

- DALY, J. J. (1965). Unpublished results.
- DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Unpublished results.
- FOUTS, P. I., HELMER, O. M., LEPKOVSKY, S. & JUKES, T. H. (1938). *J. Nutr.* **16**, 197.
- HANIC, F., ŠTEMPELOVÁ, D. & HANICOVÁ, K. (1964). *Acta Cryst.* **17**, 633.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem I. The Centrosymmetric Crystal*. A. C. A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.
- HEGSTED, D. M. & RAO, M. N. (1945). *J. Nutr.* **30**, 367.
- HSU, J. M., BUDDMEYER, E. & CHOW, B. F. (1964). *Biochem. J.* **90**, 60.
- International Tables for X-Ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.
- KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 1356.
- KORNBERG, A., TABOR, H. & SEBRELL, W. H. (1945). *Amer. J. Physiol.* **143**, 434.
- LINDQUIST, I. & NAHRINGBAUER, G. (1959). *Acta Cryst.* **12**, 638.
- LUCKEY, T. D., BRIGGS, G. M., JR., ELVEHJEM, C. A. & HART, E. B. (1945). *Proc. Soc. Exp. Biol. Med.* **58**, 340.
- NAGAKURA, S. & TANAKA, J. (1954). *J. Chem. Phys.* **22**, 236.
- PIKE, R. L. & BROWN, M. L. (1959). *J. Nutr.* **68**, 531.
- RABINOWITZ, J. C. & SNELL, E. E. (1948). *J. Biol. Chem.* **176**, 1157.
- RÉRAT, C. (1962). *Acta Cryst.* **15**, 427.
- RIGGS, T. R., COYNE, B. & CHRISTENSEN, H. N. (1953). *Biochim. Biophys. Acta* **11**, 303.
- RODWELL, V. W., VOLCANI, B. E., IKAWA, M. & SNELL, E. E. (1958). *J. Biol. Chem.* **233**, 1548.
- SIM, G. A. (1957). *Acta Cryst.* **10**, 177.
- STEBBINS, R. B. (1951). *Amer. J. Physiol.* **166**, 538.
- TROTTER, J. (1959). *Acta Cryst.* **12**, 884.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
- WOOLFSON, M. M. (1954). *Acta Cryst.* **7**, 61.

Acta Cryst. (1966). **21**, 340

Crystal Structure of Dibenzoylmethane*

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The crystal structure diffraction phase problem for dibenzoylmethane ($C_{15}H_{12}O_2$) has been solved by packing analysis. The three-dimensional scintillation counter data have been refined by anisotropic least-squares analysis. The positions of all hydrogen atoms, including the enolic hydrogen, have been found and refined by least-squares analysis. The final discrepancy index for the 865 observed reflections was 5.9%.

The molecule was found to be nonplanar, with the planes of the two phenyl groups making angles of -3.8 and $+16.9^\circ$ respectively with the enol ring. The hydrogen bond was found to be very short, 2.47 Å, and appears to be nonlinear, asymmetric, and nonstatistical. The thermal analysis showed rather large librations of the phenyl groups about their connecting bonds and a large libration of the enol ring about an axis through the carbonyl carbon atoms. Intramolecular distances were corrected for the observed librations.

The crystals are orthorhombic, space group *Pbca*, with lattice constants $a = 10.857$, $b = 24.446$, $c = 8.756$ Å, and eight molecules in the unit cell.

Introduction

Dibenzoylmethane is used as an analytical reagent for the determination of uranium (Harton & White, 1958; Maeck, Booman, Elliott & Rein, 1959). It has also been investigated for use in the determination of plutonium and neptunium (Kolthoff, Elving & Sandell, 1962) and several other metal ions because of its chelating ability. Williams, Dumke & Rundle (1962) and Engebretson & Rundle (1964) have shown that the symmetrically substituted *m*-bromo and *m*-chloro-dibenzoylmethanes are completely enolized in the crystal and possess a strong, possibly symmetric, intramolec-

ular hydrogen bond. Dibenzoylmethane crystallizes in a different space group from either the *m*-chloro or the *m*-bromo compound, with twice as many molecules in the unit cell. The unit cell of the *m*-chloro compound does not have a center of symmetry, but centers of symmetry are present in the *m*-bromo compound and in dibenzoylmethane itself.

Collection and treatment of X-ray data

Crystals suitable for X-ray analysis were obtained by recrystallization from carbon tetrachloride solution. Weissenberg and precession X-ray photographs indicated the unique centric orthorhombic space group *Pbca*. Data for the lattice constants were obtained with a single-crystal orienter-scintillation counter, which

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had been previously calibrated with an aluminum single crystal. Precise angular measurements were made for 16 reflections in the back reflection region, using chromium radiation. The lattice constants and standard deviations ($a=10.857 \pm 0.002$, $b=24.446 \pm 0.005$, and $c=8.756 \pm 0.002$) were obtained by least-squares extrapolation (Williams, 1964a) of the data using the Nelson-Riley (1945) error formula. The calculated density for eight molecules in the unit cell is 1.281 g.cm^{-3} .

Three-dimensional X-ray diffraction intensity data were taken with zirconium-filtered molybdenum radiation. All reflections that were observably above the background, up to $2\theta=50^\circ$, were scanned by the moving-crystal moving-counter (θ , 2θ coupling) measurement technique. A 100 sec scan, covering 3.33° in 2θ , was used for each reflection. Background was estimated graphically from a plot of average background versus 2θ . Because of the large b lattice constant, some overlapping of reflections occurred when the h and l indices were small. When this overlap was observed on the ratemeter charts, the reflection was rejected. The intensities of the 042 and 210 reflections were followed as standards; a nearly linear decline of about 5% was observed in both reflections. The corresponding linear decline correction was applied to all measurements. A nonlinearity correction was applied to all crude counting rates. The Lorentz and polarization corrections were made in the usual manner; no absorption or extinction correction was made. A streak correction was applied to the data (Williams & Rundle, 1964). Single-crystal orienter settings were precalculated with the program of Williams (1963). A total of 865 reflections were observed. The standard deviation of each intensity measurement was estimated by the formula

$$\sigma^2(I) = C_T + C_B + (0.03 C_T)^2 + (0.03 C_B)^2 + (0.10 C_S)^2,$$

where C_T , C_B , and C_S are respectively the total, background, and streak counts. The error in the structure factor, $\sigma(F_o)$, was calculated from $\sigma(I)$ by the finite difference method (Williams & Rundle, 1964).

Structure determination

Determination of the structure was accomplished in three stages: (1) calculation of an approximate packing structure by rigid body packing analysis; (2) verification and refinement of the packing structure by rigid body structure factor analysis; and (3) individual atom refinement by structure factor analysis.

Rigid body packing analysis

A packing function, G , was defined as a function of the six rotational and translational parameters of a molecule of assumed dimensions in the unit cell. The rotations and translations of the symmetry related molecules were expressed as functions of the orthorhombic symmetry operators of the space group. The packing function was then minimized by obtaining

expressions for the six derivatives and setting them equal to zero. The resulting set of equations in six unknowns was then solved to obtain an improved packing structure. The packing function used was

$$G = \sum [(d^0)^2 - (d^c)^2],$$

where d^0 is the expected minimum nonbonded distance, d^c is the interatomic distance for the current model, and the sum is taken over all intermolecular distances for which $d^c < d^0$. The effect of minimizing G is to make as many of the d^c as possible equal or larger than the d^0 , consistent with the unit-cell dimensions and symmetry.

Let the subscript i ($i=1, 2, 3$) refer to a set of cartesian axes, the subscript j refer to an atom of the basic molecule, and the subscript n refer to a symmetry operation transforming atom k of the basic molecule. In the simple treatment we restrict the symmetry operators T_{in} and S_{in} to translations, reflections, and twofold rotations as defined by the equation

$$X_{ikn} = T_{in} + S_{in}X_{ik},$$

where $S_{in} = \pm 1$. In this notation the square of the distance from atom j to atom k transformed by symmetry operation n is

$$(d_{jkn}^c)^2 = \sum_i (X_{ij} - T_{in} - S_{in}X_{ik})^2.$$

The square of the expected minimum interatomic distance is

$$(d_{jk}^0)^2 = (r_j + r_k)^2,$$

where r_j and r_k are the atomic radii.

The effect of a small rotation and translation of the rigid molecule is given by the matrix equation

$$\begin{bmatrix} X_{1j} \\ X_{2j} \\ X_{3j} \end{bmatrix} = \begin{bmatrix} 1 & -\theta_3 & \theta_2 \\ \theta_3 & 1 & -\theta_1 \\ -\theta_2 & \theta_1 & 1 \end{bmatrix} \begin{bmatrix} X_{1j}^0 \\ X_{2j}^0 \\ X_{3j}^0 \end{bmatrix} + \begin{bmatrix} \Delta X_1 \\ \Delta X_2 \\ \Delta X_3 \end{bmatrix},$$

where the X_{ij}^0 are the coordinates of the trial packing model, the θ_i correspond to small rotations about axis i , and the ΔX_i are translations. We may now differentiate $(d_{jkn}^c)^2$ with respect to the six variables. Table 1 shows the value of each derivative at the trial coordinates.

The packing function, G , may be minimized by expansion in a first order Taylor's series about the trial coordinates, in the same way that structure factor refinement problem is customarily treated (Cruickshank, 1959). For the generalized parameters p_i the resulting linear equations are, in matrix notation, $\mathbf{Bp} = \mathbf{c}$, where

Table 1. Derivatives of $(d_{jkn}^c)^2$

Parameter	Derivative
ΔX_1	$2C_1(1 - S_{1n})$
ΔX_2	$2C_2(1 - S_{2n})$
ΔX_3	$2C_3(1 - S_{3n})$
θ_1	$2C_2(-X_{3j}^0 + S_{2n}X_{3k}^0) + 2C_3(X_{2j}^0 - S_{3n}X_{1k}^0)$
θ_2	$2C_1(X_{3j}^0 - S_{1n}X_{3k}^0) + 2C_3(-X_{1j}^0 + S_{3n}X_{2k}^0)$
θ_3	$2C_1(-X_{2j}^0 + S_{1n}X_{2k}^0) + 2C_2(X_{1j}^0 - S_{2n}X_{1k}^0)$
where $C_i = X_{ij}^0 - T_{in} - S_{in}X_{ik}^0$	

$$B_{ij} = \sum_j \sum_k \sum_n \frac{\partial (d_{jkn}^c)^2}{\partial p_i} \frac{\partial (d_{jkn}^e)^2}{\partial p_j}$$

$$c_i = \sum_j \sum_k \sum_n \frac{\partial (d_{jkn}^c)^2}{\partial p_i} [(d_{jkn}^0)^2 - (d_{jkn}^c)^2]^2.$$

The summation is taken only over terms for which $d^c < d^0$.

Values of the nonbonded atomic radii were taken as 1.2, 1.8, and 1.4 Å for H, C and O respectively (Kitaigorodskii, 1955). Note that these values correspond to the minimum normally expected distance in the crystal. The minimum distances are compressed distances and should not be confused with the minimum in the nonbonded interatomic potential functions. In some of the dibenzoylmethane calculations the above values were increased somewhat to include more terms in the G function. The optimum values of the d^0 are those which give fastest convergence to an acceptable packing model, and these values need not correspond to the minimum of the nonbonded potential energy curve.

A more exact treatment of the rigid body packing problem would minimize the packing energy. The success of the simple packing analysis method described here led us to undertake further work in this area (Williams, 1964*b*, 1965).

In the bromo- and chloro-substituted dibenzoylmethanes the molecule was found to be nearly planar. The first packing calculations for dibenzoylmethane itself assumed planarity of the molecule, and the packing program obtained the best fit of this planar molecule in the observed unit cell. This packing model did not satisfy the diffraction data very well, and the diffraction data would not refine. The lowest value obtained for G was 113.

Packing calculations were then made for nonplanar propeller-shaped molecules with various phenyl twist angles. The lowest value of G (95.7) was found for a 7.5° phenyl twist angle. This propeller model was refined with the diffraction data using rigid body structure factor least squares.

Fig. 1 shows details of how well the best packing model obtained by minimizing the G function compares with the final model obtained by refinement of the X-ray data. In the final model, the molecule is shaped like an antipropeller, with phenyl twist angles of 3.8 and 16.9°. Notice, however, that the difference between 3.8 and 16.9 is 13.1°. In the propeller packing model with twist angles of 7.5°, the two rings are rotated 15° with respect to each other. In the Figure, the numbers not in parentheses show how much the atoms of the phenyl groups are above and below the enol ring plane for the 7.5° propeller model. The numbers in parentheses give the same information for the final molecular parameters.

It can be seen from the Figure that a small rotation about the indicated axis will fit the positions of the phenyl groups at the expense mainly of the two oxygen

atoms. In the best packing model, the phenyl carbons differed from the correct positions by an average of 0.10 Å, with a maximum of 0.16 Å. Because of the incorrect assumption of propeller shape, the fit of the oxygen atoms was not as good. The numbers in brackets in the figure show the oxygen atoms were 0.26 and 0.27 Å from their correct positions.

Rigid body structure factor analysis

The best model produced by the packing calculations yielded a discrepancy index of 28% for 379 low angle reflections. This model would not refine further by either block-diagonal or full-matrix least-squares structure factor analysis when the positions of all 17 heavy atoms were allowed to vary. Immediate convergence was obtained, however, when only the six rotational and translational parameters of the molecule were allowed to vary, with the use of the program of Hybl, described by Hybl, Rundle & Williams (1965). With this refinement method, the discrepancy index decreased to 23%. When the molecule was subdivided into three rigid-body groups (thus allowing the phenyl groups to rotate with respect to the enol ring) the discrepancy index dropped to 18% for the 379 reflections.

Individual atom refinement

The full-matrix structure factor least-squares program of Busing, Martin & Levy (1962) was used for the final refinement. The scattering factor tables of Hanson, Herman, Lea & Skillman (1964) were used. The heavy atoms were refined with allowance for anisotropic thermal motion. Only the positional parameters of the 12 hydrogen atoms were determined; an assumed temperature factor of 4.0 Å⁻² was used for the hydrogen atoms. Thus a total of 190 parameters were determined. Because of computer limitations, the least-squares matrix was calculated in two overlapping blocks, each block containing 121 parameters. On alternate cycles the block contained either the parameters from rings I and III or from rings II and III (Fig. 2), plus the scale factor. The final discrepancy

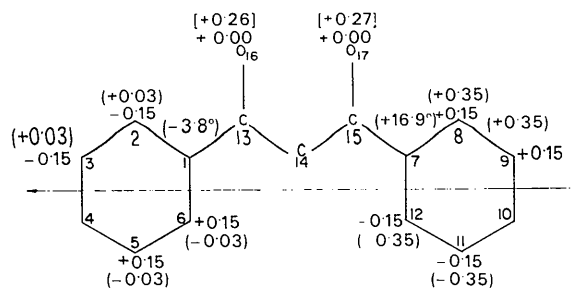


Fig. 1. Deviations (Å) of the best packing model from the final model. The numbers not in parentheses show the deviations from the plane of the enol ring for the 7.5° propeller packing model. The numbers in parentheses show the same information for the final model. The numbers in brackets indicate the deviations of the oxygen atoms in the best packing model from the observed final oxygen positions.

index for the observed reflections was 5.9%; the weighted discrepancy index was 5.0%.

Calculations of the interatomic distances, angles, and individual atom thermal analyses were made with the program of Busing, Martin & Levy (1964). Covariances between parameters were included in the error treatment, except those between parameters of atoms in ring I and in ring II. Final values of the par-

ameters are given in Table 2. A comparison of the observed and the calculated structure factors is given in Table 3. Structure factors for the final model were also calculated for all rejected reflections out to $2\theta = 50^\circ$.

Discussion

The intramolecular distances and angles are shown in Fig. 2. A thermal libration correction was applied to all distances except those involving hydrogen atoms. The libration correction is discussed below in the thermal analysis section. Table 4 shows the uncorrected distances between heavy atoms and their estimated standard deviations. The estimated standard deviations of the C-H and O-H distances are 0.05 and 0.06 Å respectively. The estimated standard deviations for the angles ranged from 0.2 to 0.6° when heavy atoms defined the angle, and from 2.8 to 4.5° when a hydrogen atom was involved in the angle.

The benzene rings have mean observed C-C and C-H bond distances of 1.389 and 0.98 Å respectively. The observed C-H distance (uncorrected for thermal libration) is in good agreement with other recent X-ray investigations (Stewart, Davidson & Simpson, 1965) but is shorter than values obtained spectroscopically and by neutron or electron diffraction (Ibers, 1961). Least-squares planes (Blow, 1960) were calculated for each ring (Table 5). The largest deviation of the carbons from the respective ring planes was 0.022 Å, and the mean magnitude of deviation was 0.010 Å. These deviations are probably not significant.

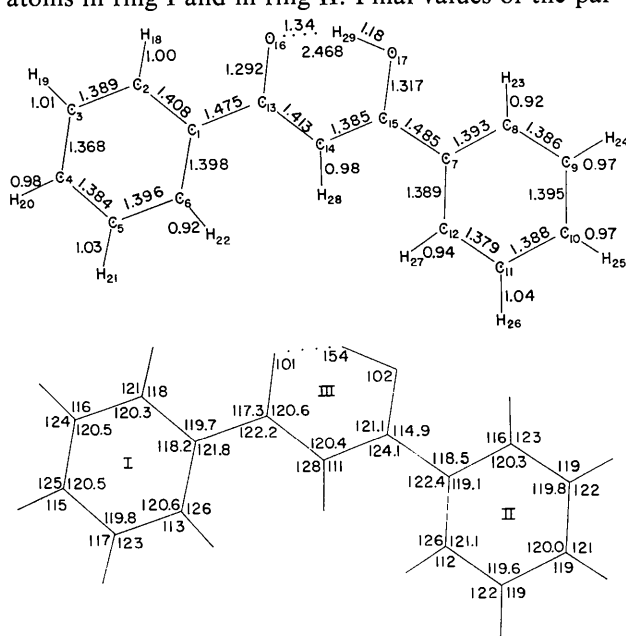


Fig. 2. The observed intramolecular distances (Å) and angles (°).

Table 2. Final values of the parameters $\times 10^5$

The form of the temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	-5777	-1876	19003	734	187	1370	-115	66	-8
C(2)	-12134	-5139	8528	992	256	1539	-55	-16	25
C(3)	7535	-10199	4373	1131	229	1831	-113	-72	-102
C(4)	3396	-11988	10034	1241	187	2076	-18	169	-69
C(5)	9997	-8812	20079	1296	166	2035	-31	-237	-28
C(6)	5514	-3712	24353	1019	191	1594	-104	-121	-27
C(7)	-3335	16173	47127	919	165	1427	43	229	83
C(8)	-10279	20505	52414	1172	185	1823	62	125	51
C(9)	-5261	24220	62532	1457	165	2461	123	157	-61
C(10)	6996	23780	66669	1816	155	1932	-51	41	-32
C(11)	13972	19476	61361	1073	185	2494	-67	19	-116
C(12)	8721	15682	51788	911	177	1984	37	200	-93
C(13)	-10661	3597	23060	750	187	1517	-119	173	55
C(14)	-4550	7085	33305	698	174	1629	-36	-101	-11
C(15)	-9208	12200	36467	776	180	1682	34	162	70
O(16)	-20853	5034	16984	760	236	2579	-21	-261	60
O(17)	-19330	13911	30089	948	228	2481	66	-126	16
H(18)	-20260	-3852	4833	848	167	1305	0	0	0
H(19)	-12941	-12440	-2644	848	167	1305	0	0	0
H(20)	7494	-15404	6953	848	167	1305	0	0	0
H(21)	18190	-10372	23951	848	167	1305	0	0	0
H(22)	10070	-2112	31957	848	167	1305	0	0	0
H(23)	-18275	20689	48970	848	167	1305	0	0	0
H(24)	-10456	27170	66327	848	167	1305	0	0	0
H(25)	10809	26473	73244	848	167	1305	0	0	0
H(26)	23072	19140	64943	848	167	1305	0	0	0
H(27)	14430	13024	48462	848	167	1305	0	0	0
H(28)	3194	6452	38663	848	167	1305	0	0	0
H(29)	-21973	10171	22218	848	167	1305	0	0	0

Table 3. Comparison of the observed structure factors and the calculated structure factors based on the parameters shown in Table 2

The first column shows the k index, the second is the observed value ($\times 10$), and the third the calculated value ($\times 10$). The first part of the table gives data which were used for the final refinement. The second part of the table gives data for reflections (up to $2\theta=50^\circ$) that were not included in the final refinement.

0, K, 0	6 115 128	10 63 75	2, K, 5	18 151 164	25 128 117	1 266 267	10 99 74	1R 88 -65	10, K, 1
4 463 -417	9 348 340	1, K, 10	1 62 -62	21 157 176	0 209 -201	2 136 -124	11 204 -220	8, K, 3	1 66 48
6 513 -505	10 250 -244	5 70 -66	2 86 102	3, K, 4	1 243 237	5 170 -175	14 138 -106	4 129 134	2 137 -148
10 948 -941	11 108 94	2, K, 0	4 98 110	0 315 319	2 109 102	6 80 -43	17 139 -146	5 219 229	3 86 81
12 599 -593	13 449 -475	0 1991 2045	5 86 -89	1 274 269	3 328 -328	1 108 114	9 78 -95	6 94 -92	4 63 -47
14 358 -339	15 105 -83	1 650 630	6 110 -95	0 7 137 133	5 267 -278	2 132 -147	12 134 119	6 275 296	6 94 -92
18 176 -170	16 91 -74	2 106 -95	7 139 143	1 274 269	9 285 288	4 319 315	14 230 309	8 150 138	7 143 -150
20 202 198	23 127 139	3 952 941	8 148 -154	5 616 -633	12 165 170	5 319 -318	15 161 155	10 104 -112	9 171 -156
22 171 -140	25 185 -183	4 200 190	9 87 -125	6 759 -760	13 175 -191	6 136 143	16 61 -49	12 106 -108	10 275 -269
24 154 141	2 106 -95	5 236 232	12 95 112	7 317 -321	14 145 -159	9 96 105	20 79 61	14 99 -51	11 99 -51
26 96 91	1, K, 2	6 369 -352	13 76 69	8 309 -307	16 586 -586	10 179 181	22 98 -104	16 63 179	12 89 -63
28 127 -126	0 176 -183	7 142 -135	15 158 -158	18 62 70	17 153 160	14 110 -101	25 103 -116	18 79 -61	14 91 -75
	2 871 838	8 359 352	16 95 94	20 79 87	19 76 83	15 188 182	9 174 -182	10 174 -182	16 87 53
	3 1956 1987	9 290 292	19 64 89	3, K, 5	21 88 -99	17 106 96	16 187 198	4 87 64	
	4 849 823	10 529 537	2, K, 6	2, K, 6	20 94 85	18 133 -127	17 86 -67	5 154 -168	
	5 546 -537	11 174 169	2, K, 6	2, K, 6	25 67 82	23 74 74	20 90 -98	6 83 -94	
	6 256 -265	12 470 484	2 129 -148	3, K, 5	26 72 45	20 115 116	2 281 282	7, K, 4	
	8 600 -633	12 470 484	3 97 96	3, K, 5	25 67 82	25 97 -92	3 91 -75	8, K, 2	
	10 240 174	13 350 -353	6 140 -141	3, K, 5	26 72 45	26 89 -58	4 321 324	9, K, 2	
	12 710 702	15 105 -83	7 137 133	4, K, 3	25 67 82	26 89 -58	5 89 -80	7, K, 4	
	14 577 549	16 144 -132	10 103 -119	4, K, 3	25 67 82	26 89 -58	6 101 -98	8, K, 2	
	20 102 -113	17 126 -114	13 186 -185	4, K, 3	25 67 82	26 89 -58	7 101 -98	9, K, 2	
	22 152 150	18 176 -183	14 100 92	4, K, 3	25 67 82	26 89 -58	8 101 -98	10, K, 2	
	24 101 -83	19 126 -114	15 158 -158	4, K, 3	25 67 82	26 89 -58	9 101 -98	10, K, 2	
	26 149 135	20 178 -180	16 95 94	4, K, 3	25 67 82	26 89 -58	10 101 -98	10, K, 2	
		21 63 -62	17 95 94	4, K, 3	25 67 82	26 89 -58	11 101 -98	10, K, 2	
		22 90 -72	18 62 70	4, K, 3	25 67 82	26 89 -58	12 101 -98	10, K, 2	
		23 327 -321	19 76 69	4, K, 3	25 67 82	26 89 -58	13 101 -98	10, K, 2	
		24 185 -179	20 148 -152	4, K, 3	25 67 82	26 89 -58	14 101 -98	10, K, 2	
		25 236 -222	21 63 -62	4, K, 3	25 67 82	26 89 -58	15 101 -98	10, K, 2	
		26 84 -70	21 63 -62	4, K, 3	25 67 82	26 89 -58	16 101 -98	10, K, 2	
			2, K, 1	4, K, 3	25 67 82	26 89 -58	17 101 -98	10, K, 2	
			1 95 102	4, K, 3	25 67 82	26 89 -58	18 101 -98	10, K, 2	
			7 81 112	4, K, 3	25 67 82	26 89 -58	19 101 -98	10, K, 2	
			13 126 127	4, K, 3	25 67 82	26 89 -58	20 101 -98	10, K, 2	
			0 159 161	4, K, 3	25 67 82	26 89 -58	21 101 -98	10, K, 2	
			2 82 93	4, K, 3	25 67 82	26 89 -58	22 101 -98	10, K, 2	
			5 105 110	4, K, 3	25 67 82	26 89 -58	23 101 -98	10, K, 2	
			6 117 120	4, K, 3	25 67 82	26 89 -58	24 101 -98	10, K, 2	
			10 203 196	4, K, 3	25 67 82	26 89 -58	25 101 -98	10, K, 2	
			11 63 -43	4, K, 3	25 67 82	26 89 -58	26 101 -98	10, K, 2	
			9 118 114	4, K, 3	25 67 82	26 89 -58	27 101 -98	10, K, 2	
			10 94 -99	4, K, 3	25 67 82	26 89 -58	28 101 -98	10, K, 2	
			11 81 102	4, K, 3	25 67 82	26 89 -58	29 101 -98	10, K, 2	
			15 61 -63	4, K, 3	25 67 82	26 89 -58	30 101 -98	10, K, 2	
			15 61 -63	4, K, 3	25 67 82	26 89 -58	31 101 -98	10, K, 2	
			2, K, 9	4, K, 3	25 67 82	26 89 -58	32 101 -98	10, K, 2	
			2 115 -106	4, K, 3	25 67 82	26 89 -58	33 101 -98	10, K, 2	
			3 64 -47	4, K, 3	25 67 82	26 89 -58	34 101 -98	10, K, 2	
			10, K, 8	4, K, 3	25 67 82	26 89 -58	35 101 -98	10, K, 2	
			2 79 -62	4, K, 3	25 67 82	26 89 -58	36 101 -98	10, K, 2	
			3 100 -77	4, K, 3	25 67 82	26 89 -58	37 101 -98	10, K, 2	
			4 100 -90	4, K, 3	25 67 82	26 89 -58	38 101 -98	10, K, 2	
			0 114 -110	4, K, 3	25 67 82	26 89 -58	39 101 -98	10, K, 2	
			10 206 187	4, K, 3	25 67 82	26 89 -58	40 101 -98	10, K, 2	
			11 104 -95	4, K, 3	25 67 82	26 89 -58	41 101 -98	10, K, 2	
			1 199 -188	4, K, 3	25 67 82	26 89 -58	42 101 -98	10, K, 2	
			2 418 -419	4, K, 3	25 67 82	26 89 -58	43 101 -98	10, K, 2	
			3 551 -524	4, K, 3	25 67 82	26 89 -58	44 101 -98	10, K, 2	
			4 498 -479	4, K, 3	25 67 82	26 89 -58	45 101 -98	10, K, 2	
			2 117 93	4, K, 3	25 67 82	26 89 -58	46 101 -98	10, K, 2	
			11 5 94	4, K, 3	25 67 82	26 89 -58	47 101 -98	10, K, 2	
			6 380 -375	4, K, 3	25 67 82	26 89 -58	48 101 -98	10, K, 2	
			7 229 223	4, K, 3	25 67 82	26 89 -58	49 101 -98	10, K, 2	
			8 253 258	4, K, 3	25 67 82	26 89 -58	50 101 -98	10, K, 2	
			9 597 586	4, K, 3	25 67 82	26 89 -58	51 101 -98	10, K, 2	
			10 582 -582	4, K, 3	25 67 82	26 89 -58	52 101 -98	10, K, 2	
			6 327 313	4, K, 3	25 67 82	26 89 -58	53 101 -98	10, K, 2	
			11 146 138	4, K, 3	25 67 82	26 89 -58	54 101 -98	10, K, 2	
			7 171 -165	4, K, 3	25 67 82	26 89 -58	55 101 -98	10, K, 2	
			13 270 -284	4, K, 3	25 67 82	26 89 -58	56 101 -98	10, K, 2	
			14 177 181	4, K, 3	25 67 82	26 89 -58	57 101 -98	10, K, 2	
			15 175 184	4, K, 3	25 67 82	26 89 -58	58 101 -98	10, K, 2	
			2 171 156	4, K, 3	25 67 82	26 89 -58	59 101 -98	10, K, 2	
			16 105 78	4, K, 3	25 67 82	26 89 -58	60 101 -98	10, K, 2	
			17 123 -109	4, K, 3	25 67 82	26 89 -58	61 101 -98	10, K, 2	
			19 88 -85	4, K, 3	25 67 82	26 89 -58	62 101 -98	10, K, 2	
			4 90 -95	4, K, 3	25 67 82	26 89 -58	63 101 -98	10, K, 2	
			5 198 205	4, K, 3	25 67 82	26 89 -58	64 101 -98	10, K, 2	
			8 179 197	4, K, 3	25 67 82	26 89 -58	65 101 -98	10, K, 2	
			9 345 -358	4, K, 3	25 67 82	26 89 -58	66 101 -98	10, K, 2	
			10 324 -333	4, K, 3	25 67 82	26 89 -58	67 101 -98	10, K, 2	
			11 134 122	4, K, 3	25 67 82	26 89 -58	68 101 -98	10, K, 2	
			12 227 234	4, K, 3	25 67 82	26 89 -58	69 101 -98	10, K, 2	
			15 156 -149	4, K, 3	25 67 82	26 89 -58	70 101 -98	10, K, 2	
			16 128 127	4, K, 3	25 67 82	26 89 -58	71 101 -98	10, K, 2	
			17 95 95	4, K, 3	25 67 82	26 89 -58	72 101 -98	10, K, 2	
			18 140 130	4, K, 3	25 67 82	26 89 -58	73 101 -98	10, K, 2	
			20 139 -138	4, K, 3	25 67 82	26 89 -58	74 101 -98	10, K, 2	
			21 162 -158	4, K, 3	25 67 82	26 89 -58	75 101 -98	10, K, 2	
			23 319 -338	4, K, 3	25 67 82	26 89 -58	76 101 -98	10, K, 2	
			26 62 -50	4, K, 3	25 67 82	26 89 -58	77 101 -98	10, K, 2	
			1 287 -283	4, K, 3	25 67 82	26 89 -58	78 101 -98	10, K, 2	
			2 309 -305	4, K, 3	25 67 82	26 89 -58	79 101 -98	10, K, 2	
			3 263 263	4, K, 3	25 67 82	26 89 -58	80 101 -98	10, K, 2	
			4 136 -128	4, K, 3	25 67 82	26 89 -58	81 101 -98	10, K, 2	
			5 127 117	4, K, 3	25 67 82	26 89 -58	82 101 -98	10, K, 2	
			6 224 -232	4, K, 3	25 67 82	26 89 -58	83 101 -98	10, K, 2	
			8 232 230	4, K, 3	25 67 82	26 89 -58	84 101 -98	10, K, 2	
			9 285 288	4, K, 3	25 67 82	26 89 -58	85 101 -98	10, K, 2	
			10 438 448	4, K, 3	25 67 82	26 89 -58	86 101 -98	10, K, 2	
			11 364 365	4, K, 3	25 67 82	26 89 -58	87 101 -98	10, K, 2	
</									

Table 3 (cont.)

Table with multiple columns containing numbers and alphanumeric labels (e.g., 0, K, 0, 2, 1, K, 1, etc.). The table is organized into a grid-like structure with labels on the left and numerical values in the main body.

The molecule as a whole is nonplanar; the plane of benzene ring I makes an angle of -3.8° with the plane of the enol ring, while the plane of benzene ring II makes an angle of $+16.9^\circ$ with the enol ring. The magnitude and sense of the nonplanarity can be read from Table 5. If plane III is used as a reference, it can be seen from the Table that ring I has been bent down-

Table 4. Intramolecular distances and their estimated standard deviations

Atoms	Distance (uncorrected)	Distance (corrected)
C(1)—C(2)	$1.398 \pm 0.007 \text{ \AA}$	1.408 \AA
C(2)—C(3)	1.383 ± 0.007	1.389
C(3)—C(4)	1.358 ± 0.007	1.368
C(4)—C(5)	1.375 ± 0.007	1.384
C(5)—C(6)	1.390 ± 0.007	1.396
C(6)—C(1)	1.387 ± 0.007	1.398
C(7)—C(8)	1.380 ± 0.007	1.393
C(8)—C(9)	1.381 ± 0.007	1.386
C(9)—C(10)	1.383 ± 0.008	1.395
C(10)—C(11)	1.377 ± 0.007	1.388
C(11)—C(12)	1.374 ± 0.007	1.379
C(12)—C(7)	1.376 ± 0.007	1.389
C(1)—C(13)	1.482 ± 0.006	1.475
C(13)—C(14)	1.404 ± 0.007	1.413
C(14)—C(15)	1.377 ± 0.006	1.385
C(15)—C(7)	1.490 ± 0.007	1.485
C(13)—O(16)	1.277 ± 0.005	1.292
C(15)—O(17)	1.302 ± 0.005	1.317
O(16)—O(17)	2.460 ± 0.005	2.468

Table 5. Distances from the least-squares planes and equations of the planes in \AA

Distances to atoms defining the plane are asterisked

Atom	I	II	III
C(1)	0.019*		-0.059
C(2)	-0.013*		-0.104
C(3)	0.002*		-0.175
C(4)	0.004*		-0.243
C(5)	0.003*		-0.232
C(6)	-0.014*		-0.164
C(7)		-0.003*	0.028
C(8)		-0.015*	0.373
C(9)		0.022*	0.428
C(10)		-0.011*	0.058
C(11)		-0.006*	-0.293
C(12)		0.013*	-0.291
C(13)	-0.031	0.277	-0.017*
C(14)	-0.026	0.319	0.006*
C(15)	-0.109	-0.015	0.008*
O(16)	-0.062	-0.022	0.014*
O(17)	-0.193	-0.373	-0.011*
H(18)	0.03		-0.02
H(19)	0.05		-0.14
H(20)	-0.06		-0.36
H(21)	0.00		-0.29
H(22)	0.09		-0.06
H(23)		-0.03	0.57
H(24)		0.04	0.70
H(25)		-0.04	0.04
H(26)		0.01	-0.53
H(27)		-0.03	-0.59
H(28)	-0.00	0.53	-0.01
H(29)	-0.19	-0.32	-0.05

$$(I) \quad -0.4769X - 0.4296Y - 0.7668Z - 1.753 = 0$$

$$(II) \quad -0.2826X - 0.5544Y - 0.7828Z - 1.144 = 0$$

$$(III) \quad -0.5174X - 0.3779Y - 0.7678Z - 1.834 = 0$$

ward in addition to a rotation about the C(1)—C(13) bond. This is shown by the negative deviations of C(1) and C(4) from the ring III plane. On the other hand, C(7) and C(10) are more nearly in the ring III plane, so that ring II is primarily only rotated about the C(7)—C(15) bond.

Three types of factor primarily operate to determine the angles of the benzene ring planes with respect to the enol ring plane. The first is the repulsive forces between compressed atoms which can be relieved by such rotations. Between ring I and ring III these compressed distances are: H(22)—H(28), 2.30; C(6)—H(28), 2.79; C(14)—H(22), 2.75; C(6)—C(14), 2.96; O(16)—H(18), 2.42; and C(2)—O(16), 2.76 \AA . The compressed distances between ring II and ring III are: H(27)—H(28), 2.19; C(12)—H(28), 2.60; C(14)—H(27), 2.85; C(12)—C(14), 3.02; O(17)—H(23), 2.34; and C(8)—O(17), 2.72 \AA . These distances present a mixed picture of repulsion relief, since (for example) while the C—C distance increases in going from ring I to ring II, the C—O distance decreases. The four angles C(6)—C(1)—C(13), C(1)—C(13)—C(14), C(12)—C(7)—C(15), and C(7)—C(15)—C(14) have increased slightly from 120° to allow some repulsion relief.

The second factor, which operates to oppose the rotation of the phenyl groups, is the conjugation energy between the rings (Fischer-Hjalmars, 1963). There are available rough estimates for the magnitude of this energy as a function of the rotation angle in biphenyl (Bartell, 1962), which give some indication of the energy of rotation in the present phenyl-enol conjugated system. The C(1)—C(13) and C(7)—C(15) bond lengths of 1.475 and 1.485 \AA are normal for single bonds between trigonal carbon atoms (Dewar & Schmeising, 1960).

The third factor is the effect of the crystal packing. With the aid of a computer it is possible to sum potential energies of interaction with neighboring molecules (Williams, 1964*b*). Such a packing summation is only meaningful to the extent that reliable non-bonded interatomic potential functions are available. The molecular packing is considered in more detail below.

The enol ring presents a consistent picture of a non-linear, asymmetric, and nonstatistical hydrogen bonded system. In this picture the double bonds are partly localized between C(13)—O(16) and C(14)—C(15), and the enolic hydrogen is attached to O(17). The differences of 0.025 \AA in the C—O distances, 0.028 \AA in the C—C distances, and 0.16 \AA in the O—H distances are individually barely outside experimental error. The hydrogen is significantly off the O(16)—O(17) line (by 0.25 \AA) with a C(15)—O(17)—H(29) angle of 102° and an O(16)—H(29)—O(17) angle of 154° .

The short O—O distance of 2.468 \AA is similar to the corresponding distances of 2.475 and 2.464 \AA found in bis(*m*-chlorobenzoyl)methane and bis(*m*-bromobenzoyl)methane. The short O—O distance in these molecules can be correlated with the conjugation energy

and the near planarity of these molecules which result in the repulsions between nonbonded atoms discussed above. These repulsions increase the C(1)–C(13)–C(14) and C(7)–C(15)–C(14) angles, forcing the oxygen atoms closer together. Hydrogen bonds in this length range have been described by other workers as either symmetric or asymmetric, usually depending upon the crystal symmetry of the bond (Speakman & Mills, 1961). Rundle (1964) has recently summarized the available data on short O–H–O hydrogen bonds.

Thermal analysis

An examination of the directions and amplitudes of the principal axes of the observed anisotropic atomic vibrations indicated that the molecule could reasonably be subdivided thermally into the three ring components. The method of Cruickshank (1956) was applied to find the rigid body translations and librations of each ring, using the computer program of Gantzel, Coulter & Trueblood (1964). Coupling of the benzene ring systems to the enol ring was introduced by allowing

the center of libration to move along the C(1)–C(4) and C(7)–C(10) bonds until the best least-squares fit was obtained. Similarly, the center of libration of the enol ring was allowed to move along the line joining the mid-points of O(16)–O(17) and C(13)–C(15). The best fit of the rigid body thermal model was such that about 90% of the magnitudes of the observed atomic anisotropic temperature factors was accounted for. The minima with respect to the position of the center of libration were not sharply defined. For ring I the librational center was located at 0.6 Å from C(1) in the direction of C(4), while for ring II the center was located 0.2 Å from C(7) in the direction of C(10). This difference between the location of the librational centers of the two rings is consistent with the molecular packing. Ring I is sandwiched between two molecules, while ring II extends into the end packing region (Fig. 4) where it has more space available to wag. This larger wagging motion moves the librational center of ring II more towards C(7).

The librational center of the enol ring was located at the mid-point of C(13)–C(15). Table 6 summarizes

Table 6. Results of the rigid body thermal analysis

The translational tensor T						
Ring	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
I	0.0555	0.0526	0.0481	–0.0135	0.0032	0.0040
II	0.0564	0.0389	0.0581	0.0004	0.0162	0.0061
III	0.0343	0.0544	0.0622	–0.0055	0.0064	0.0092

Principal axes of T and their direction cosines relative to the cell axes

Ring	Axis	R.M.S. amplitude	$\cos \theta_1$	$\cos \theta_2$	$\cos \theta_3$
I	1	0.260 Å	0.7415	–0.6707	–0.0163
	2	0.225	0.3136	0.3250	0.8922
	3	0.195	0.5931	0.6667	–0.4513
II	1	0.272	–0.6701	–0.1333	–0.7302
	2	0.209	–0.6554	0.5682	0.4976
	3	0.188	–0.3486	–0.8120	0.4681
III	1	0.262	–0.0728	–0.5260	–0.8474
		0.228	–0.4097	0.7904	–0.4555
		0.175	–0.9093	–0.3140	0.2730

The librational tensor ω (radians²)

Ring	ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{13}	ω_{23}
I	0.0086	0.0124	0.0053	–0.0020	–0.0009	0.0042
II	0.0062	0.0125	0.0127	0.0032	0.0057	0.0055
III	0.0014	0.0228	0.0108	0.0019	0.0003	0.0090

Principal axes of ω and their direction cosines relative to the cell axes

Ring	Axis	R.M.S. amplitude	$\cos \theta_1$	$\cos \theta_2$	$\cos \theta_3$
I	1	7.0°	0.3257	–0.8566	–0.4002
	2	5.1	0.9454	0.2920	–0.1444
	3	3.3	0.0064	0.4251	–0.9051
II	1	8.3	–0.4010	–0.6064	–0.6867
	2	5.0	–0.3086	0.7952	–0.5220
	3	3.1	–0.8626	–0.0025	0.5059
III	1	9.5	0.0703	0.8812	0.4674
	2	4.5	0.1253	0.4570	–0.8806
	3	2.0	0.9896	–0.1205	0.0783

the results obtained by the thermal analysis. In Fig. 3 the results are shown stereographically, looking down the c axis of the cell.

The rigid body librations show a definite pattern of maximum libration about the bonds connecting the rings. This pattern reassures us that the thermal parameters derived from the experimental data have validity and are not merely reflecting various experimental errors. Rings I and II have different crystalline environments. As noted above, ring I is sandwiched between molecules. Ring II is not thus sandwiched, and there-

fore it is reasonable to expect ring II to show a greater libration about its connecting bond than ring I. The enol ring shows an especially large libration of 9.5° about the C(13)-C(15) line. This result is also quite reasonable in view of the smaller size of the oxygen atoms relative to the carbons. Since the perpendicular distance between molecules is determined largely by the C-C interactions, the enol ring is allowed to librate in the extra space thus provided.

The intramolecular distances (except those involving hydrogen) were corrected for thermal foreshortening

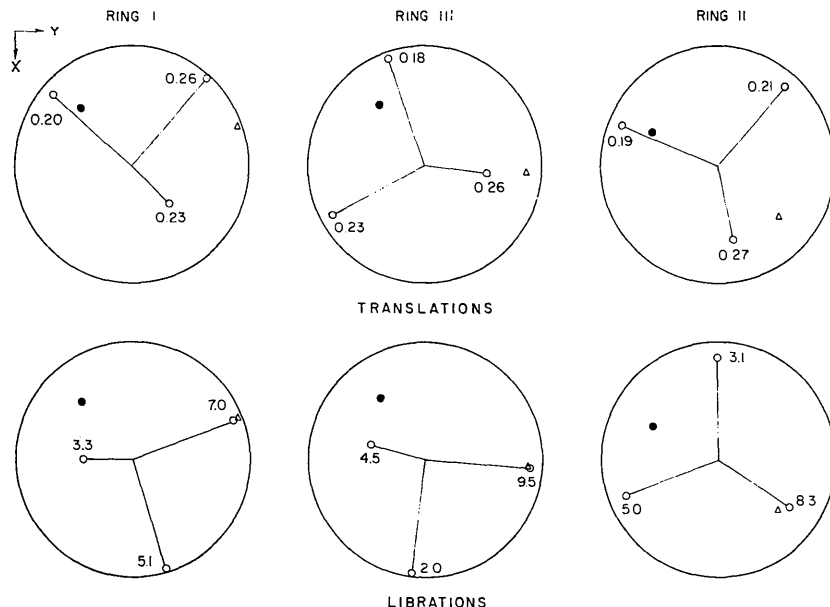


Fig. 3. Thermal stereograms of the observed rigid body translations and librations. The direction of the principal axes of translation or libration is shown stereographically for each of the three rings. The r.m.s. magnitude of translation (\AA) or libration ($^\circ$) is shown by each axis. The triangles show the directions of the C(7)-C(13), C(13)-C(15), C(15)-C(7) bonds for rings I, III, and II, respectively. The solid circles show the direction of the normals to the best least-squares planes for each ring.

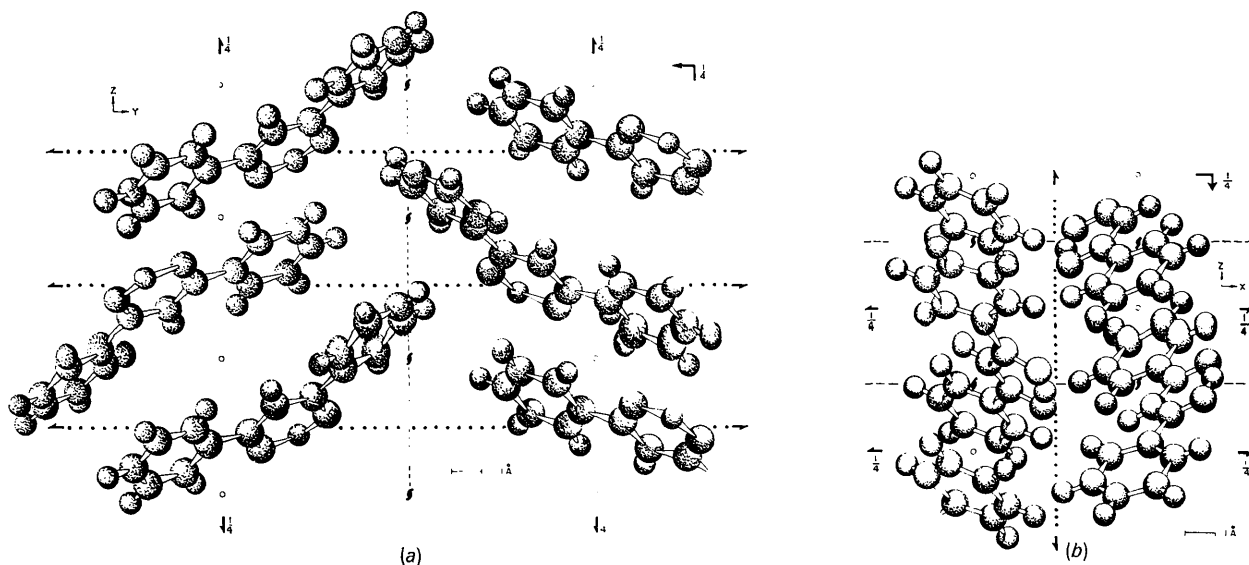


Fig. 4. (a) The structure looking down the x axis. The dimer stacking through centers of symmetry in the z direction is shown. The end interlocking of the phenyl rings II in the y direction is also shown. (b) The structure looking down the y axis. The absence of interlocking in the x direction is shown.

by the method of Cruickshank (1961). The magnitude of the correction varied from 0.005 to 0.015 Å, with the largest correction applying to the lengths of the C–O bonds.

Packing of the molecules

Fig. 4 shows how the molecules are arranged in the unit cell. The structure may be viewed as if it were made up of packing dimers, the molecules of the packing dimer being related by a center of symmetry. These dimers are stacked along z and interlock with each other in the y direction. The thickness of the dimer controls the length of the c lattice constant, while the end interlocking is controlled by the twofold screw in the y direction, the z glide in the y direction, and the b lattice constant. Table 7 shows by symmetry type the short intermolecular distances.

Table 7. Short intermolecular distances (Å) classified by symmetry type

The specified symmetry operation is applied to the second atom of the pair. There is an equivalent distance with the atoms interchanged, using the same symmetry operation with a negative translation part.

- Glide plane at $y=b/4$, translation $c/2$.
H(24)–C(8), 3.21; H(24)–C(15), 3.14; H(24)–O(17), 2.67;
H(25)–C(7), 3.16; H(25)–C(12), 3.16.
- Glide plane at $z=c/4$, translation $a/2$.
C(6)–H(18), 3.20; H(21)–C(2), 2.92; H(21)–H(18), 2.75;
H(22)–C(2), 3.22; H(22)–O(16), 2.71; H(22)–H(18), 2.47;
H(27)–O(16), 2.86; H(27)–H(29), 2.44; H(28)–O(16), 2.88;
H(28)–H(29), 3.00.
- Screw axis at $y=b/4$, $z=c/2$, translation $a/2$.
C(11)–H(23), 3.21; H(26)–H(23), 2.92.
- Screw axis at $x=0$, $z=c/4$, translation $b/2$.
C(9)–H(20), 3.07; H(24)–H(20), 2.75.
- Screw axis at $x=a/4$, $y=0$, translation $c/2$.
C(11)–H(21), 3.15; H(26)–C(4), 3.13; H(26)–C(5), 3.16;
H(26)–H(20), 2.40; H(26)–H(21), 2.47; H(27)–H(21), 2.99.
- Screw axis at $x=-a/4$, $y=0$, translation $c/2$.
C(15)–H(19), 3.17; O(17)–H(19), 2.47; H(23)–H(19), 2.87;
H(29)–H(19), 2.80.
- Inversion center at $x=0$, $y=0$, $z=c/2$.
C(5)–C(7), 3.46.

Phenyl ring I and the enol ring are directly on top of one another in the packing dimer, while phenyl ring II hangs off each end. Thus phenyl ring I is relatively constrained and is only twisted at a 3.8° angle. Phenyl ring II extends into the end interlocking region and is more free to twist there. The observed twist of 16.9° is such that the edges of the rings are brought more parallel to x , allowing more efficient interlocking.

There is no interlocking in the x direction. The molecular interfaces are through the x glides normal to z and through screw axes in the x direction. All intermolecular distances appear to be normal van der Waals contacts.

If bis(*m*-bromo- or bis(*m*-chloro-benzoyl)methane crystallized with the same packing structure as dibenzoylmethane itself, there would be considerably less congregation of halogen atoms. In the bromo compound the bromines are arranged in sheets, in the chloro

compound the chlorine atoms are arranged in chains, while the *meta* hydrogen atoms in dibenzoylmethane itself are relatively isolated. Thus it appears that the magnitude of the halogen–halogen dispersion attraction is a controlling factor determining the packing structure. We have made approximate calculations of the packing energy of dibenzoylmethane in the three space groups and have obtained packing energies in the correct sequence $E(Pbca) < E(Pca2_1) < E(Pnca)$. More quantitative packing calculations are planned for this system.

References

- BARTELL, L. S. (1962). *Tetrahedron*, **17**, 265.
 BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE, a Fortran Crystallographic Function and Error Program*. USAEC Report ORNL-TM-306.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, a Fortran Crystallographic Least-squares Program*. USAEC Report ORNL-TM-305.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1959). In *International Tables for X-ray Crystallography*, Vol. II, p. 326. Birmingham: Kynoch Press.
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
 DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96.
 ENGBRETSON, G. R. & RUNDLE, R. E. (1964). *J. Amer. Chem. Soc.* **86**, 574.
 FISCHER-HJALMARS, I. (1963). *Tetrahedron*, **19**, 1805.
 GANTZEL, P., COULTER, C. & TRUEBLOOD, K. (1964). IBM 709 or 7090 Program UCLATO1, private communication.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
 HARTON, C. A. & WHITE, J. C. (1958). *Anal. Chem.* **30**, 1779.
 HYBL, A., RUNDLE, R. E. & WILLIAMS, D. E. (1965). *J. Amer. Chem. Soc.* **87**, 2779.
 IBERS, J. A. (1961). *Acta Cryst.* **14**, 853.
 KITAIGORODSKII, A. I. (1955). *Organic Chemical Crystallography*. New York: Consultants Bureau.
 KOLTHOFF, I. M., ELVING, P. J. & SANDELL, E. B. (1962). *Treatise on Analytical Chemistry*. Part II, Vol. 9, p. 160.
 MAECK, W. J., BOOMAN, G. L., ELLIOTT, M. C. & REIN, J. E. (1959). *Anal. Chem.* **31**, 1130.
 NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
 RUNDLE, R. E. (1964). *Journal de Physique*, **25**, 487.
 SPEAKMAN, J. C. & MILLS, H. H. (1961). *J. Chem. Soc.* p. 1164.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 WILLIAMS, D. E., DUMKE, W. L. & RUNDLE, R. E. (1962). *Acta Cryst.* **15**, 627.
 WILLIAMS, D. E. (1963). *Single Crystal Orienter Angles Program SCO-6*. Unpublished research.
 WILLIAMS, D. E. & RUNDLE, R. E. (1964). *J. Amer. Chem. Soc.* **86**, 1660.
 WILLIAMS, D. E. (1964a). *LCR-2, a Fortran Lattice Constant Refinement Program*. USAEC Report IS-1052.
 WILLIAMS, D. E. (1964b). *PACK2, a Fortran Crystallographic Molecular Packing Program*. USAEC Report IS-1042.
 WILLIAMS, D. E. (1965). *Science*, **147**, 605.