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## Dynamical Scattering and Electron Crystallography – *Ab Initio* Structure Analysis of Copper Perbromophthalocyanine

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### Abstract

Electron diffraction intensity data were collected at 1200 kV from thin epitaxially oriented crystals of copper perbromophthalocyanine ( $C_{32}Br_{16}CuN_8$ ) in a projection down molecular columns. Measured cell constants for the projection with *mmm* symmetry are  $d_{100} = 17.88$  (9),  $b = 26.46$  (15) Å. The structure was determined by Fourier refinement after three heavy-atom positions were identified in an initial potential map. In addition to the copper and halogens, all light-atom positions were found. Although the final *R* value for all data is 0.41, *n*-beam dynamical calculations for crystal thicknesses corresponding to the estimated sample dimension account for the observed amplitudes that deviate most from their kinematical values.

### Introduction

Is electron crystallography possible? That is to say, can electron diffraction intensity data from thin microcrystals be exploited for quantitative *ab initio* structure analyses in much the same way as X-ray crystal-structure determinations are carried out? Since the early work of Rigamonti (1936), there have been numerous attempts to answer this question, including the comprehensive program on organic compounds begun by Vainshtein and his co-workers in Moscow (Vainshtein, 1964).

Although the first use of direct phasing techniques to solve a structure with electron diffraction intensities was reported 15 years ago (Dorset & Hauptman, 1976), only recently has successful application of this

technique to a number of representative organic structures shown (Dorset, 1991) that the above questions can be answered affirmatively if the compounds investigated are composed of light atoms such as carbon, nitrogen and oxygen. These analyses show that, after initial determination of atomic positions, the structures can be refined by Fourier techniques (and possibly also constrained least-squares techniques) to produce a reasonable packing scheme in which the constituent molecules are found to have chemically meaningful bond distances and angles. If microcrystals are the only preparations available (as in linear polymers), electron crystallographic techniques can be used to obtain reasonably accurate molecular architectures.

Because of dynamical scattering, the presence of heavy atoms in an organic structure may, on the other hand, make a structure analysis difficult or impossible. This was anticipated by the direct phasing analysis of simulated electron diffraction data from the disodium salt of an organic sulfinate (Dorset, Jap, Ho & Glaeser, 1979). Analysis of a 60 kV data set from thiourea (Dvoryankin & Vainshtein, 1960) has shown that the phase estimates obtained from the computed triplet and quartet structure invariants are correct, but the dynamical-scattering contribution from the sulfur atom can affect the accuracy of bond distances and angles calculated from the atomic positions found in the potential maps (Dorset, 1991). Use of shorter electron wavelengths may be helpful, as demonstrated in the structure determination of copper perchlorophthalocyanine with high-voltage electron diffraction intensity data. By low-dose electron

microscopy, Uyeda, Kobayashi, Suito, Harada & Watanabe (1972) were initially able to identify the molecular quatrefoil shape when thin epitaxially nucleated crystals were tilted  $26.5^\circ$  around a unit-cell  $b$  ( $=26 \text{ \AA}$ ) axis. Unit-cell constants measured from electron diffraction patterns were found to be  $a = 19.62$ ,  $b = 26.04$ ,  $c = 3.76 \text{ \AA}$ ,  $\beta = 116.5^\circ$ . (For this determination, two types of crystal are grown that give nearly orthogonal views of the molecular packing.) The molecular planes are oriented parallel to the unit-cell (001) plane, thus the space group is either  $C2/m$  or  $C2/c$ . Averaged higher-resolution images (Uyeda, Kobayashi, Ishizuka & Fujiyoshi, 1978–1979) obtained later at 500 kV were able to resolve the positions of the Cu and Cl heavy atoms but not the C or N positions of the organic residue. These lighter-atom positions were determined only when direct phasing techniques, followed by Fourier refinement, were applied to the 1200 kV electron diffraction intensity data (Dorset, Tivol & Turner, 1991) and the resultant crystal structure was found to have bond distances and angles consistent with the X-ray structures of similar compounds. Recently, another technique for achieving an atomic-resolution structure for this compound was discussed (Fan, Xiang, Li, Pan, Uyeda & Fujiyoshi, 1991), which employed image deconvolution to obtain crystallographic phases to  $2 \text{ \AA}$  resolution and the multisolution computer-program package *RANTAN* (Yao, 1981) enabled them to carry out a phase determination to  $1 \text{ \AA}$  resolution of the electron diffraction pattern. Of course, there may be heavy-atom derivatives where even high-voltage electrons will not ensure that the observed intensities are adequately close to the kinematical limit. In that case, criteria other than the minimization of the crystallographic  $R$  factor must be used to evaluate the progress of a structure determination. One such example is discussed in this paper, which describes the crystal structure analysis of copper perbromophthalocyanine, which is isomorphous to the perchloro analog studied previously.

#### Materials and methods

Thin (001) plate microcrystals of copper perbromophthalocyanine,  $C_{32}Br_{16}CuN_8$ , were epitaxially nucleated from the vapor phase on a KCl crystal substrate. This growth was carried out in an Edwards 306A vacuum coater at  $ca\ 1.33 \times 10^{-2}$  Pa by sublimation *in vacuo* from an electrically heated perforated molybdenum boat. The freshly cleaved KCl crystal face was first outgassed by heating to ensure that the nucleation surface would be atomically clean. Growth of these crystals and their molecular-resolution electron-microscope images have been described by Fryer & Holland (1984), who also demonstrated that the copper perchloro- and perbromophthalocyanines were structurally isomorphous. Optically, the epitax-

ial films were estimated to be about  $100 \text{ \AA}$  thick. These were coated with a thin carbon film, floated on a clean water surface to separate them from the KCl substrate, picked up with bare 300-mesh copper electron-microscope grids and allowed to dry in air.

Selected-area electron diffraction patterns (Fig. 1) were obtained from epitaxially oriented (001) crystalline plate specimens tilted  $26^\circ$  in a holder that also enables a rotation of the grid to orient the proper crystal projection (along [001]) relative to the electron beam (Turner, Barnard, McCauley & Tivol, 1991). Thus one could find the  $hk0$  diffraction pattern (Fig. 1). The accelerating voltage selected on the AEI EM-7 electron microscope was 1200 kV. Precautions were taken to minimize the radiation dosage to the specimen by control of illumination with the condenser lenses and electron-gun bias setting (also inserting suitably small apertures) and recording the diffraction patterns with a sensitive photographic emulsion (DuPont Cronex Lo-dose Mammography film). Intensity measurements were made using a Joyce Loebel MkIIC flatbed microdensitometer and integrating under the peaks. There was no Lorentz correction applied to the 168 observed intensities.

After calculation of normalized structure factors from the observed intensity data in the usual way

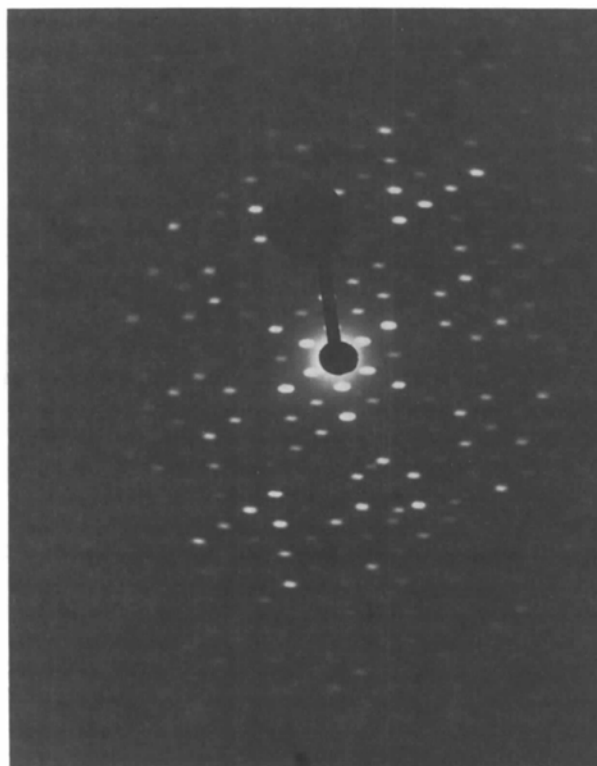


Fig. 1. Electron diffraction pattern from an epitaxially oriented crystal of copper perbromophthalocyanine tilted  $26^\circ$  around the unit-cell  $b$  axis. Accelerating voltage: 1200 kV.

(Hauptman, 1972), direct phasing was attempted using probabilistic estimates of three- and four-phase structure invariants (Hauptman, 1972; Hauptman & Green, 1976) for the centered projection in plane group *cm̄m*. A full description of this methodology in electron crystallography has been published earlier (Dorset, 1991). After identification of a molecular fragment in the first potential map, Fourier refinement was carried out by evaluation of potential maps calculated from the estimated phase  $\alpha_c$  of the observed structure factors using expressions

$$\rho(r) = (1/V) \sum_h \sum_k |M| \exp i\alpha_c \exp (-2\pi i h x + k y),$$

where

$$|M| = |F_o|, \quad |F_o| - |F_c| \quad \text{or} \quad 2|F_o| - |F_c|.$$

*N*-beam dynamical calculations were carried out using the multislice method of Cowley & Moodie (1959) *via* a computer program package purchased from Arizona State University. As usual, this involves the phase grating expression (Cowley, 1981)

$$q(x, y) = \exp [-i\sigma\psi(x, y)\Delta z],$$

where  $\sigma$  is an interaction term, dependent upon the electron wavelength, and  $\psi(x, y)$  is the projected potential distribution of the crystal slice. Since the perbromo- compound is isostructural with copper perchlorophthalocyanine (Uyeda, Kobayashi, Ishizuka & Fukiyoshi, 1978–1979), it is assumed that the slice thickness  $\Delta z$  is 3.76 Å.

### Structure analysis

With an internal gold powder diffraction standard, the lattice constants measured for the projection down the molecular columns in this structure were  $d_{100} = 17.88$  (9),  $b = 26.46$  (15) Å with the implied  $\beta$ -angle values of 116°, *i.e.* 90 + 26° tilt used to project down the molecular columns, and the unit-cell *a* axis of 19.89 Å would be oriented parallel to the molecular planes (see Uyeda, Kobayashi, Suito, Harada & Watanabe, 1972). [As mentioned above, the tilt angle needed to orient the correct projection down the molecular columns was determined by Fryer & Holland (1984).] The rectangular projection was determined to have *cm̄m* plane-group symmetry from the  $h + k = 2n + 1$  absences in the experimental diffraction pattern (Fig. 1) and the *mm* symmetry of the molecule.

Evaluation of triplet and quartet structure invariants was used in an attempt to determine phase values for 29 reflections. As was shown in subsequent dynamical-scattering calculations, the effective change of numerous normalized structure-factor magnitudes adversely affected the success of the phase determination so that 15 of the 29 estimates were incorrect. Hence, the direct phase determination is not successful. Nevertheless, certain features of the

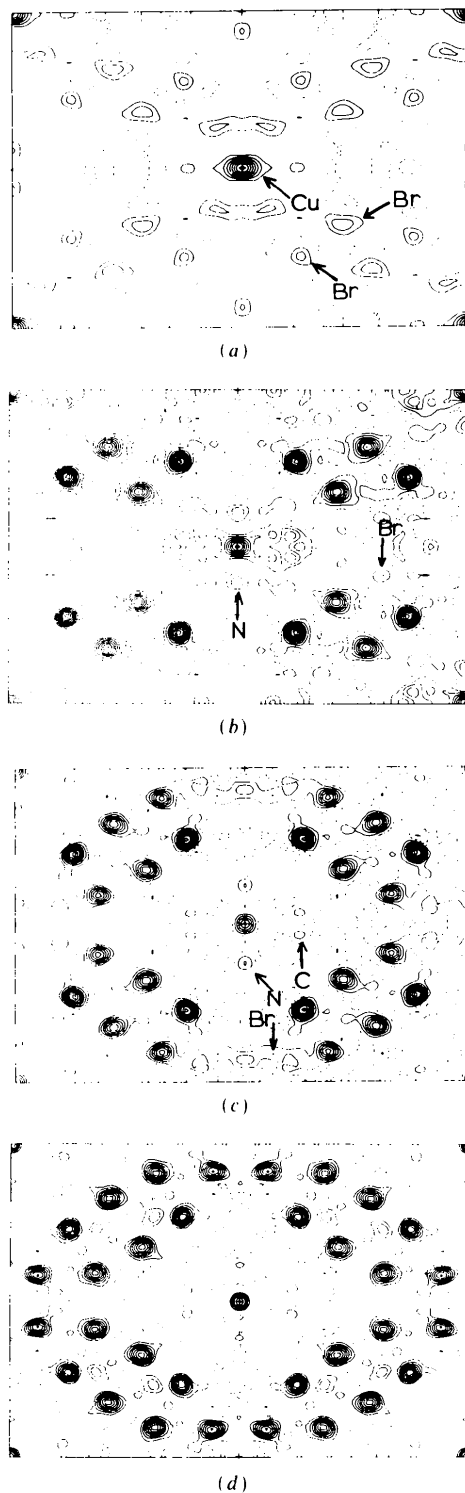
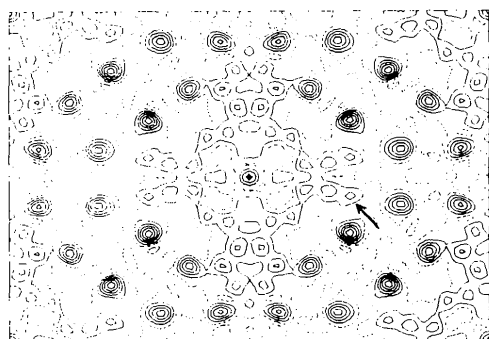
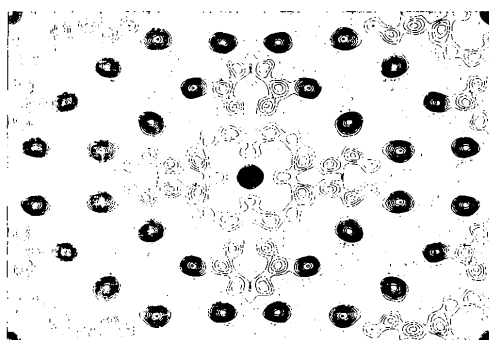


Fig. 2. Early stages of structure analysis. (a) Initial map from 29 phased structure factors in which the positions of a Cu atom and two Br atoms are recognized. (b) First potential map based on 168 structure factors phased from heavy-atom positions in (a). Additional Br- and N-atom positions are visible. (c) Subsequent potential map showing final Br-atom position and two light-atom positions. (d) Potential map with all heavy atoms well resolved.

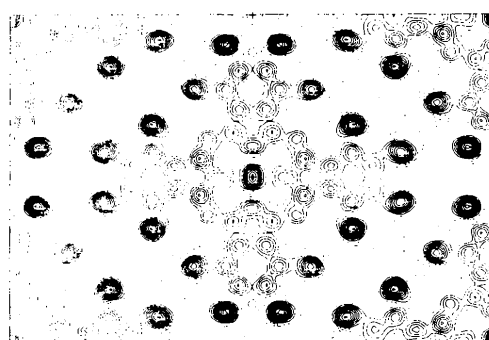
structure could be discerned in the first potential map, based on the initial phase estimate (Fig. 2*a*), especially when the molecular geometry was used as a guideline. (A similar procedure would be used in X-ray determinations of organic molecules, for which the molecular architecture is known, so that the positions of reasonable fragments can be picked from the initial map.) A second map (Fig. 2*b*) was calculated with phase estimates for all 168 unique reflections found from a kinematic structure-factor calculation



(a)



(b)



(c)

Fig. 3. Final stages of Fourier refinement. (a) Potential map after all atom positions located directly by refinement procedure and one benzene C atom added to theoretical position (arrow). One additional aromatic C atom is required. (b) Structure giving lowest *R* factor. Some light-atom positions are not well resolved. (c) Best potential map clearly showing all atomic positions.

with input positions for the Cu and two Br atoms, as deduced from the initial map. In the second map, a third Br-atom position as well as an N-atom position were found for a subsequent structure-factor calculation. The new phase estimate led to a third potential map (Fig. 2*c*) from which the fourth unique Br-atom position was determined as well as that of a C atom. When atoms were correctly positioned, their density in the map was well resolved (Fig. 2*d*). A subsequent difference map based on  $|F_o| - |F_c|$  located four more C atoms and the other two N atoms.

The Fourier refinement progressed until all but two C-atom positions were located in the potential map. At this point difference maps based on  $2|F_o| - |F_c|$  or  $|F_o| - |F_c|$  were not useful for finding the remaining atoms so that these C atoms had to be inserted at positions expected for a tilted benzene ring. Their presence was confirmed by the contour levels of the subsequent maps (Fig. 3*a*). Attempts to refine this structure further by reduction of the crystallographic *R* factor began to fail at this point. For example, the structure in Fig. 3(*b*) corresponds to  $R = 0.36$  whereas that in Fig. 3(*c*) gives  $R = 0.41$ . (Here isotropic temperature factors  $B_{Cu} = 2.0$ ,  $B_N = 4.0$ ,  $B_C = 4.0$  and  $B_{Br} = 6.0 \text{ \AA}^2$  were used for the structure-factor calculations.) Clearly, the latter map contains better resolved atomic peaks, as determined by the number of density contours, and this was taken to be the correct structure. This presumption was justified by the calculation bond distances and angles (Fig. 4).

Although the derived structure is not as accurate as the one determined for the perchloro derivative (Dorset, Tivol & Turner, 1991), the bond angles and distances calculated from the atomic positions in the

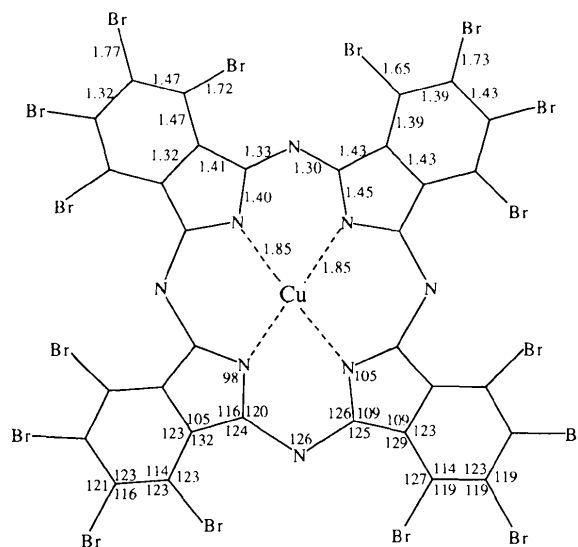


Fig. 4. Bond distances and angles calculated from projected coordinates in Table 1 and assuming a  $26^\circ$  tilt of the molecular plane around the *b* axis.

Table 1. Projected atomic positions for  $C_{32}Br_{16}CuN_8$ 

Atom	$x/a$	$y/b$
Cu	0.000	0.000
Br1	0.081	0.302
Br2	0.157	0.202
Br3	0.271	0.120
Br4	0.405	0.057
N1	0.000	0.070
N2	0.093	0.000
N3	0.117	0.090
C1	0.136	0.042
C2	0.203	0.025
C3	0.265	0.055
C4	0.327	0.025
C5	0.055	0.106
C6	0.036	0.158
C7	0.074	0.202
C8	0.036	0.246

map of Fig. 3(c) (see Table 1) and assuming a  $26^\circ$  tilt of the planar molecule were not greatly different from the values determined by X-ray crystallography for similar compounds. The average distances found in this study and the comparable values found for an unhalogenated copper phthalocyanine (Brown, 1968) are:

Bond	Bond lengths ( $\text{\AA}$ )	
	This study	X-ray structure
Aromatic C–C	1.40 (6)	1.39 (2)
Pyrrole C–C	1.42 (1)	1.45 (2)
Pyrrole C–N	1.43 (4)	1.37 (1)
Azo C–N	1.32 (1)	1.330 (4)

The average C–Br distance,  $1.72(5) \text{\AA}$ , on the other hand, is significantly smaller than the value of  $1.85(1) \text{\AA}$  expected for aromatics (Sutton, 1958). (Attempts to find new Br positions in difference maps were not successful.) The Cu–N distances are closer to the values found for the perchloro analog ( $1.83 \text{\AA}$ ) than those found for the unhalogenated compound ( $1.93 \text{\AA}$ ).

The final structure can be further corroborated by  $n$ -beam dynamical calculations. Although we stipulated that initial structure-factor calculations for the phase grating should be carried out at  $3.0 \text{\AA}^{-1}$  resolution and had carried out the multislice calculation with an aperture of  $1.36 \text{\AA}^{-1}$ , we have specifically monitored a set of 54 reflections within the Miller-index range  $h \leq 10$ ,  $k \leq 9$ . In the multislice calculations, intensities were sampled at intervals of 10 slices up to 50 slices. At the maximum thickness of  $188 \text{\AA}$ , the total summed intensity was 98.58% of the incident beam after the multislice calculation.

As shown in Table 2, the match of computed and observed structure factors was appreciably improved for crystal thickness in the region of 113 to  $150 \text{\AA}$ , consistent with our optical estimate of the sample thickness. As found before in our analysis of the  $n$ -paraffins (Dorset, 1976*a, b*), the multislice calculation correctly indicated which reflections should be

Table 2. Structure factors for  $C_{32}Br_{16}CuN_8$ 

$hk$	$ F_o $	$ F_c $	$ F_{\text{dyn}} $		
			$t = 37.6 \text{\AA}$	$t = 112.8 \text{\AA}$	$t = 150.0 \text{\AA}$
02	1.86	0.71	0.81	1.29	1.65
04	1.66	1.24	1.23	1.35	1.49
06	0.70	0.24	0.24	0.34	0.40
08	1.47	2.13	2.09	1.79	1.57
11	2.02	0.78	0.88	1.53	1.98
13	0.98	0.72	0.73	0.93	1.09
15	0.29	0.20	0.24	0.19	0.21
17	0.57	0.99	0.97	0.84	0.78
19	1.27	1.50	1.45	1.28	1.14
20	1.28	0.44	0.47	0.68	0.84
22	2.40	1.73	1.76	2.09	2.40
24	0.47	1.20	1.18	1.04	0.99
26	0.41	0.16	0.24	0.44	0.57
28	0.61	1.16	1.15	1.04	0.99
31	1.24	1.01	1.00	0.87	0.80
33	0.42	0.69	0.71	0.71	0.76
35	1.41	1.90	1.85	1.56	1.35
37	1.33	1.67	1.62	1.38	1.22
39	0.36	0.19	0.24	0.19	0.20
40	1.12	1.17	1.15	1.00	0.88
42	0.44	0.40	0.41	0.48	0.58
44	1.46	1.84	1.79	1.53	1.34
46	0.35	0.09	0.00	0.16	0.23
48	1.51	3.04	2.97	2.61	2.36
51	0.64	0.81	0.81	0.81	0.83
53	0.27	0.13	0.00	0.19	0.24
55	1.65	1.93	1.88	1.62	1.41
57	0.96	1.50	1.45	1.29	1.20
59	0.93	1.35	1.32	1.18	1.07
60	1.95	2.16	2.12	1.81	1.59
62	0.51	0.51	0.24	0.28	0.36
64	1.37	0.54	1.32	1.16	1.04
66	0.67	0.95	0.94	0.82	0.75
68	0.65	0.76	0.73	0.68	0.63
71	1.81	2.00	1.94	1.67	1.50
73	0.82	1.18	1.18	1.13	1.12
75	0.49	0.48	0.53	0.82	1.01
77	1.17	1.42	1.38	1.20	1.08
79	0.76	0.13	0.34	0.76	0.99
80	0.82	0.09	0.00	0.22	0.29
82	1.36	1.22	1.19	1.04	0.96
84	0.55	0.63	0.62	0.54	0.51
86	0.45	0.72	0.71	0.72	0.74
88	0.38	0.23	0.34	0.68	0.84
91	0.33	0.58	0.57	0.72	0.81
93	1.62	1.52	1.48	1.29	1.17
95	0.52	0.42	0.41	0.38	0.36
97	0.66	0.65	0.62	0.56	0.50
99	0.48	0.07	0.00	0.12	0.16
10,0	0.28	0.01	0.00	0.31	0.38
10,2	0.86	1.25	1.22	1.06	0.94
10,4	0.17	0.46	0.47	0.38	0.32
10,6	0.15	0.06	0.00	0.24	0.31
10,8	0.28	0.24	0.24	0.31	0.25
$R$		0.39	0.37	0.27	0.26

most changed by dynamical scattering, *viz* the 020, 040, 110, 200 and 480. The best match to the data subset lowers the  $R$  value from 0.39 to 0.26, a value consistent with electron crystallographic structure analyses of other compounds with 'quasi-kinematical' data sets. [The failure to lower the  $R$  factor further in the analyses of such organic structures is probably due to the additional data perturbation from secondary scattering (Cowley, Rees & Spink, 1951).] The match of dynamical data to the observed structure-factor magnitudes is shown in Fig. 5 for various crystal thicknesses.

### Discussion

In an early discussion of the use of direct phasing techniques in electron crystallography (Dorset, 1978), it was proposed that structure analyses with electron diffraction data that impose kinematical phases on observed dynamical structure-factor magnitudes may be much more effective for visualizing atomic detail than the averaging of high-resolution images, even when using an electron microscope with the best possible objective-lens transfer function. This is because the dynamical perturbations to the diffracted beams are first expressed as phase distortions, which can severely degrade the quality of the image before the wave amplitudes are greatly changed from their kinematical values. In fact, such a phase distortion is mentioned as being a significant perturbation to 500 kV images from copper perchlorophthalocyanine by Uyeda, Kobayashi, Ishizuka & Fujiyoshi (1978–1979). By contrast, analysis of electron diffraction data from this compound has been shown to yield an atomic-resolution structure (Dorset, Tivol & Turner, 1991).

Given this assumption, it is still difficult to understand *prima facie* why the structure analysis worked so well for copper perbromophthalocyanine. Dynamical scattering from *ca* 100 Å thick crystals is significant, even at 1200 kV, degrading the match between kinematical and observed structure factors. The direct phase determination is not really successful although, with knowledge of molecular architecture, one can find a fragment with which to begin a successful Fourier refinement. Scrutiny of the total data set reveals that dynamical scattering significantly changes the values of 11 of the 168 measured intensities so that the computed *R* value is 0.35 for the remaining 157 reflections. Five of these reflections,

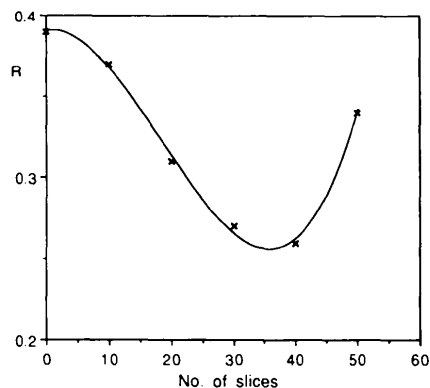


Fig. 5. Crystallographic *R* factor comparing observed structure factors to structure factors calculated using kinematical assumption (shown at zero thickness) or by multislice *n*-beam calculation monitored at intervals of ten slices where each slice is 3.76 Å thick. As usual  $R = \sum |F_o| - k \sum |F_c| / \sum |F_o|$  where *k* is a scale factor such that  $\sum |F_o| = k \sum |F_c|$ . Here the calculated  $|F_c|$  may be a kinematical or dynamical data set.

which account for the largest deviation from kinematical wave amplitudes, occur at  $d^* \leq 0.15 \text{ \AA}^{-1}$ . Hence the high-resolution reflections are less affected by dynamical scattering and, as demonstrated, the structure can be refined, even if the crystallographic residual for the total data set is rather large. Nevertheless, the use of the crystallographic *R* factor as the sole criterion for a successful structure refinement can lead to a false structure, as found earlier with thiourea (Dorset, 1991). The best procedure is to find models where the atomic peak positions in computed Fourier maps are well resolved and have the most contour levels.

It is apparent from the analysis of a dozen examples so far that electron crystallographic determinations of unknown molecular crystal structures are far from being 'the stuff of fantasy'. If conditions for collection of the best possible intensity data are recognized, there is no reason why such analyses cannot be carried out in a way comparable to X-ray crystal structure determinations. The example discussed in this paper represents a data set collected at conditions near the limit for successful structure determination.

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## Direct Methods in Electron Crystallography – Structure Analysis of Boric Acid

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### Abstract

Direct phasing methods based on the probabilistic estimate of triplet and quartet structure invariants are used to determine the crystal structure of boric acid from room-temperature electron diffraction data published by Cowley [*Acta Cryst.* (1953), **6**, 522–529] and also new low-temperature data collected at or below 128 K. In either instance, the resulting structure is the monolayer found earlier and the bond distances and angles for heavy atoms computed from the atomic coordinates agree well with three-dimensional X-ray and neutron diffraction determinations. H-atom positions are not accurately defined, however. A reason for the monolayer structure resulting from the analysis of electron diffraction data is suggested, given the continuous reciprocal-lattice rods observed in diffraction patterns from tilted crystals also seen earlier at room temperature.

### Introduction

In the 1950s the utility of electron diffraction intensity data for crystal structure analysis was anticipated with considerable enthusiasm, especially for the materials where the favorable scattering-factor ratio would permit a more accurate determination of H-atom positions than is possible by X-ray crystallography (Cowley, 1953*a*). A number of structures were determined (Cowley, 1953*b*; Vainshtein, 1964) from such data but, due to the difficulties experienced in finding phases for the measured structure-factor amplitudes, contemporary X-ray structures were used to define the heavy-atom positions and the H-atom positions were then sought in the subsequent electrostatic potential maps. Unfortunately, this reasonable procedure has often created an unfavorable impression

of the electron diffraction technique in the crystallographic community, an impression that is amplified by the relative complexity of the scattering theory and, thus, the number of corrections that sometimes need to be made to the measured data. That is to say, it is commonly thought by many crystallographers that valid *ab initio* structure analyses with electron diffraction intensity data are not possible.

Recently, this laboratory has investigated the use of direct phasing techniques for determining crystal structures from observed electron diffraction intensities, including a reassessment of data sets that were used in the earlier analyses. As has been shown (Dorset, 1991*a*), direct phase analysis of published electron diffraction data from 2,5-diketopiperazine (2,5-piperazinedione) (Vainshtein, 1955) yields a structure that is very close to the one found by an X-ray determination. Similar results were obtained (Dorset, 1991*b*) in the reanalysis of urea (Lobachev & Vainshtein, 1961) and thiourea (Dvoryankin & Vainshtein, 1960), although some influence of dynamical scattering was indicated in the latter case. Nevertheless, direct phasing methods, based on the evaluation of three- and four-phase invariants, are found to be remarkably robust when used with electron diffraction intensity data, even when they are somewhat perturbed by multiple scattering.

Among the earliest studies of hydrogen-bonded structures by electron diffraction, boric acid was found (Cowley, 1953*b*) to have a disordered layer stacking and the hydrogen-bonding scheme was quite different from the one suggested originally by Zachariasen (1934), since the possibility of nonlinear linkages is suggested in the final potential maps. This structure has not been verified in subsequent X-ray (Zachariasen, 1954; Gajhede, Larsen & Rettrup,