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Crystal and Molecular Structure of *p,p'*-Dimethoxybenzophenone by the Direct Probability Method

By I. L. Karle, H. Hauptman, J. Karle and A. B. Wing
U.S. Naval Research Laboratory, Washington, D.C., U.S.A.

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The structure of *p,p'*-dimethoxybenzophenone has been determined from X-ray single-crystal data. The space group is $P2_1/a$ and there are eight molecules in the unit cell. The cell parameters are $a = 16{\cdot}43$, $b = 16{\cdot}03$, $c = 9{\cdot}62$ Å, $\beta = 100° 15'$. The phases of the largest 270 normalized structure factors, $E_{\mathbf{h}}$, were determined directly by probability methods (Hauptman & Karle). A Fourier map with these $E_{\mathbf{h}}$ as coefficients revealed the structure, which was improved by the least-squares method. A line connecting the methoxy oxygens within a molecule is almost parallel to the b axis and a second molecule is shifted by approximately $\frac{1}{2}c$ from the first, except that the corresponding benzene rings of the adjacent molecules are twisted in opposite directions. The methyl carbons lie almost in the planes of the adjacent benzene rings.

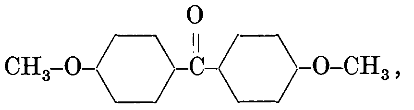
Also included in this paper is a discussion of the limitations of Σ_1 for $P2_1/a$ and the theoretical basis for the use of an E map.

1. Introduction

By this time several structures have been determined using the direct probability method presented in Monograph I (Hauptman & Karle, 1953). Christ, Clark & Evans (1954) have found the structure of colemanite and Christ & Clark (1956) have found the structure of meyerhofferite. Bertaut & Blum (1956) have derived the forms for Σ_1, Σ_2 and Σ_3 of Monograph I appropriate to the space group *Bbmm*, and have applied them to solving the structure of Ti_2CaO_4.

Vand & Pepinsky (1953) purported to demonstrate the failure of the methods based on the joint probability distributions of Monograph I by means of a simple planar four-atom structure. However, Bertaut (1955), using the probability formulas appropriate to the correct space group, *p4m*, easily obtained the true structure, thus nullifying the claim based on this four-atom problem.

The X-ray structure analysis of *p,p'*-dimethoxybenzophenone,



the most complex structure thus far studied by direct probability methods, is described in this paper. Signs for the largest normalized structure factors (E) were determined directly from the magnitudes of the intensities alone by the probability methods of Monograph I. These signs were used to compute a three-dimensional E map, which revealed the structure immediately. The coordinates obtained from this map were then improved using a three-dimensional least-squares procedure. A note concerning this structure has been published by us (Karle, Hauptman, Karle & Wing, 1957).

2. Experimental measurements

The crystals used in this investigation were grown by Mr C. E. Miller of Bell Telephone Laboratories. Dr S. Geller suggested that we apply the probability methods to this material and supplied us with crystallographic data and preliminary diffraction photographs.

The crystals were colorless, opaque needles with the c axis as the needle axis. The dimensions of the unit cell were obtained from rotation and Weissenberg photographs. The crystallographic data are:

$$a = 16{\cdot}43,\ b = 16{\cdot}03,\ c = 9{\cdot}62\ \text{Å},\ \beta = 100°\ 15',$$
$$\text{space group } P2_1/a,\ Z = 8\ ,$$
$$\varrho(\text{X-ray}) = 1{\cdot}289,\ \ \varrho(\text{physical}) = 1{\cdot}259\ .$$

There are 30 carbon atoms, 6 oxygen atoms, and 28 hydrogen atoms in general positions in an asymmetric unit.

Equi-inclination Weissenberg photographs were taken about the three crystallographic axes, using nickel-filtered copper radiation. Five exposure sequences were made of each layer. The intensities were estimated visually, using a calibrated comparison strip, and corrections were made for Lorentz and polarization factors, obliquity, α_1, α_2 resolution and spot size (Wing & Birks, 1954). 5527 independent reflections were measured, almost the entire copper sphere, of which 1261 intensities were observed to be zero. The data were corrected for vibrational motion and placed on an absolute scale by means of a K curve (Karle & Hauptman, 1953; see also Wilson, 1949), thus giving $F_{\mathbf{h}}^2$. From these, the magnitudes of the normalized structure factors were computed by means of

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2/\varepsilon \sum_{j=1}^{N} f_{j\mathbf{h}}^2\ , \qquad (2{\cdot}1)$$

where, for space group $P2_1/a$, $\varepsilon = 2$ when $\mathbf{h}$ is $h0l$ or $0k0$ and $\varepsilon = 1$ otherwise, N is the number of atoms in the unit cell, and f_j is the atomic scattering factor of the jth atom.

The theoretical probability distribution of a structure factor in a centrosymmetric crystal predicts 32% of all $|E| > 1$, 5% of all $|E| > 2$, and 0·3% of all $|E| > 3$. The actual distribution of $|E|$ for this crystal was found to be 25% greater than 1, 6% greater than 2 and 1·4% greater than 3. Theoretically, for a centrosymmetric crystal the following averages occur:

$$\langle |E| \rangle = 0{\cdot}798,\ \langle E^2 \rangle = 1{\cdot}0 \ \text{ and } \ \langle |E^2-1| \rangle = 0{\cdot}968\,.$$

For this crystal the values for these averages were:

$$\langle |E| \rangle = 0{\cdot}675,\ \langle E^2 \rangle = 0{\cdot}986, \ \text{ and } \ \langle |E^2-1| \rangle = 1{\cdot}17\,.$$

3. Determination of the phases

Sign determination by the probability formulas in Monograph I* requires only the knowledge of the space group, and the magnitudes of the normalized structure factors. The chemical composition of the unit cell, although useful, is not required for the structure determination. To facilitate the determination of the phases, the E_{hkl} were arranged in order of descending E magnitudes in groups where the indices were $g0g$, $0g0$, ggg, ggu, guu, gug, ugu, ugg, uug, and uuu (g = even, u = uneven). The E^2-1 values were also listed. It was immediately apparent from the E values that the reflections with l even were considerably stronger than those with l odd. Furthermore, in the groups ggg and ugu the reflections with $k=4, 8, 12, \ldots$ were much stronger than those with $k = 2, 6, 10, \ldots$ and in the groups ugg and ggu all the strong reflections had $k = 2, 6, 10, \ldots$. There was no particular pattern for k odd. Since an ordered distribution of normalized intensities (E^2) with respect to the k index existed for this crystal, it was necessary to examine the effect it would have on the phase-determining formulas.

The square of the normalized structure factor for $P2_1/a$ for the case of equal atoms is

$$\begin{aligned} E^2_{hkl} &= F^2_{hkl} \Big/ \sum_{j=1}^{N} f_j^2 \\ &= \frac{16}{N} \sum_{j=1}^{N/4} \genfrac{}{}{0pt}{}{\cos^2}{\sin^2} 2\pi(hx_j+lz_j) \genfrac{}{}{0pt}{}{\cos^2}{\sin^2} 2\pi k y_j \\ &\quad + \frac{16}{N} \sum_{j \neq j'}^{N/4} \genfrac{}{}{0pt}{}{\cos}{\sin} 2\pi(hx_j+lz_j) \genfrac{}{}{0pt}{}{\cos}{\sin} 2\pi(hx_{j'}+lz_{j'}) \\ &\quad \times \genfrac{}{}{0pt}{}{\cos}{\sin} 2\pi k y_j \genfrac{}{}{0pt}{}{\cos}{\sin} 2\pi k y_{j'}\,, \end{aligned} \tag{3·1}$$

where the cosine terms apply to the case where $h+k$ is even and the sine terms to $h+k$ odd. Using various trigonometric relations, (3·1) can be rewritten in the form

$$E^2_{hkl}-1 = (-1)^{h+k} \frac{1}{N^{\frac{1}{2}}} E_{2h,\,0,\,2l}+R \tag{3·2}$$

or

$$(-1)^{h+k}(E^2_{hkl}-1) = \frac{1}{N^{\frac{1}{2}}} E_{2h,\,0,\,2l}+(-1)^{h+k}R\,, \tag{3·3}$$

where

$$\begin{aligned} R = \frac{4}{N} \sum_{j=1}^{N/4} &[(-1)^{h+k}+\cos 4\pi(hx_j+lz_j)] \cos 4\pi k y_j \\ &+ \frac{4}{N} \sum_{j \neq j'}^{N/4} \{(-1)^{h+k} \cos 2\pi[h(x_j+x_{j'})+l(z_j+z_{j'})] \\ &+ \cos 2\pi[h(x_j-x_{j'})+l(z_j-z_{j'})]\} \\ &\times \{(-1)^{h+k} \cos 2\pi k(y_j+y_{j'})+\cos 2\pi k(y_j-y_{j'})\}\,. \end{aligned}$$

Upon averaging over the index k, expressions (3·2) and (3·3) become

$$\langle E^2_{hkl}-1 \rangle_k = \langle R_1 \rangle_k+\langle R_2 \rangle_k+\langle R_3 \rangle_k \tag{3·4}$$

and

$$\langle (-1)^{h+k}(E^2_{hkl}-1) \rangle_k = \frac{1}{N^{\frac{1}{2}}} E_{2h,\,0,\,2l}+\langle R_4 \rangle_k+\langle R_5 \rangle_k+\langle R_6 \rangle_k \tag{3·5}$$

where we find, for example,

$$\langle R_1 \rangle_k = \frac{4}{N} \sum_{\nu \neq \nu'}^{N/4} \cos 2\pi[h(x_\nu-x_{\nu'})+l(z_\nu-z_{\nu'})]\,, \tag{3·6}$$

$$\langle R_4 \rangle_k = \frac{4}{N} \sum_{\nu \neq \nu'}^{N/4} \cos 2\pi[h(x_\nu+x_{\nu'})+l(z_\nu+z_{\nu'})]\,, \tag{3·7}$$

and the indices ν and ν' range over those values of $j = 1, 2, \ldots, N$ for which $y_\nu-y_{\nu'} = 0$, ($y_\nu \neq 0$ or $\frac{1}{2}$). In other words, the subscripts ν, ν' refer only to those pairs of atoms whose y coordinates ($\neq 0$ or $\frac{1}{2}$) are the same. Similar expressions are obtained for $\langle R_2 \rangle_k$ and $\langle R_5 \rangle_k$ with $y_\nu+y_{\nu'} = 0$ ($y_\nu \neq 0$ or $\frac{1}{2}$) and for $\langle R_3 \rangle_k$ and $\langle R_6 \rangle_k$ with $y_\nu = y_{\nu'} = 0$ or $\frac{1}{2}$. In the general case where $y_\nu \neq \pm y_{\nu'}$ and $y_\nu \neq 0$ or $\frac{1}{2}$, then all the remainder terms $\langle R_n \rangle_k$ reduce to zero. Consequently, in the general case, the value of (3·4) is zero, and (3·5) becomes the phase-determining formula Σ_1 for $P2_1/a$ (Hauptman & Karle, 1953). Obviously, if many pairs of atoms in the asymmetric unit have the same y coordinate or are in the planes $y = 0$ or $\frac{1}{2}$, the remainder term in (3·5) can become significant and the signs for $E_{2h,\,0,\,2l}$ determined from Σ_1 may not be reliable.

An estimate of the feasibility for using Σ_1 in $P2_1/a$ can be made from the value of the quantity $\langle |\langle E^2_{hkl}-1 \rangle_k| \rangle_{h,l}$, which is first averaged over k for fixed h, l and then over all h, l. If the y coordinates of the atoms are not equal to 0 or $\frac{1}{2}$ or to each other, then the above quantity should have a value near zero. Deviations from zero are expected since a finite number of data are used in the averages. In this crystal, however, the value of the average was 0·608, two to three times the value to be expected from the size of sample used if the magnitudes of no two y

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* Since the solution of this crystal structure, more powerful phase-determining formulas have been derived (see Hauptman & Karle, 1957, 1958 and Karle & Hauptman, 1957, 1958).

coordinates were identical. Thus the conditions for the exact validity of Σ_1 for $P2_1/a$ were not fulfilled. Therefore, the use of this formula would require the establishment of a high level of rejection, i.e. a sign would be accepted only if the value of Σ_1 were unusually large when compared with its standard deviation. As it turned out, the values of Σ_1 for $P2_1/a$ were sufficiently large for only three of the E_{g0g}, the magnitudes of which were too small to be useful in the early stages of the phase-determining procedure. Accordingly Σ_1 for $P2_1/a$ was not useful, and it was decided to treat the crystal as if it were in $P\bar{1}$.

A similar analysis can be made for the Σ_1 formula for $E_{0,2k,0}$ in which case atoms having both the same x and z coordinates introduce a limitation. For this crystal the value of $\langle|\langle E^2_{hkl}-1\rangle_{h,l}|\rangle_k$ was 0·221, a value several times larger than that expected from the number of terms in this average. Accordingly, only one sign was determined using this formula, $E_{0,12,0} = -2\cdot41$. As it happened this sign was not useful in the earlier stages of the phase determination, but later on played the role of corroborating phases obtained otherwise.

The Σ_1 formula in space group $P\bar{1}$ is not subject to the same limitations as Σ_1 in $P2_1/a$. Therefore the initial phases from which the rest of the phases were obtained were determined using Σ_1 for $P\bar{1}$,

$$sE_{2\mathbf{h}} \sim s(E^2_{\mathbf{h}}-1)\ , \qquad (3\cdot8)$$

where s symbolizes 'sign of' and $\sim$ means 'probably is'. Here a phase is determined only from the magnitude of one other reflection. In order to have a high probability that the phase indication is correct, it is necessary that both $E_{2\mathbf{h}}$ and $E^2_{\mathbf{h}}-1$ have large magnitudes. Since the largest negative value that E^2-1 can have is -1, whereas the positive values can be much greater than $+1$, only positive signs are obtained with Σ_1 in a structure of this complexity. For this crystal, signs for four reflections were accepted with this formula. They are listed in Table 1.

Table 1

2**h**	$E_{2\mathbf{h}}$	**h**	$E^2_{\mathbf{h}}-1$	$P_+(E_{2\mathbf{h}})$ (*a*)	$P_+(E_{2\mathbf{h}})$ (*b*)
$\bar{4}$ 4 10	3·19	$\bar{2}$25	+7·04	0·87	0·97
10 4 4	3·18	522	+10·61	0·94	~1·00
12 4 6	2·97	623	+9·00	0·90	~1·00
8 4 2	2·35	421	+6·93	0·80	0·84

$P_{(+)}(E_{2\mathbf{h}})$ indicates the probability that a particular sign is positive. Values in column (*a*) were computed from the hyperbolic tangent formula of Woolfson (1954) and those in column (*b*) from (3·29) in Monograph I. Both formulas give approximate values of the probability but they are sufficiently accurate to indicate whether a sign should be accepted. A more accurate value of the probability can be obtained by taking higher-order approximations in deriving the joint probability (see (3·03) and p. 43 in Monograph I).

Next, formula Σ_3 was used to expand the table of signs,

$$sE_{2\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{2\mathbf{k}}(E^2_{\mathbf{h}+\mathbf{k}}-1)\ . \qquad (3\cdot9)$$

In this formula, the signs of several $E_{2\mathbf{k}}$ must be known in order to determine the sign of an $E_{2\mathbf{h}}$. Again, only reflections with large E values are examined so that the probability of assigning a correct sign is high. An example of applying Σ_3 to find the sign of $E_{\bar{12},8,8}$ is shown in Table 2. For this application it is convenient to have a numerical listing of all the indices in dictionary order with their $|E|$ and E^2-1 values, in order to look up the necessary $E^2_{\mathbf{h}+\mathbf{k}}-1$ terms. From the 10, 4, 4 term alone, the $P_+(E_{\bar{12},8,8})$ is 0·88. When the other $E_{2\mathbf{k}}$ with known signs were included in the summation, the $P_+(E_{\bar{12},8,8})$ rose to almost certainty.

Only those signs were accepted for which the corresponding probability was high. Of course, there were some $E_{2\mathbf{h}}$ for which Σ_3 was indeterminate. After quite a few + signs had been assigned, it was possible to get − signs from Σ_3 with a high probability. An example is illustrated in Table 3.

Since E^2-1 cannot be greater than -1 in the negative direction, many negative terms are needed to get a large $P_-(E_{2\mathbf{h}})$. The one term alone in the example gave $P_-(E_{2\mathbf{h}}) = 0\cdot61$. It was found, however, that a great majority of the contributing terms gave an indication of a negative sign.

Table 2

2**h** =	$\bar{12}$ 8 8		($E_{2\mathbf{h}} = 5\cdot67$)		
2**k** =	10 4 4	10 $\bar{4}$ 4	$\bar{10}$ $\bar{4}$ $\bar{4}$	$\bar{10}$ 4 $\bar{4}$	($E_{2\mathbf{k}} = +3\cdot18$)
h+**k** =	$\bar{1}$ 6 6	$\bar{1}$ 2 6	$\bar{11}$ 2 2	$\bar{11}$ 6 2	
$E^2_{\mathbf{h}+\mathbf{k}}-1$ =	+0·04	+3·45	−1·00	+13·35	

$$sE_{2\mathbf{h}} \sim +3\cdot18(+0\cdot04+3\cdot45-1\cdot00+13\cdot35)+\ldots$$

Table 3

2**h** =	0 8 2		($E_{2\mathbf{h}} = 3\cdot00$)		
2**k** =	$\bar{12}$ 8 8	$\bar{12}$ $\bar{8}$ 8	12 8 $\bar{8}$	12 $\bar{8}$ $\bar{8}$	($E_{2\mathbf{k}} = +5\cdot67$)
h+**k** =	$\bar{6}$ 8 5	$\bar{6}$ 0 5	6 8 $\bar{3}$	6 0 $\bar{3}$	
$E^2_{\mathbf{h}+\mathbf{k}}-1$ =	−0·79	−0·86	−0·92	−0·99	

$$sE_{2\mathbf{h}} \sim +5\cdot67(-0\cdot79-0\cdot86-0\cdot92-0\cdot99)+\ldots$$

When about 15–25 signs had been found with Σ_3, they were reiterated in Σ_3 to check for internal consistency. At this point there were a sufficient number of known signs to use Σ_2,

$$sE_{\mathbf{h}} \sim s \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h+k}} \,. \qquad (3\cdot10)$$

In this formula, the signs of both $E_{\mathbf{k}}$ and $E_{\mathbf{h+k}}$ need to be known in order to obtain the sign of $E_{\mathbf{h}}$. Again, only the terms with the largest E values were used to establish a basic set of signs. The signs determined by Σ_3 were confirmed by using Σ_2 whenever possible, e.g. the signs of $\bar{4}$, 4, 10 and 8, 4, 2 were assigned from Σ_1 and they combined to give the sign of $\overline{12}$, 8, 8:

$$\begin{array}{r} \bar{4}\ \ 4\ \ 10 \\ \bar{8}\ \ 4\ \ \ \bar{2} \\ \hline \overline{12}\ \ 8\ \ \ 8 \end{array} \qquad\qquad \begin{array}{l} E_{\mathbf{k}} = +3\cdot19 \\ E_{\mathbf{h+k}} = +2\cdot35 \\ \hline E_{\mathbf{h}} = 5\cdot67 \end{array}$$

$$sE_{\overline{12},8,8} \sim (+3\cdot19)(+2\cdot35)$$

The probability that $E_{\overline{12},8,8}$ is + is 0·99 and is in agreement with the positive result from Σ_3. As many combinations of Σ_2 as possible should be used for every sign determined. For the $E_{\mathbf{h}}$ with the largest magnitudes, there should be extremely few, if any, inconsistent sign indications with Σ_2. As one proceeds to smaller magnitudes of $E_{\mathbf{h}}$, then some contradictions will occur and, at times, the sign may be indeterminate.

So far, the only signs determined have been in the group *ggg* (including 0*g*0 and *g*0*g*). It seems to be a good policy to determine the signs of only the largest E_{ggg} and then to proceed to the largest $E_{\mathbf{h}}$ in the other groups. Otherwise a false pattern of signs may be established which will be found to give large inconsistencies in the other groups. In order to begin in the other groups, it is necessary to arbitrarily assign three signs which fix the origin (Monograph I). Ordinarily, the largest $E_{\mathbf{h}}$ are chosen for the assigned signs. In this crystal, the *ugg* group had large E values, hence the largest, $E_{\overline{13},6,4} = 7\cdot17$, was made positive. The next largest *ugg* was $\overline{11}$, 6, 6 and Σ_2 with the known signs from the *ggg* group was used to determine its sign. There were two contributors:

$$\begin{array}{r} \overline{13}\ 6\ 4 \\ \bar{2}\ 0\ \bar{2} \\ \hline \overline{11}\ 6\ 6 \end{array} \quad \begin{array}{c} (+7\cdot17) \\ (+3\cdot69) \\ \hline 6\cdot53 \end{array} \quad \text{and} \quad \begin{array}{r} \overline{13}\ \ \bar{6}\ 4 \\ 2\ 12\ 2 \\ \hline \overline{11}\ \ 6\ 6 \end{array} \quad \begin{array}{c} (-7\cdot17) \\ (-2\cdot29) \\ \hline 6\cdot53 \end{array}$$

$$sE_{\overline{11},6,6} \sim (+7\cdot17)(+3\cdot69) + (-7\cdot17)(-2\cdot29)$$

With the signs for $\overline{13}$, 6, 4 and $\overline{11}$, 6, 6, signs for many more E_{ugg} were determined with Σ_2. Arbitrary signs were also assigned to the largest *uug* and *ggu* reflections and others in these groups were determined with Σ_2. Finally, the signs in the four remaining groups were dependent upon the signs already obtained. For instance, in the *gug* group, combinations such as *ugg*+*uug*, *ggu*+*guu*, *ugu*+*uuu*, and *ggg*+*gug* were used in Σ_2.

Two hundred and seventy signs with $|E| > 2$ were assigned using Σ_1, Σ_2 and Σ_3. Some cross checking for consistency in groups other than *ggg* was performed using Σ_3. Since the sign determination was carried out by hand computing, it was not feasible to apply Σ_3 very extensively. Of the 270 phases, all but one subsequently proved to be correct.

In a set of 1732 Σ_2 combinations which were used to determine the signs, there were 116 contradictions to the correct sign. These contradictions did not usually interfere with the sign determination since there were several stronger terms indicating the correct sign. Table 4 lists the number of exceptions to Σ_2 and the corresponding $E_1E_2E_3/N^{\frac{1}{2}}$ product associated with them, where N is the number of atoms in the unit cell. The exceptions are related to $E_1E_2E_3/N^{\frac{1}{2}}$ since this quantity occurs in the probability expression for Σ_2 and since it is in a normalized form applicable to any crystal.

Table 4

$E_1E_2E_3/N^{\frac{1}{2}}$	Exceptions
5·0–11·0	0
4·0– 4·9	1
3·0– 3·9	9
2·0– 2·9	29
1·0– 1·9	77

The largest exception had a value of 4·8 and it was the only exception out of 144 terms in the range 4·0–11·0. The exceptions followed an expected distribution in that the number was relatively small for large $E_1E_2E_3/N^{\frac{1}{2}}$ values and larger for smaller $E_1E_2E_3/N^{\frac{1}{2}}$ values.

4. Structure

The 270 reflections (6% of the non-zero data) for which signs had been determined were used to compute a three-dimensional E map. This is a Fourier in which the $E_{\mathbf{h}}$ rather than the $F_{\mathbf{h}}$ are used as coefficients. The E map was characterized by 37 main peaks, two of which were fairly weak. One of the weak peaks was spurious whereas the other 36 peaks were identified with the atoms of the two molecules in the asymmetric unit. The average weight of the six O atoms was 310, the average weight of the thirty C atoms was 266, and the rapidly oscillating background rarely reached ±100.

The coordinates of the atoms as read from the E map were subjected to a preliminary least-square refinement on the IBM 704, using the program prepared by D. Sayre. About 1100 structure-factor magnitudes sampled throughout the copper sphere of data (every fifth reflection ordered on $\sin\theta$) were used. One temperature factor per atom was used and the 28 hydrogen atoms in the asymmetric unit were omitted. At present, the R factor for the 1100 reflections used in the least-squares procedure, including all the zero reflections, is 22%*. The R factor for all 5527

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* At this point it became apparent that the least-squares procedure was diverging owing to approximations in the program, and the computation was terminated.

Table 5. *Fractional atomic parameters*

	Molecule I				Molecule II		
Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
O	0·432	0·680	0·077	O	0·434	0·686	0·585
O	0·225	0·370	0·220	O	0·227	0·376	0·731
O	0·435	0·064	0·067	O	0·424	0·069	0·543
C(CH$_3$)	0·429	0·751	0·185	C(CH$_3$)	0·381	0·763	0·578
C(CH$_3$)	0·387	0·985	0·062	C(CH$_3$)	0·419	0·995	0·629
C(CO)	0·292	0·372	0·174	C(CO)	0·294	0·378	0·678
C	0·398	0·607	0·112	C	0·396	0·612	0·612
C	0·361	0·595	0·225	C	0·311	0·608	0·611
C	0·327	0·515	0·239	C	0·282	0·526	0·631
C	0·329	0·451	0·149	C	0·328	0·457	0·651
C	0·366	0·467	0·040	C	0·412	0·466	0·650
C	0·404	0·545	0·013	C	0·446	0·544	0·625
C	0·327	0·289	0·135	C	0·330	0·296	0·649
C	0·278	0·219	0·116	C	0·327	0·228	0·730
C	0·311	0·140	0·091	C	0·357	0·153	0·708
C	0·394	0·137	0·099	C	0·391	0·145	0·594
C	0·445	0·204	0·107	C	0·397	0·210	0·498
C	0·410	0·282	0·137	C	0·367	0·286	0·531

reflections is 26%, and 22% if the reflections read to be zero are omitted. It would be worth while to refine the structure further both with three-dimensional Fouriers and with least squares, using anisotropic temperature factors and the complete set of data.

The present atomic coordinates are listed in Table 5. The two molecules in an asymmetric unit are illustrated in Fig. 1, a projection along the *a* axis, $\frac{1}{4} \le x \le \frac{1}{2}$.

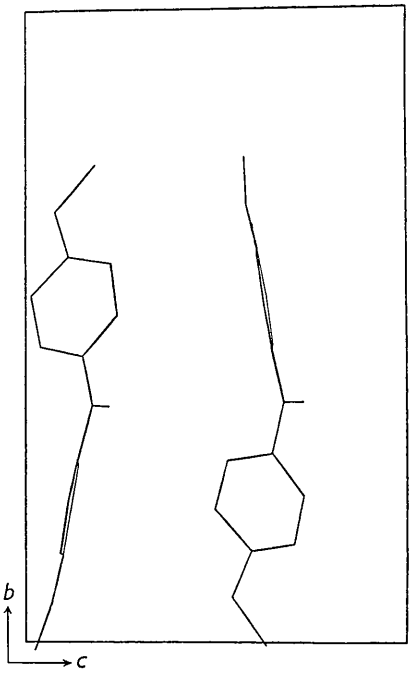

Fig. 1. Projection of an asymmetric unit along the *a* axis, $\frac{1}{4} \le x \le \frac{1}{2}$.

The three oxygen atoms in each molecule lie near the

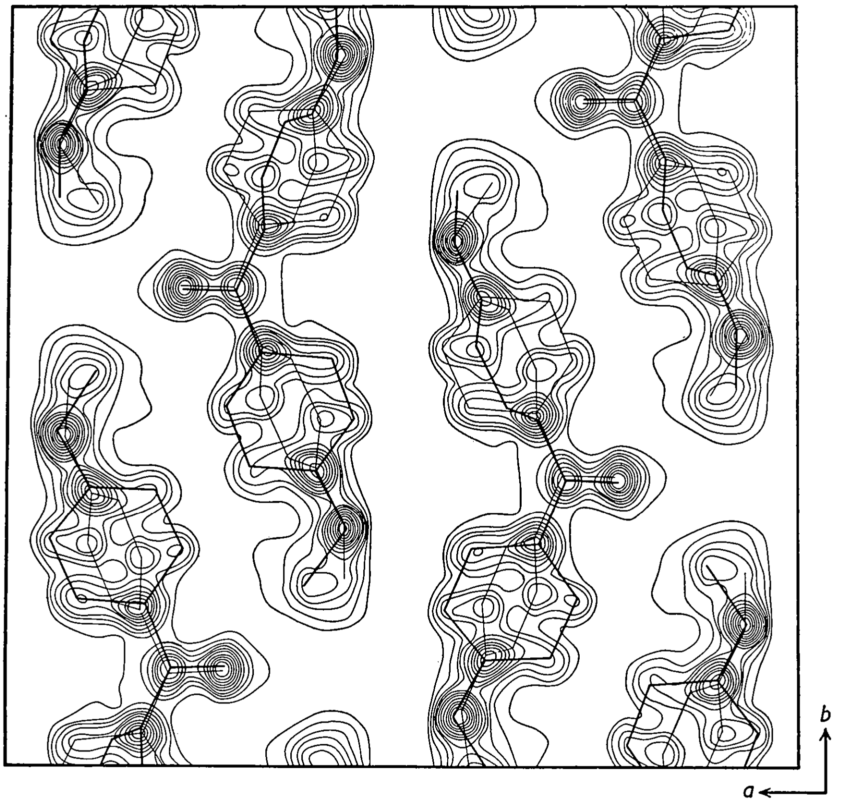

Fig. 2. Electron-density projection on (001). The pairs of superimposed molecules are separated by approximately $\frac{1}{2}c$. The coordinates of the line drawings were taken from the preliminary three-dimensional least-squares refinement.

202 planes. The molecules are related to each other approximately by a shift of $z+\frac{1}{2}$ and a reflection through $y=\frac{3}{8}$. The carbon atoms in the methoxy groups are very nearly in the same plane as the adjacent benzene rings. The top ring in molecule I and the bottom ring in molecule II are rotated about 38° out of the planes formed by the three oxygen atoms in each molecule, whereas the bottom ring in molecule I and the top ring in molecule II are rotated about 24° out of the plane of oxygen atoms.

Fig. 2 illustrates the contents of the unit cell as viewed down the c axis. The pairs of superimposed molecules are separated by approximately $\frac{1}{2}c$. The coordinates of the line drawings were taken from the least-squares refinement. The signs for the electron-density projection were derived from these coordinates where $R=20\%$ for the z projection, including all terms. The same reflections and signs were used to compute the E map (E_{hk0} instead of F_{hk0} for the coefficients in the Fourier series) which is illustrated in Fig. 3. A comparison of the E map with the F map shows the much greater resolution of atoms in the superposed benzene rings and methyl groups in the E map. The contours near the centers of the atoms were not drawn owing to the fairly rough grid used in computing the series. The contours in the E map are on an arbitrary scale spaced by a value of 1, with the lowest contour at 2. The background oscillates very rapidly but does not exceed ±2.

The shortest intermolecular distances are between an oxygen and oxygen in methoxy groups at 3·41 Å and an oxygen and carbon at 3·45 Å. The average bonded distances with their average deviations at the present stage of refinement are listed in Table 6.

Table 6

Bond type	Average distance (Å)	Average deviation (Å)
C–C, ring	1·378	0·030
C–C, non-ring	1·475	0·030
C–O, aromatic	1·405	0·025
C–O, aliphatic	1·500	0·028
C=O	1·280	0·010

The C–O–C angles are 115° and the $C_{ar.}$–C–$C_{ar.}$ angle in the ketone group is 123°, which is the same as that found in p,p'-diiodobenzophenone (Manthey, Plieth & Singewald, 1952).

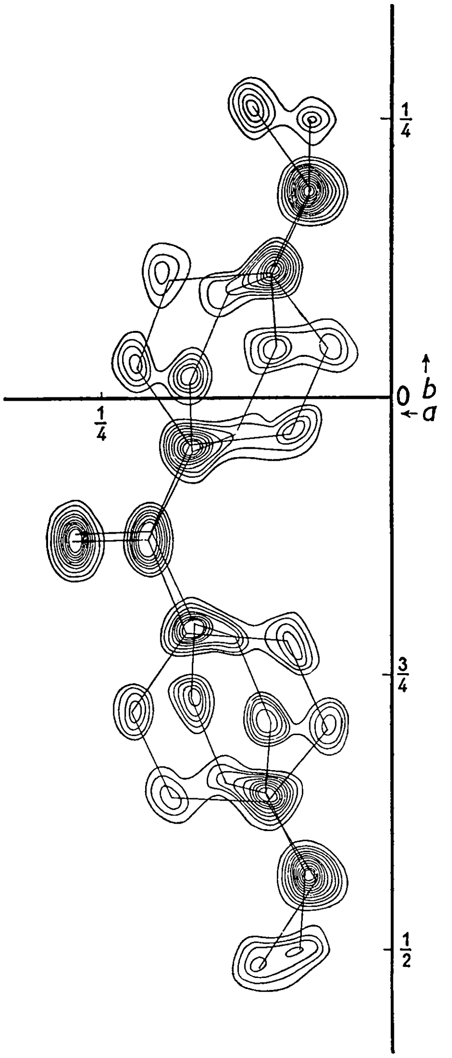

Fig. 3. An E map projection on (001). The same reflections and signs were used to compute the E map as those used in the F map, Fig. 2. The increased resolution over that in Fig. 2 is of interest.

5. Theoretical basis for E maps

The value of removing the effect of the electron distribution and vibration in sharpening peaks in a Fourier series is well known. To our knowledge this sharpening has been applied mainly to the calculation of a Patterson series. It has been seen in this paper that it is worth while to compute sharpened Fourier series representing atomic positions using on the one hand only the largest E values as coefficients and on the other hand all E values contained within a particular sphere in reciprocal space. A Fourier series computed from a restricted number of large E's is well adapted for use with direct methods of phase determination since the phases of the largest E's are the ones which are most easily determined. We present here the theoretical significance of such a calculation.

We define the structure factor

$$F_{\mathbf{h}_\mu}=X_{\mathbf{h}_\mu}+iY_{\mathbf{h}_\mu}\,, \tag{5·1}$$

where

$$X_{\mathbf{h}_\mu}=\sum_{j=1}^{N/n} f_{j\mathbf{h}_\mu}\xi_{j\mathbf{h}_\mu}\,, \tag{5·2}$$

$$Y_{\mathbf{h}_\mu}=\sum_{j=1}^{N/n} f_{j\mathbf{h}_\mu}\eta_{j\mathbf{h}_\mu}\,, \tag{5·3}$$

N is the number of atoms in the unit cell, n is the symmetry number, $f_{j\mathbf{h}_\mu}$ is the atomic scattering factor, and the values of the real and imaginary parts $X_{\mathbf{h}_\mu}$ and $Y_{\mathbf{h}_\mu}$ of the structure factor $F_{\mathbf{h}_\mu}$ are known to be

$A_{\mathbf{h}_\mu}$ and $B_{\mathbf{h}_\mu}$ respectively. The ξ and η are the trigonometric functions of the atomic coordinates listed in *International Tables* (1952) for the various space groups. It was shown (Karle & Hauptman, 1954) that the most probable values of the coordinates x_k, y_k, z_k of those atoms characterized by the atom scattering factor f_k coincide (to good approximation) with the principal maxima of

$$\exp\left\{\sum_{\mu=1}^{m}\frac{-(A_{\mathbf{h}_\mu}-f_{k\mathbf{h}_\mu}\xi_{k\mathbf{h}_\mu})^2-(B_{\mathbf{h}_\mu}-f_{k\mathbf{h}_\mu}\eta_{k\mathbf{h}_\mu})^2}{2m_2\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}}\right\}, \quad (5\cdot4)$$

where, subject to $m_2 \neq 0$,

$$m_2 = m_2^0 = \int_0^1\int_0^1\int_0^1 \xi^2_{j\mathbf{h}_\mu}dx_jdy_jdz_j$$

or

$$m_2 = m_0^2 = \int_0^1\int_0^1\int_0^1 \eta^2_{j\mathbf{h}_\mu}dx_jdy_jdz_j\,. \quad (5\cdot5)$$

In the cases that either m_2^0 or m_0^2 equals zero, m_2 equals the non-zero moment. If we take the logarithm of (5·4) and expand the squares, we obtain

$$\sum_{\mu=1}^{m}\frac{1}{2m_2\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}}\left(-A^2_{\mathbf{h}_\mu}-B^2_{\mathbf{h}_\mu}+2f_{k\mathbf{h}_\mu}(A_{\mathbf{h}_\mu}\xi_{k\mathbf{h}_\mu}+B_{\mathbf{h}_\mu}\eta_{k\mathbf{h}_\mu}) -f^2_{k\mathbf{h}_\mu}(\xi^2_{k\mathbf{h}_\mu}+\eta^2_{k\mathbf{h}_\mu})\right)\,. \quad (5\cdot6)$$

As pointed out by Bullough & Cruickshank (1954), the main term in (5·6) is

$$\sum_{\mu=1}^{m}\frac{f_{k\mathbf{h}_\mu}}{m_2\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}}\left(A_{\mathbf{h}_\mu}\xi_{k\mathbf{h}_\mu}+B_{\mathbf{h}_\mu}\eta_{k\mathbf{h}_\mu}\right), \quad (5\cdot7)$$

the first two terms of (5·6) being a numerical constant and the last is space-group, though not structure, dependent, and is also not expected to have an important effect upon the maxima. The last term is seen to be a numerical constant for space group $P1$.

Expression (5·7) is a Fourier series and we are interested in seeing how the coefficients of the real and imaginary parts are related to the normalized structure factor $E_{\mathbf{h}_\mu}$, defined by

$$E_{\mathbf{h}_\mu} = \frac{F_{\mathbf{h}_\mu}}{\left((m_2^0+m_0^2)\sum\limits_{j=1}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}} = \frac{X_{\mathbf{h}_\mu}+iY_{\mathbf{h}_\mu}}{\left((m_2^0+m_0^2)\sum\limits_{j=1}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}}\,. \quad (5\cdot8)$$

If we ignore numerical constants, we have for the coefficients of the first and second terms in (5·7), respectively

$$\frac{f_{k\mathbf{h}_\mu}}{\left(\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}}\cdot\frac{A_{\mathbf{h}_\mu}}{\left(\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}}, \quad (5\cdot9)$$

and

$$\frac{f_{k\mathbf{h}_\mu}}{\left(\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}}\cdot\frac{B_{\mathbf{h}_\mu}}{\left(\sum\limits_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}\right)^{\frac{1}{2}}}\,. \quad (5\cdot10)$$

The first term in the product (5·9) is the same as the first term of (5·10). It is essentially a constant and if all atoms are assumed to have the same shape, it is an exact constant. Now consider the second terms in (5·9) and (5·10). The numerators are the known values of the real and imaginary parts of the structure factor and the sum in the denominators differs from the sum in (5·8) by a single term. We may conclude that the coefficients in (5·7) are proportional to $E_{\mathbf{h}_\mu}$ and we are thus led to the significance of an E map, namely: The maxima of an E map answer the following question: 'What are the most probable values of the atomic coordinates given the values of any set of structure factors?'.

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