

## The Crystal Structures of Deoxyanisoin and *p,p'*-Dimethoxybenzophenone

BY H. G. NORMENT AND ISABELLA L. KARLE

*U.S. Naval Research Laboratory, Washington 25, D.C., U.S.A.*

(Received 10 November 1961)

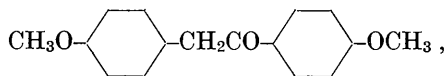
The structure of deoxyanisoin has been determined directly from the intensities by the application of probability methods to obtain the phases. Three-dimensional X-ray single-crystal data were used. The space group is  $P2_1/c$ ,  $Z=4$  and the cell dimensions are

$$a = 15.13, b = 5.506, c = 21.94 \text{ \AA}; \beta = 133^\circ 50'.$$

The molecules lie extended along the  $\bar{4}04$  planes. Planes through the benzene rings make an angle of  $62^\circ$  with each other. The carbonyl group and the methoxy groups are coplanar with the adjacent benzene ring.

The structure of *p,p'*-dimethoxybenzophenone previously determined has been refined by least squares using 5527 independent reflections. Bond lengths and angles are compared with those in deoxyanisoin.

Deoxyanisoin,



itself a weak estrogen, is used as an intermediate in the synthesis of stilbestrol, which is a non-steroid with high estrogenic activity. The analysis of its crystal and molecular structure was undertaken to compare it with the structure of *p,p'*-dimethoxybenzophenone (Karle, Hauptman, Karle & Wing, 1958), whose molecular formula is similar except for the absence of the methylene group. The latter compound has two molecules in the asymmetric unit whereas deoxyanisoin has one. Due to a lack of computing facilities at the time the structure of *p,p'*-dimethoxybenzophenone was determined, it was refined only on one-fifth of the total data. All the data available in the copper sphere have now been used in a least-squares refinement with isotropic temperature factors. The new coordinates, bond lengths, and other structural features are reported in this paper.

### DEOXYANISOIN

#### Experimental measurements

Impure deoxyanisoin, purchased from Bios Laboratories, Inc., was recrystallized twice from ethyl alcohol which yielded colorless crystals with a sharp melting point at  $111.5^\circ\text{C}$ . Long, virtually flawless, prisms with almost square cross sections were grown by slow evaporation of solvent from an acetone solution. The prism faces are parallel to the (100) and ( $\bar{1}02$ ) planes.

The crystals were found to be monoclinic, space group  $P2_1/c$ , with unit cell parameters:

$$a = 15.13 \pm 0.02, b = 5.506 \pm 0.017, c = 21.94 \pm 0.06 \text{ \AA};$$

$$\beta = 133^\circ 50' \pm 1'; Z = 4;$$

$$\rho_c = 1.288, \rho_o = 1.287 \text{ g.cm.}^{-3} \text{ (Rose \& Williams, 1959).}$$

The unit-cell parameters were determined by least squares from zero-layer Weissenberg photographs from two crystals, one mounted on its  $b$  axis and the other on its  $a$  axis, both calibrated by superposition of a Weissenberg pattern of a small, carefully aligned,  $\alpha$ -quartz crystal mounted on its  $a$  axis.

Complete sets of Weissenberg intensity data were collected about both the  $a$  and  $b$  axes using  $\text{Cu } K\alpha$  radiation. The  $b$  axis data were collected from a crystal prepared by rounding the edges off a short section of prism, cross section about 0.3 mm., by rolling on Crocus cloth. The  $a$  axis data were collected from a much smaller, irregularly shaped crystal. A Nonius Wiebenga type goniometer was used, and for the upper layer  $b$  axis data, the reflections were integrated horizontally to compensate for spot compaction. The  $a$  axis reflections were integrated both horizontally and vertically so that the spot shape corresponded as closely as possible with the shape of the spots on the zero layer  $b$  axis photographs. The multiple film technique was used with a single sheet of 0.003" aluminum foil as interleaving. Thus, with a five film pack in a standard Nonius camera, an intensity range of 50,000 to 1 is easily obtained on a single exposure. Of the 3073 reflections within the copper sphere, 2931 (95%) were observed. Intensities were estimated visually with the aid of a calibrated film strip prepared from a selected reflection in the usual way.

The intensity data were punched on IBM cards directly from the primary data sheets and processed on the IBM 704 computer using the data reduction program of Norment (1961). The computer output yielded directly the scaled and averaged data in structure factor and normalized structure factor form.

The theoretical probability distributions of the structure factors for a centrosymmetric crystal and various averages are listed in Table 1 together with actual values for deoxyanisoin ( $A$ ), *p,p'*-dimethoxybenzophenone ( $B$ ), and *N*-benzyl-1,4-dihydronicotin-

Table 1. *Distribution and averages for normalized structure factors for A (deoxyanisoin), B (p,p'-dimethoxybenzophenone), and C (N-benzyl-1,4-dihydronicotinamide)*

	Theor.	A	B	C
<i>N</i>		76	144	64
<i>N/Z</i>		19	36	16
No. of data		2931	5527	2014
Sp. Gr.		<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/a</i>	<i>P2<sub>1</sub>/c</i>
$\langle  E  \rangle_{av.}$	0.798	0.665	0.675	0.807
$\langle E^2 \rangle_{av.}$	1.000	0.968	0.986	1.017
$\langle  E^2 - 1  \rangle_{av.}$	0.968	1.15	1.17	1.033
$ E  > 1$	32.0%	22.4	25.0	25.0
$ E  > 2$	5.0	5.6	6.0	4.5
$ E  > 3$	0.3	1.6	1.4	0.8

amide (*C*) (I. L. Karle, 1961). The average values of  $|E|$  and  $|E^2 - 1|$  for deoxyanisoin differ considerably from the theoretical values obtained for a random distribution of atoms in a unit cell. Nevertheless they are quite similar to those of (*B*), whose chemical formula is similar to (*A*). The averages for (*C*), however, are fairly close to the theoretical values. The percentage of  $|E|$ 's greater than 1.0 has been found in each case to be smaller than that predicted for a crystal with atoms at random positions, whereas the number of  $|E|$ 's greater than 3.0 is larger, a circumstance which is advantageous for the application of statistical methods for phase determination.

### Determination of the phases

A preliminary step to phase determination is the examination of the data for rational dependence (Hauptman & Karle, 1959; and Hauptman, Karle & Karle, 1960). This arises from special, simple relationships among the atomic coordinates and the effect is exaggerated if the data are limited. Rational dependence can interfere with the application of  $\Sigma_1$  and  $\Sigma_3$  (Hauptman & Karle, 1953). Ideally,  $\langle E^2 \rangle_{av}$  for all subsets of *hkl* should be near 1.0. In this crystal, the  $\langle E^2 \rangle_{av}$  for the subset *gkl* is considerably larger than that for *ukl* (where *g* is even and *u* is odd) indicating the existence of several pairs of atoms with  $\Delta x \sim \frac{1}{2}$ . Furthermore, the  $\langle E^2 \rangle_{av}$  for the subsets *h3u*, *h1g*, and *h5g* are large whereas the  $\langle E^2 \rangle_{av}$  for *h3g* is small, consistent with atoms at or near  $y = n/6$ .

Table 2. *Application of  $\Sigma_1$ :*

$$sE_{2h,0,2l} \sim s \sum_k (-1)^{k+l} (E_{hkl}^2 - 1)$$

<i>2h,0,2l</i>	<i>hkl</i>	$(-1)^{k+l}(E_{hkl}^2 - 1)$
$\bar{4}04$ ( $E = 5.7$ )	$\bar{2}02$	-1.00
	$\bar{2}12$	-12.45
	$\bar{2}22$	+3.30
	$\bar{2}32$	+0.88
	$\bar{2}42$	+2.53
	$\bar{2}52$	-27.45
	$\bar{2}62$	-1.00
	$\bar{2}72$	-0.02
		-35.21

The data should have been corrected for rational dependence in order to apply the probability formulas to obtain an initial set of phases. For expediency, however, it was found that after assigning three phases to fix the origin (Hauptman & Karle, 1953),  $106-$ ,  $252+$ , and  $2,3,13+$ , and obtaining two phases with  $\Sigma_1$ ,  $\bar{4}04-$  and  $060+$ , with an almost certain probability that they are correct (see Table 2 for example), then only two other phases assigned arbitrarily,  $\bar{8},4,18p$  and  $\bar{6}46q$ , were needed for employing  $\Sigma_2$  to obtain a sufficient number of phases to determine the structure. Each of the seven initial phases had  $|E| > 3.5$  and they were applied in  $\Sigma_2$  to determine the phases of those reflections with the largest  $|E|$  values in order to insure the greatest probability that they be correct. As many  $\Sigma_2$  combinations as possible were used to determine a single phase. Rarely was a phase determination based on a single contribution. As expected, some  $\Sigma_2$  contributors occasionally indicated an incorrect answer. Table 3 shows a compilation of the  $\Sigma_2$  contributors to the first 140 phases determined in this fashion. The quantity  $E_1E_2E_3/N^{3/2}$  is related to the probability that the phase indication of the single contributor is correct. The number of correct and incorrect indications is listed in the second and third columns. According to the usual pattern, the  $\Sigma_2$  contributors with the largest  $E_1E_2E_3/N^{3/2}$  values are generally correct. The number of disagreements increases as the value of  $E_1E_2E_3/N^{3/2}$  decreases. In this set of 140 phases, two were subsequently found to be incorrect. A total of 250 phases were determined with six in error.

Table 3.  $\Sigma_2$  distribution

$E_1E_2E_3/N^{3/2}$	Agreements	Exceptions
$\geq 8.0$	33	0
7.0-7.9	25	0
6.0-6.9	33	0
5.0-5.9	60	1
4.0-4.9	101	0
3.0-3.9	134	3
2.0-2.9	249	14
$< 2.0$	219	30

Thirty *h0l* reflections were used to obtain an electron density projection on (010).<sup>\*</sup> Since many phases were determined as *p* or *q*, from the arbitrarily assigned phases  $\bar{8},4,18$  and  $\bar{6}46$ , it was necessary to compute four projections for the four possible sign combinations of *p* and *q*. Each of the four projections revealed the molecule equally well. The differences in the four projections were that the molecule was either shifted along the  $\bar{4}04$  direction or that it was rotated  $180^\circ$  about its pseudo-center of symmetry. Structure factor calculations immediately revealed that the combination with both *p* and *q* positive was the correct one. A projection on (100) using the phases originally determined yielded all of the *y* coordinates.

\* Electron density projections were computed on the NAREC computer, U.S. Naval Research Laboratory.

## Refinement

After several cycles of two-dimensional Fourier refinement, the  $R$  factor for all non-zero observed  $h0l$  reflections was 29%. Five cycles of least squares refinement, performed on the IBM 704 using the

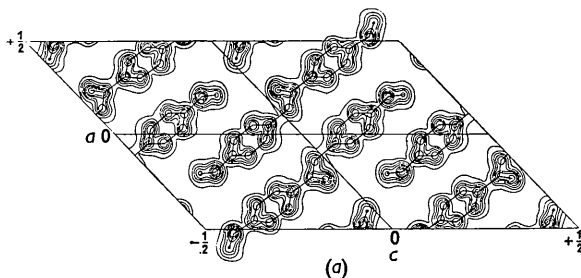
Table 4a. Fractional coordinates for deoxyanisoin referred to the monoclinic axes and isotropic temperature factors

Atom	$x$	$y$	$z$	$B$
C <sub>1</sub>	0.2278	0.8377	0.0806	3.55
C <sub>2</sub>	0.3077	0.8343	0.1744	3.07
C <sub>3</sub>	0.3897	1.0253	0.2229	3.56
C <sub>4</sub>	0.4641	1.0324	0.3100	3.74
C <sub>5</sub>	0.4544	0.8450	0.3481	3.53
C <sub>6</sub>	0.3739	0.6515	0.3007	3.87
C <sub>7</sub>	0.2998	0.6482	0.2138	3.62
C <sub>8</sub>	0.6008	1.0337	0.4841	5.60
C <sub>9</sub>	0.1375	0.6306	0.0314	3.91
C <sub>10</sub>	0.0514	0.6522	0.9357	3.33
C <sub>11</sub>	0.9673	0.8409	0.8902	3.95
C <sub>12</sub>	0.8848	0.8469	0.8030	3.76
C <sub>13</sub>	0.8863	0.6617	0.7599	3.49
C <sub>14</sub>	0.9683	0.4738	0.8034	3.83
C <sub>15</sub>	0.0519	0.4712	0.8919	3.71
C <sub>16</sub>	0.7913	0.4880	0.6269	5.06
O <sub>1</sub>	0.5215	0.8331	0.4326	4.46
O <sub>2</sub>	0.7989	0.6838	0.6734	4.25
O <sub>5</sub>	0.2384	0.9994	0.0481	5.08

Table 4b. Estimated hydrogen atom positions

The hydrogen atoms are given the same numbers as the carbon atoms to which they are attached. The positions are illustrated in Fig. 3. All were assigned an isotropic temperature factor of  $4.0 \text{ \AA}^2$  for the structure factor calculations

Atom	$x$	$y$	$z$
3	0.402	0.198	0.192
4	0.528	0.167	0.343
6	0.357	0.478	0.325
7	0.238	0.490	0.175
8 <sub>1</sub>	0.452	0.690	0.042
8 <sub>2</sub>	0.333	0.562	0.030
8 <sub>3</sub>	0.367	0.500	0.455
9 <sub>1</sub>	0.198	0.598	0.047
9 <sub>2</sub>	0.085	0.482	0.047
11	0.035	0.013	0.078
12	0.170	0.023	0.227
14	0.015	0.665	0.230
15	0.117	0.152	0.422
16 <sub>1</sub>	0.220	0.650	0.353
16 <sub>2</sub>	0.268	0.448	0.437
16 <sub>3</sub>	0.117	0.560	0.357



program NUXR5 (Van den Hende & Pepinsky, 1961), reduced the  $R$  factor for the same set of  $h0l$  reflections to 14%. Using the least squares  $x$  and  $z$  parameters and the  $y$  parameters determined from the  $a$  axis Fourier projection, the  $R$  factor for 921 of the lowest order non-zero observed three-dimensional data was computed to be 19%. Three cycles of least-squares refinement on the set of 921 data, followed by three cycles on all of the 2157 non-zero observed data, followed by one cycle with hydrogen atoms included in the structure factor calculations, resulted in an  $R$  factor of 16% for the set of 2157 reflections. In all of the above refinement, structure factors were calculated and refined with individual isotropic temperature factors for each atom.\* The data input to the least-squares refinement calculations was taken directly from the output of the initial data processing calculation.

The refined atomic parameters for the heavy atoms are given in Table 4a. The hydrogen atom positions given in Table 4b are not refined. They were estimated using molecular models at a latter stage of the refinement for the purpose of including hydrogen atoms in the structure factor computations.

## Structure

Electron density projections on (010) and (100) are illustrated in Figs. 1(a) and (b), respectively. The molecules are extended along the  $(\bar{4}04)$  planes in such a manner that the carbonyl group and the methoxy groups are coplanar with the adjacent benzene rings. Planes through the benzene rings make an angle of  $62^\circ 15'$  with each other. The carbonyl oxygen is surrounded by hydrogens from the methyl groups of adjacent molecules. The projection along the  $a$  axis shows that all atoms lie near  $y = n/6$ . The four pairs of atoms which are nearly superimposed in the projection are separated by  $x \sim \frac{1}{2}$ . Bond lengths and angles for the deoxyanisoin molecule are shown in Figs. 2(a) and (b). Standard deviations in bond lengths (including the uncertainties in cell parameters) are  $0.01 \text{ \AA}$  and in bond angles  $0.6^\circ$ .

\* A microfilmed copy of the observed and calculated structure factors has been deposited at the Library of Congress, Washington, D.C. (Reel No. 7203).

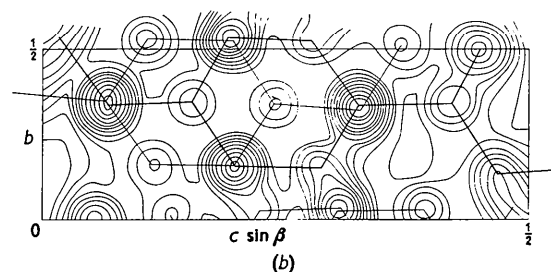


Fig. 1. (a) Electron-density projection on (010) for deoxyanisoin. (b) Electron-density projection on (100). Contour intervals are at  $1 \text{ e.}\text{\AA}^{-2}$  with zero contour omitted.

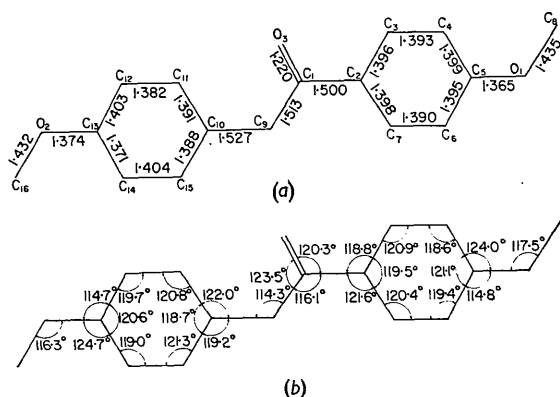


Fig. 2. (a) Bond lengths in deoxyanisoin. Standard deviation is 0.01 Å. (b) Bond angles in deoxyanisoin. Standard deviation is 0.6°.

The mean planes through the two benzene rings are described by the equations

$$0.70903X' - 0.50790Y' - 0.48918Z' + 0.24626 = 0 \quad (1)$$

$$-0.65538X' - 0.52277Y' + 0.54513Z' + 3.3118 = 0 \quad (2)$$

where  $X'$ ,  $Y'$ , and  $Z'$  refer to orthogonal axes such that

$$X' = ax \sin \beta, \quad Y' = by, \quad \text{and} \quad Z' = ax \cos \beta + cz.$$

The deviations of the ring atoms and the atoms of the adjacent methoxy and carbonyl groups from the mean planes through the benzene rings are listed in Table 5. The r.m.s. deviation of the ring atoms from coplanarity is 0.0039 Å for ring (1) and 0.0029 Å for ring (2). The carbon atom in each methoxy group is twisted by 0.11–0.13 Å from the plane of the adjacent ring.

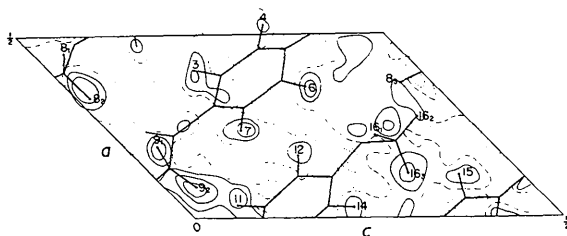


Fig. 3.  $(F_o - F_c)$  synthesis on (010) for deoxyanisoin. Zero contour broken, negative contours dotted. Contour interval is 0.25 e. Å<sup>-2</sup>.

Fig. 3 shows a difference synthesis on (010). The position of the molecule is outlined and the expected positions of the hydrogen atoms are indicated. Hydrogens 9<sub>1</sub> and 9<sub>2</sub> attached to the methylene group and all the hydrogens attached to the benzene rings are revealed by peaks of electron density. Of the six hydrogens attached to methyl groups, the positions of 16<sub>2</sub>, 16<sub>3</sub>, 8<sub>2</sub> and 8<sub>3</sub> are indicated by peaks, whereas there is no indication of 8<sub>1</sub> and 16<sub>1</sub>. The negative areas occur mainly inside benzene rings, between C–O bonds and near the carbonyl oxygen.

Table 5. Distances of atoms from the average planes through the benzene rings in deoxyanisoin

Ring 1		Ring 2	
Atom	$\Delta$ (Å)	Atom	$\Delta$ (Å)
C <sub>2</sub>	+0.0001	C <sub>10</sub>	+0.0041
C <sub>3</sub>	+0.0004	C <sub>11</sub>	-0.0012
C <sub>4</sub>	+0.0029	C <sub>12</sub>	0.0000
C <sub>5</sub>	-0.0067	C <sub>13</sub>	-0.0018
C <sub>6</sub>	+0.0073	C <sub>14</sub>	+0.0044
C <sub>7</sub>	-0.0040	C <sub>15</sub>	-0.0053
OCH <sub>3</sub> {	O <sub>1</sub> -0.0171	OCH <sub>3</sub> {	O <sub>2</sub> +0.0246
	C <sub>3</sub> -0.1107		C <sub>16</sub> +0.1298
CO {	C <sub>1</sub> -0.0306		C <sub>9</sub> +0.1030
	O <sub>3</sub> +0.0024		

## *p,p'*-DIMETHOXYBENZOPHENONE

### Refinement

The crystallographic data for *p,p'*-dimethoxybenzophenone are:

$$a = 16.43, \quad b = 16.03, \quad c = 9.62 \text{ \AA};$$

$$\beta = 100^\circ 15'; \quad P2_1/a, \quad \text{and} \quad Z = 8.$$

The structure was solved in 1957 by obtaining phases with the direct probability method. (Karle, Hauptman, Karle & Wing, 1958). At that time, approximate coordinates were reported since the structure consisting of 36 atoms was refined using only 1100 reflections, one-fifth of the total data, with an  $R$  factor of 22% (including zero reflections). The complete set of data of 5527 reflections has now been processed through several cycles of least square refinement using the same program as for the refinement of deoxyanisoin. Only the carbon and oxygen atoms were included and only isotropic temperature factors were considered since the number of parameters for 28 additional hydrogen atoms and anisotropic temperature factors presented a formidable problem for the computers available to us. The new  $R$  factor for all the observed reflections is 18.0%, and 21.6% if the non-observed reflections are included.\* The new coordinates are listed in Table 6.

The three oxygen atoms of each molecule lie almost in the 202 planes. The two molecules in the asymmetric unit are related to each other by a shift of very nearly  $z + \frac{1}{2}$  and a reflection through  $y = \frac{3}{8}$ .

The mean planes through the four benzene rings, which are labeled in Table 6, are described by the equations

$$-0.86988X' + 0.29843Y' - 0.39264Z' + 2.6503 = 0 \quad (1)$$

$$-0.17127X' + 0.16877Y' - 0.97064Z' + 0.46993 = 0 \quad (2)$$

$$-0.18017X' - 0.15885Y' - 0.97070Z' + 7.2752 = 0 \quad (3)$$

$$-0.89141X' - 0.25184Y' - 0.37669Z' + 7.9287 = 0 \quad (4)$$

\* A microfilmed copy of the observed and calculated structure factors has been deposited at the Library of Congress, Washington, D.C. (Reel No. 7203).

Table 6. Fractional coordinates for *p,p'*-dimethoxybenzophenone referred to the monoclinic axes and isotropic temperature factors

Molecule 1				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O <sub>1</sub>	0.4327	0.6809	0.0815	4.23
O <sub>2</sub>	0.2258	0.3699	0.2202	4.87
O <sub>3</sub>	0.4344	0.0629	0.0680	3.95
C <sub>4</sub> (CH <sub>3</sub> )	0.4310	0.7496	0.1752	5.40
C <sub>18</sub> (CH <sub>3</sub> )	0.3878	0.0123	0.0522	5.75
C <sub>11</sub> (CO)	0.2890	0.3702	0.1719	3.28
C <sub>5</sub>	0.3980	0.6080	0.1100	3.18
C <sub>6</sub>	0.3596	0.5937	0.2257	3.40
C <sub>7</sub>	0.3250	0.5158	0.2426	3.27
C <sub>8</sub>	0.3283	0.4509	0.1484	2.80
C <sub>9</sub>	0.3687	0.4663	0.0341	3.40
C <sub>10</sub>	0.4020	0.5440	0.0144	3.37
C <sub>12</sub>	0.3268	0.2895	0.1365	2.91
C <sub>13</sub>	0.2768	0.2177	0.1161	3.37
C <sub>14</sub>	0.3105	0.1404	0.0926	3.29
C <sub>15</sub>	0.3950	0.1352	0.0924	3.17
C <sub>16</sub>	0.4464	0.2048	0.1135	3.53
C <sub>17</sub>	0.4112	0.2817	0.1344	3.19

Molecule 2				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O <sub>19</sub>	0.4340	0.6871	0.5833	4.07
O <sub>20</sub>	0.2290	0.3764	0.7347	5.29
O <sub>21</sub>	0.4242	0.0701	0.5466	4.49
C <sub>22</sub> (CH <sub>3</sub> )	0.3860	0.7612	0.5648	5.64
C <sub>36</sub> (CH <sub>3</sub> )	0.4207	0.0023	0.6318	6.93
C <sub>29</sub> (CO)	0.2907	0.3776	0.6818	3.69
C <sub>23</sub>	0.3955	0.6148	0.6075	2.95
C <sub>24</sub>	0.3110	0.6076	0.6106	3.45
C <sub>25</sub>	0.2793	0.5297	0.6334	3.44
C <sub>26</sub>	0.3281	0.4584	0.6507	2.77
C <sub>27</sub>	0.4122	0.4671	0.6480	3.20
C <sub>28</sub>	0.4468	0.5447	0.6281	3.37
C <sub>30</sub>	0.3287	0.2974	0.6484	2.95
C <sub>31</sub>	0.3258	0.2287	0.7353	3.69
C <sub>32</sub>	0.3571	0.1527	0.7071	3.48
C <sub>33</sub>	0.3922	0.1432	0.5882	3.46
C <sub>34</sub>	0.3955	0.2099	0.4989	3.35
C <sub>35</sub>	0.3653	0.2867	0.5296	3.24

Table 7. Distances of atoms from the average planes through the benzene rings in *p,p'*-dimethoxybenzophenone

Ring 1		Ring 2	
Atom	$\Delta$ (Å)	Atom	$\Delta$ (Å)
C <sub>5</sub>	+0.0031	C <sub>12</sub>	+0.0007
C <sub>6</sub>	-0.0071	C <sub>13</sub>	-0.0064
C <sub>7</sub>	+0.0031	C <sub>14</sub>	+0.0064
C <sub>8</sub>	+0.0062	C <sub>15</sub>	-0.0007
C <sub>9</sub>	-0.0098	C <sub>16</sub>	-0.0051
C <sub>10</sub>	+0.0063	C <sub>17</sub>	+0.0050
OCH <sub>3</sub> { O <sub>1</sub>	+0.0113	OCH <sub>3</sub> { O <sub>3</sub>	+0.0349
C <sub>4</sub>	+0.0078	C <sub>18</sub>	-0.0241

Ring 3		Ring 4	
Atom	$\Delta$ (Å)	Atom	$\Delta$ (Å)
C <sub>23</sub>	+0.0071	C <sub>30</sub>	+0.0038
C <sub>24</sub>	+0.0031	C <sub>31</sub>	+0.0037
C <sub>25</sub>	-0.0092	C <sub>32</sub>	-0.0041
C <sub>26</sub>	+0.0074	C <sub>33</sub>	-0.0017
C <sub>27</sub>	+0.0031	C <sub>34</sub>	+0.0093
C <sub>28</sub>	-0.0105	C <sub>35</sub>	-0.0096
OCH <sub>3</sub> { O <sub>19</sub>	+0.0457	OCH <sub>3</sub> { O <sub>21</sub>	+0.0180
O <sub>22</sub>	+0.0340	C <sub>36</sub>	+0.0481

where *X'*, *Y'* and *Z'* refer to orthogonal axes such that

$$X' = ax \sin \beta, \quad Y' = by, \quad \text{and} \quad Z' = ax \cos \beta + cz.$$

The deviations of the ring atoms and the adjacent methoxy groups from the mean planes through the benzene rings are listed in Table 7. The r.m.s. deviation from the planes of the atoms in the four rings is 0.0062 Å. In this molecule the methoxy groups are closer to the planes through the adjacent benzene rings than the similar groups in deoxyanisoin. The angle between the planes of the two rings in molecule 1 is 54° 25' and that in molecule 2 is 55° 30'. A plane through the carbonyl group and the two adjacent carbon atoms makes an angle of 35° 37' with ring 1 and 24° 15' with ring 2 in molecule 1, and 25° 50' with ring 3 and 35° 22' with ring 4 in molecule 2. Thus the carbonyl group is not centrally located between the planes of the adjacent benzene rings. In deoxyanisoin, the carbonyl group lies in the plane

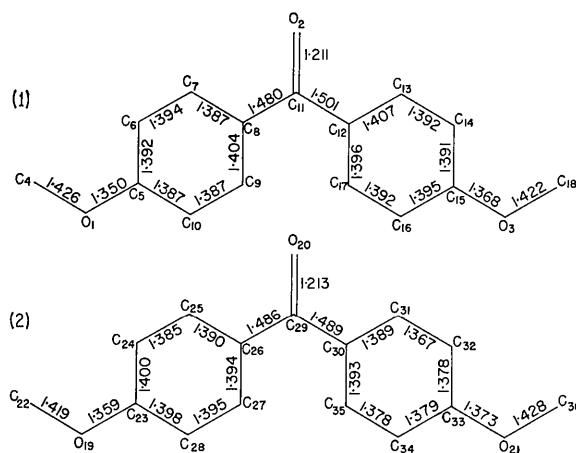


Fig. 4. Bond lengths in *p,p'*-dimethoxybenzophenone for the two molecules in the asymmetric unit. Standard deviation is 0.01 Å.

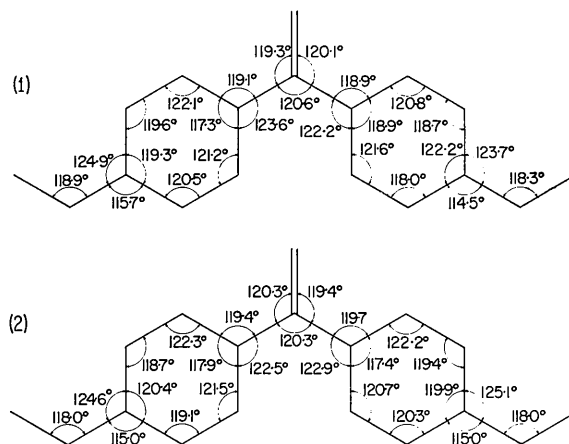


Fig. 5. Bond angles in *p,p'*-dimethoxybenzophenone for the two molecules in the asymmetric unit. Standard deviation is 0.6°.

of the adjacent ring. Bond lengths and bond angles for the two molecules of *p,p'*-dimethoxybenzophenone are shown in Figs. 4 and 5.

### Discussion

The similarities in the distances and angles in the three molecules of the two compounds studied is quite striking. The six O-CH<sub>3</sub> bond lengths range from 1.419 to 1.435 Å, the six O-C<sub>ar</sub> bond lengths range from 1.350 to 1.374 Å, the five OC-C<sub>ar</sub> distances range from 1.480 to 1.501 Å, and the three C=O distances are 1.211, 1.213 and 1.220 Å. The C<sub>ar</sub>-C<sub>ar</sub> in deoxyanisoin average 1.392 Å and in *p,p'*-dimethoxybenzophenone 1.390 Å. The six C-O-C<sub>ar</sub> angles range from 116.3° to 118.9°. The O-C<sub>ar</sub>-C<sub>ar</sub> angles are unequal about the C<sub>ar</sub>-O bond and enlarged on the side of the methyl group, the enlargement probably due to steric hindrance between hydrogens on the ring and in the methyl group. These angles range from 123.7° to 125.1° in the three molecules. The deoxyanisoin molecule almost behaves as if it had a center of symmetry between C<sub>1</sub> and C<sub>9</sub>, judging from the similarity in the values of the angles at either end of the molecule. Even the C-C-C angle in the tetrahedral methylene group has been enlarged to nearly equal the C-C-C angle in the planar carbonyl group.

The environment of the molecules in the unit cell is quite similar in the two compounds. The planes of the rings in different molecules make angles of 60°-62° with each other. The carbonyl groups are surrounded by hydrogens from the methyl groups of adjacent molecules. The closest intermolecular approach in deoxyanisoin is 3.46 Å between methyl carbons atoms of adjacent molecules and the next closest is 3.54 Å for O<sub>3</sub>-C<sub>16</sub> and 3.56 Å for O<sub>2</sub>-C<sub>3</sub>.

Similarly in *p,p'*-dimethoxybenzophenone close approaches are found between the carbonyl oxygens and carbons of the methyl groups (3.47-3.53 Å) and between the methoxy oxygens and ring carbon atoms (3.41-3.54 Å). The closest approach of 3.38 Å is between O<sub>3</sub> and the atom related to it by a center of symmetry.

The isotropic temperature factors for both molecules are also quite similar. The average *B* values for all carbons except those in the methyl groups, for the methyl carbons, methoxy oxygens, and carbonyl oxygens are 3.64, 5.34, 4.35 and 5.08 for deoxyanisoin and 3.25, 5.93, 4.19 and 5.08 for *p,p'*-dimethoxybenzophenone. In each molecule, there is considerably more vibration at the terminal methoxy groups and in the central carbonyl than in the rings.

### References

- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3. Brooklyn: Polycrystal Book Service.
- HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 846.
- HAUPTMAN, H., KARLE, I. L. & KARLE, J. (1960). *Acta Cryst.* **13**, 451.
- KARLE, I. L., HAUPTMAN, H., KARLE, J. & WING, A. B. (1958). *Acta Cryst.* **11**, 257.
- KARLE, I. L. (1961). *Acta Cryst.* **14**, 497.
- NORMENT, H. G. (1961). Abstracts Amer. Cryst. Assoc. Meeting, Boulder, Colorado; U.S. Naval Research Laboratory Report # 5739, Washington, D.C.
- ROSE, H. A. & WILLIAMS, J. G. (1959). *Anal. Chem.* **31**, 478.
- VAN DEN HENDE, J. H. & PEPINSKY, R. (1961). *NUXR5: Crystallographic Least-Squares Refinement Program for the IBM 704*, Crystal Research Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania.

*Acta Cryst.* (1962). **15**, 878

## Structural Features of Some Phases Related to Cementite

BY B. ARONSSON AND S. RUNDQVIST

*Institute of Chemistry, University of Uppsala, Uppsala, Sweden*

(Received 29 September 1961)

Investigations during the last few years have shown that a number of phases, especially borides, of the seventh and eighth group metals are isomorphous with cementite or crystallize in structures closely related to that of cementite. In this paper the recently obtained structural data are summarized and discussed. The influence of the radius ratio on trends in interatomic distances and lattice parameters is particularly considered. On basis of the presented data some general remarks on 'complicated' interstitial phases are also made.

### 1. Introduction

During the last few years the crystal structures of borides, silicides and phosphides of the seventh and

eighth group metals have been studied at this Institute with the principal aim of providing accurate data for a discussion of the crystal chemistry of these phases. In this paper the structures of a number of metal-rich