA}$  observed in dibenzoylmethane<sup>1</sup> and tetraacetylene,<sup>2</sup> respectively, and indicates the presence of a strong intramolecular hydrogen bond. The hydrogen atom (H5) is unambiguously located in an asymmetric position near O2, and is situated significantly off the line between the two oxygen atoms. The angle  $\text{O1}\cdots\text{O2}-\text{H5}$  is  $16 \pm 1^\circ$ .

If the individual distances in the enol ring are considered to be independently determined, the two C-C and C-O bonds are significantly different. Owing to the large thermal parameters of the oxygen atoms, and because the two C-C distances have C3 in common, this assumption is, however, rather unwarranted. On the other hand, the present investigation is in full agreement with previous investigations,<sup>1-3</sup> as to the asymmetry and bond lengths of the enol ring. Furthermore, the hydrogen atom (H5) is localized asymmetrically. There are therefore reasons to believe that the asymmetries and the observed differences in the enol ring are real. The question is whether the observed bond

distances are due to conjugation or to a statistical distribution. The idea of conjugation in the ring seems to be very likely and is supported by the following arguments; the carbon skeleton in the enol ring seems fairly rigid and the enol ring is planar within the experimental error. A statistical distribution could either arise from dynamic interchange between the two possible *cis* isomers or from a disordered structure containing both isomers arranged at random in a static distribution. The static model does not seem probable; the calculated value for the barrier in malondialdehyde is only 0.5 kcal/mol,<sup>16</sup> and NMR investigations in solution<sup>17</sup> indicate rapid interconversion between the *cis*-enols I and II.

Although the statistical models do not seem likely, they cannot be excluded; the effects of statistical disorder and thermal motion are additive in the total mean-square displacement.<sup>18</sup> The presence of disorder may therefore not necessarily lead to abnormal thermal parameters.

*Acknowledgement.* The author wishes to thank cand.real. P. Groth and cand.real. B. Klewe for many stimulating discussions and helpful suggestions.

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Received April 3, 1971.