

respect to \mathbf{T} : $\theta_1 = A$ and $\theta_2 = \{B_x, B_y, B_z\}$. Thus there are three AR's of \mathbf{T} , A, E_a, E_b , resulting from A and obtained by engendering with the IR's of $\mathbf{T}/\mathbf{D}_2 = \mathbf{C}_3$ and one three-dimensional representation F obtained by inducing with B_x . Obviously these AR's of \mathbf{T} are themselves IR's of \mathbf{T} .

The IR's of \mathbf{T} are now classified into three orbits relative to \mathbf{O} : $\theta_1 = A$, $\theta_2 = \{E_a, E_b\}$ and $\theta_3 = F$. Representation A gives rise to two IR's A_1, A_2 of \mathbf{O} obtained by engendering with the IR's of $\mathbf{O}/\mathbf{T} = \mathbf{C}_2$ and E_a can be seen to induce the representation E . The two three-dimensional representations F_1, F_2 of \mathbf{O} are obtained from F from the IR's of $\mathbf{O}/\mathbf{T} = \mathbf{C}_2$ and by noting that $(C_4^x)^2 = C_2^x$. The matrices thus obtained for the generating elements of the degenerate species of \mathbf{T} and \mathbf{O} are given below Tables 2 and 3.

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A Simple Direct Method for Solving Centrosymmetric Projections

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Fourier syntheses with a very few properly chosen terms can often represent structures quite well in projection. The use of triple-product relationships is shown to optimize the choice of terms for such a synthesis while minimizing the necessary number of sign combinations. The application of this method is demonstrated in the solutions of three structures: (1) 2,3-dimethoxybenzoic acid (orthovertic acid); (2) (\pm) -2,4,6-trimethylpimelic acid; (3) morpholinium nitrate.

Several methods for solving crystal structures using only a very few structure factors have been put forward. These include Lonsdale's (1929) classic solution of hexamethylbenzene, Robertson's (1945) solution of coronene, and Woolfson's (1954) method of permutation syntheses. We wish to call attention to what we believe to be the optimal method of using a few structure factors, based on Cochran's (1952) discussion of the representation of electron density by Fourier series.

Lonsdale's method, used later by Robertson, depends on the recognition that if $|U_{hkl}|$ is near the maximum value of 1.0, then *all* the atomic centres must lie on or close to the crests of that Fourier component of the electron density. If there are several such U_{hkl} , what may be called geometrical Fourier summations can then be made, and a molecular model fit to those regions where crests coincide, the correct set of signs being found by trial and error. Figs. 1 and 2 show such

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syntheses for hexamethylbenzene and for coronene. Since, however, reflexions with $|U|$ near 1.0 usually arise from special structural features, they are generally quite rare, and without such outstandingly strong reflexions this method cannot be applied.

Woolfson's method of permutation syntheses is completely general, but has other severe limitations. The grounds for selection of terms included in the syntheses are left somewhat vague. The choice of signs is based not on any crystallographic information but solely on a combinatorial analysis. It is accepted in advance that one sign in seven may be wrong, in order to limit the number of combinations that need be tried, which even so is rather large (for example, 256 syntheses for 16 terms).

The method we propose relies first of all on the fact that, in projection down a reasonably short axis, the usual numerical Fourier summation made with quite a small number of properly chosen terms can be sufficient to reveal all or most of a structure. The terms should be chosen from the largest E 's, as these in gen-

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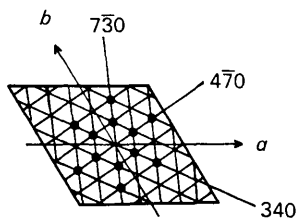


Fig. 1. Hexamethylbenzene, $C_6(CH_3)_6$, $P\bar{1}$; $a=9.010$, $b=8.926$, $c=5.344$ kX; $\alpha=44.5$, $\beta=116.7$, $\gamma=119.6^\circ$; $Z=1$. Molecular plane $\sim(001)$. Signs are $340+$; $470+$; $730+$.

eral provide syntheses with far more significant detail than those made with the largest F 's, as illustrated below. The key point is to select a set of large E 's with signs strongly linked through triple-product relationships. First, this maximizes the probability of having one synthesis with *all* signs correct. Second, it minimizes the number of sign combinations needed. Third, this procedure tends to give the best representation of a physical structure possible with a series containing only a few terms, since it tends to maximize

$$\int_V \rho_{\text{POINT ATOM}} dV = \frac{1}{V^2} \sum_h \sum_{h'} E_h E_{h'} E_{h+h'}$$

a condition formulated by Cochran (1952). Note that in hexamethylbenzene the three reflexions used satisfy a triple-product relationship, and that among the seven reflexions used for coronene there are five such relationships (one of which, however, fails).

We have successfully applied these ideas to three nearly-equal-atom structures, each containing on the order of 50 atoms in the unit cell:

- (1) 2,3-dimethoxybenzoic acid (orthovertic acid, OVA)
- (2) (\pm) -2,4,6-trimethylpicelic acid (TMPA)
- (3) morpholinium nitrate (MN).

All three crystals belong to space group $P2_1/c$ with $Z=4$. Unit cell parameters are given in Table 1. Detailed reports of the structures will be published elsewhere.

Table 1. Unit cell parameters of OVA, TMPA and MN

	OVA	TMPA	MN	
a	8.34	12.45	6.73	Å
b	7.05	7.10	10.31	Å
c	16.76	13.41	11.72	Å
β	111.2°	101.7°	121.9°	

In OVA, our first attempt, there were no triple-product relationships at all among the eight largest E_{h0l} , $|E| > 1.8$. Defining an origin with two signs still meant too large a number of maps, 64, to make and choose among. Rather desperately turning to the largest F_{h0l} , anticipating poor resolution, we found two weak relationships. Eight maps were thus required using the seven terms we chose. The maps were indeed poor (one

of the triple-product relationships failed), but it was possible, assuming that the structure consisted of dimers hydrogen-bonded across centres of symmetry, to fit a model to two of the maps, and one of the two proposed structures proved to be correct on refinement.

This was disappointing, in that it might appear that only special features of this structure had led to its solution. To test our premises, we made, after the solution was obtained, two Fourier syntheses, using the

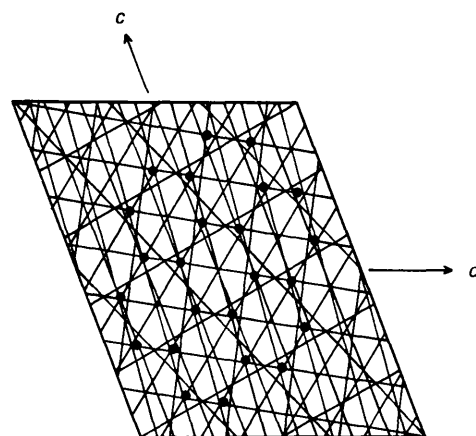


Fig. 2. Coronene, $C_{24}H_{12}$, $P2_1/a$; $a=16.10$, $b=4.695$, $c=10.15$ Å; $\beta=110.8^\circ$; $Z=2$. Signs are $207+$; $405-$; $602-$; $10,0,3-$; $14,0,8+$; $16,0,1+$; $16,0,0+$.

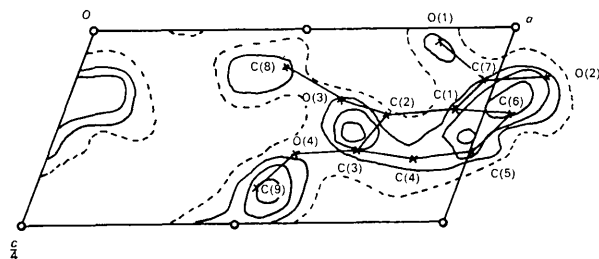


Fig. 3. OVA $\rho(010)$ F map.

F used:	004	-59	102	67	104	-72	$20\bar{8}$	-48
	$20\bar{6}$	-45	200	43	304	-52	$40\bar{6}$	40

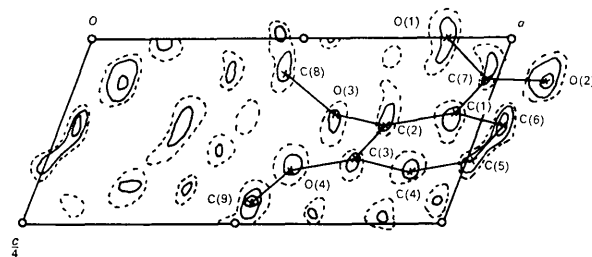


Fig. 4. OVA $\rho(010)$; E map.

E used:	304	-1.9	506	2.0	604	1.9	$70\bar{1}\bar{2}$	2.2
	706	2.3	$80\bar{8}$	-1.8	$80\bar{6}$	-2.0	806	1.9

eight largest F_{h0l} and the eight largest E_{h0l} with correct signs. These are shown in Figs. 3 and 4. While the F map has some information, the E map is extremely well resolved, all 13 atoms being clearly shown in a

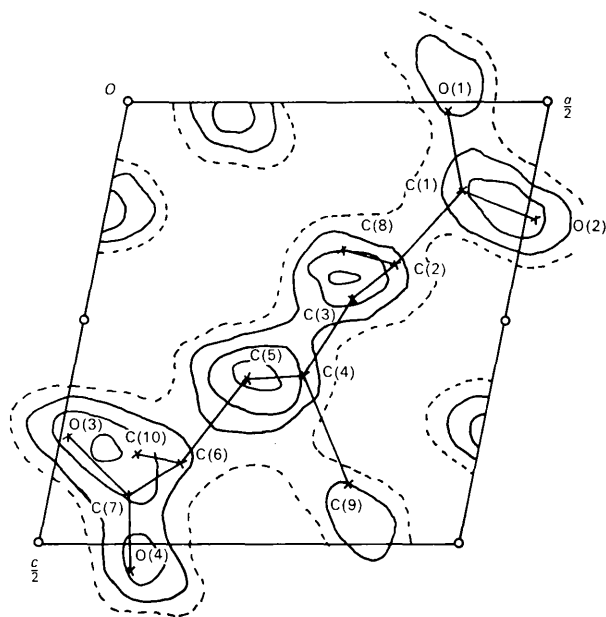


Fig. 5. TMAPA $\rho(010)$ F map.

F used:	102	57	208	53	202	122	204	-59
	406	52	404	-99	402	-68	402	-59

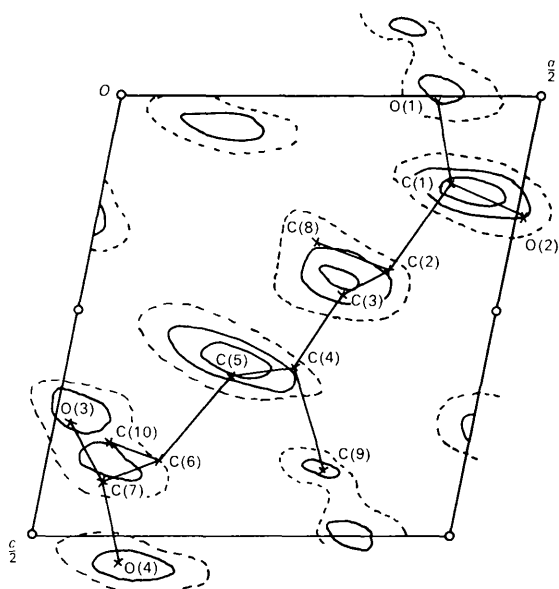


Fig. 6. TMAPA $\rho(010)$ E map.

E used:	1,0,10	-1.84	208	2.85	202	2.65	204	-1.70
	3,0,12	1.79	406	2.16	404	-3.06	402	-1.76

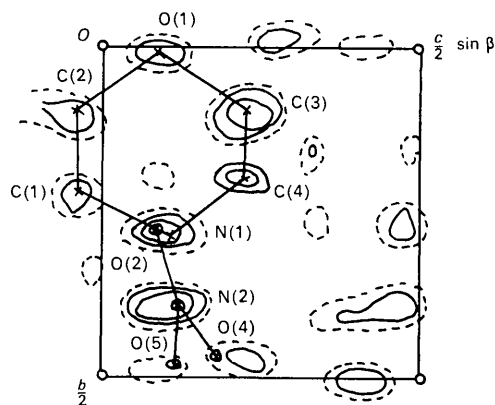


Fig. 7. MN $\rho(100)$ E map.

E used:	018	1.55	023	-1.44	075	1.91
	083	2.64	095	-1.63	0,10,0	2.40
	0,10,6	-1.28	0,11,2	-3.01		

map with only eight terms. Indeed, the eight-term E map is even better resolved than the final F synthesis using all the zero-layer reflexions. It convinced us of the utility of E syntheses with only a few terms. It was apparent, however, that successful application of our ideas demanded the use of triple-product relationships.

Therefore, in TMAPA, from 15 $|E_{h0l}| > 1.5$ we selected eight related so that phases could be assigned using only three symbols. One of the eight maps was clearly the best, showing both carboxyl groups near centres of symmetry, forming hydrogen bonds, as anticipated. Trials with a model showed the best way to place all the atoms, and the projection refined straight away. For comparison, we also tried the method with eight F_{h0l} . Accepting several Σ_1 indications that the structure invariant $40\bar{4}$ was negative reduced the number of sign combinations to eight. The best F map, Fig. 5, corresponds closely with the best E map, Fig. 6, because in this rather unusual case there are six terms common to the two syntheses.

In MN the shortest axis (100) projection has symmetry pgg . From among the $|E_{0kl}| > 1.2$ we chose eight which could be assigned phases using only one symbol. Of the two maps the better was quite obvious and is shown in Fig. 7. Our interpretation was again correct, and refinement proceeded smoothly.

We realize, of course, that simple centrosymmetric structures such as these can be solved fairly easily, in three dimensions, by other means. Its minimal requirements of time and effort, however, recommend our method as an alternative to be borne in mind, especially since its success in these three very different structures show it to be independent of any structural peculiarities. A particularly useful application of this method might be to centrosymmetric projections in non-centrosymmetric space groups such as $P2_1$ or $P2_12_12_1$, as a basis for the complete solution. Whether an extension of these ideas to three dimensions is possible and the limits of structural complexity to which

this approach is applicable can only be tested by more trials in the future. Finally, there would seem to be a clear value in this method for laboratories with only modest or no machine computation facilities, and for students being trained in methods of crystal-structure analysis.

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On the Reliability of the Σ_2 Relation. II. Artificial Structures in $P2_1/c$

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It is shown that for structures in which the coordinates of atoms have been randomly generated, the probability formula gives an underestimate of the experimental probability of the Σ_2 relation. Concentration of atoms in planes increases the number of reliable triplet sign relations. Although the presence of a non-crystallographic centre of symmetry results in a larger number of triplet relations with high $E_H E_K E_{H-K}$ values, the percentage of failures is increased compared with random structures.

Introduction

In the first paper of this series (Schenk, 1973) it was shown that for real structures in $P2_1/c$ the probability formula

$$p_+(|E_H E_K E_{H-K}|) = \frac{1}{2} + \frac{1}{2} \tanh(\sigma_3 \sigma_2^{-3/2} |E_H E_K E_{H-K}|) \quad (1)$$

(Cochran & Woolfson, 1955) deviates markedly from the true result. In a number of cases the probabilities

(1) were found to be overestimates of the experimental probabilities. Therefore (1) and the related expression for multiple sign indications are of doubtful reliability for practical sign determinations.

The discrepancies between theory and practice exist because the theory is derived assuming the positions of atoms to be random variables, whilst in practice they are not. The first purpose of this paper is to show that for randomly generated structures in $P2_1/c$ the probabilities (1) are underestimates of the true probabilities. For these model structures the Patterson func-

Table 1. Total number (nr.) of triplet sign relations above a variable $E_3 = \sigma_2^{-3/2} \sigma_3 |E_H E_K E_{H-K}|$ value with the percentage (%) of correct sign relations for structures 1 to 7, which were randomly generated

E_3	Structure 1		Structure 2		Structure 3		Structure 4		Structure 5		Structure 6		Structure 7	
	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%
15														
10														
8														
6														
5														
4.0														
3.6	1	100	1	100					3	100	2	100		
3.2	1	100	1	100	1	100	2	100	3	100	2	100	1	100
2.8	5	100	2	100	3	100	2	100	10	100	2	100	1	100
2.6	8	100	5	100	5	100	5	100	11	100	2	100	3	100
2.4	12	100	12	100	11	100	11	100	20	100	7	100	4	100
2.2	22	100	16	100	20	100	18	100	31	100	14	100	9	100
2.0	32	100	24	100	39	100	36	100	52	100	29	100	28	100
1.8	65	100	56	100	74	100	62	98.4	79	100	52	100	49	100
1.6	123	98.4	93	100	151	98.7	123	97.6	151	100	111	100	88	97.7
1.4	266	98.1	201	99.5	323	98.1	266	96.6	290	98.3	216	99.1	181	98.9
1.2	511	97.6	394	98.2	615	97.9	530	97.0	510	96.9	423	97.4	371	97.3
1.0	1149	96.2	879	95.2	1188	95.5	1128	94.1	1034	95.1	968	95.0	842	96.1
0.9	1644	95.0	1313	94.1	1686	94.2	1682	93.1	1521	93.9	1425	93.8	1278	94.8
0.8	2508	92.9	2038	92.3	2508	92.2	2611	91.5	2238	92.4	2169	92.0	2013	92.0
0.7	3803	90.5	3070	90.1	3704	90.0	4009	89.2	3412	90.5	3364	90.0	3118	89.9