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Application of a multi-solution method for determination of phases for non-centrosymmetric crystals.

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A program has been written for direct phase determination for non-centrosymmetric crystals by a multi-solution technique. The method was successfully applied in the solution of two structures.

The tangent formula (Karle & Hauptman, 1956),

$$\tan\theta_{\mathbf{h}} = \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin(\theta_{\mathbf{k}}+\theta_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos(\theta_{\mathbf{k}}+\theta_{\mathbf{h}-\mathbf{k}})},$$

has been employed successfully for phase determination for many non-centrosymmetric crystals (Karle & Karle, 1964, 1966, 1968; Oh & Maslen, 1968; Cooper, Norton & Hauptman, 1969). Success of this formula is dependent upon the existence of several correctly determined phases prior to its application.

The $\sum_2$ formula (Karle & Karle, 1964, 1966),

$$\theta_{\mathbf{h}} \simeq \langle \theta_{\mathbf{k}}+\theta_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}},$$

has been used with varying degrees of success to obtain these initial phases (Karle & Karle, 1964, 1966, 1968; Oh & Maslen, 1968) following the assignment of appropriate phases to a specified number of reflections to fix the origin and enantiomorph (Hauptman & Karle, 1956; Karle & Hauptman, 1956). The hazards of this approach have been pointed out by Oh & Maslen (1968) and by Germain & Woolfson (1968).

We have utilized a modification of a procedure described by Germain & Woolfson (1968) in which, following assignment of phases to fix the origin, additional initial phases for use in the tangent formula are specified by a permutation technique. Rather than use a maximum of four possible phases per starting reflection, we preferred to use six, thus allowing a more accurate calculation of phases in the initial stages when few reflections are involved. A two-stage procedure is followed in which phases determined for a limited number of reflections with the highest E's (stage 1) are subsequently used to calculate remaining phases (stage 2).

Each possible phase combination for the starting reflections is used to calculate phases for a limited number of reflections. Normally six cycles of the tangent formula were performed. Following each cycle an increasing percentage of the most reliable new phases determined are incorporated as input for the next cycle (*e.g.* 40, 60, 75, 85 %). In accordance with the criterion of Germain & Woolfson the best determined phases are considered as those with the highest values of

$$z_{\mathbf{h}}=[\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\sin(\theta_{\mathbf{k}}+\theta_{\mathbf{h}-\mathbf{k}})]^2+[\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\cos(\theta_{\mathbf{k}}+\theta_{\mathbf{h}-\mathbf{k}})]^2.$$

All phases are accepted for the last two cycles. The initial (non-origin determining) phases are only allowed to vary after three cycles.

Phases of those models with the highest figures of merit $C\ (=\sum_{\mathbf{h}} Z_{\mathbf{h}}$; Germain & Woolfson, 1968), chosen so as to include 10 % of the total number, are then used to calculate the phases of the remaining reflections for each of these models. In this second stage 60 and 80 % of new phases determined are accepted on the first and second cycles respectively, and all phases refined on the following two cycles. At the end of the last iteration of each model the reliability indices

$$R=\frac{\sum_{\mathbf{h}} ||E_{\mathbf{h}}|_{\text{obs}}-|E_{\mathbf{h}\text{calc}}|}{|\sum_{\mathbf{h}} |E_{\mathbf{h}}|_{\text{obs}}} \quad \text{(Karle \& Karle, 1956)}$$

and C are calculated.

Zonal reflections, whose phases are fixed by space-group symmetry, are automatically set equal to the expected value closest to which they are calculated, provided they differ from this value by no more than a threshold amount (set at 70° in the examples below). Those reflections whose phases vary from the expected value by more than the threshold angle are not used in the following cycle to calculate other phases. In the examples below, no zonal reflections were rejected in the final cycle for the correct model.

The structures of tetrolic acid ($C_4O_2H_4$; $P2_1$) and p,p'-dimethylchalcone ($C_{17}O_1H_{16}$; $P2_12_12_1$) have been solved and will be published at a later date.

For tetrolic acid phases were assigned to 3 appropriate reflections to fix the origin. Four other reflections with high E values which entered into many combinations and which were of different parity from each other and from the origin-determining reflections were chosen. One of the reflections was assigned 3 possible phases (30, 90, and 150° – this reflection was chosen to fix the enantiomorph). The other three reflections were each assigned 6 phases (30, 90, 150, 210, 270, and 330°). 648 models were therefore computed. As the molecule is small it was necessary to determine phases for only 90 reflections; therefore the procedure was terminated at the end of the first stage.

Two models with equally high C values each gave a plausible structure, one the enantiomorph of the other. The phase angle of the reflection chosen to fix the enantiomorph was, by chance, close to 0° in one and close to 180° in the enantiomorph. Therefore in choosing possible phases of 30, 90 and 150° for this reflection, both structures were determined by the refinement procedure.

For p,p'-dimethylchalcone, three appropriate origin-determining reflections were chosen, plus a zonal reflection to fix the enantiomorph. Four other reflections were chosen, 3 of them being given 6 possible phases each and the last one 4 phases (45, 135, 225, 315°). 150 phases were determined for each of the 864 models and, in turn, used to generate 400 phases (for the models with highest C values) in the second stage. An E-map computed using the phases of a model with the lowest R value (0·20) yielded the correct

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structure. The C value for this model, although quite high, was not the highest. It therefore seems that the R index is a more reliable criterion than C.

E-maps for both structures were easily interpretable. All atoms were located without any ambiguity.

The tangent program was written in FORTRAN code for a 32 K microsecond computer by the authors of this paper. It is capable of calculating 150 phases for one model (6 cycles) in 40 seconds and 400 phases for one model (4 cycles) in 2·4 minutes.

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Refinement of the crystal structure of phosphorus pentabromide, PBr_5.

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The crystal structure of PBr_5 has been refined from 607 reflexions. The cell dimensions are: $a = 5{\cdot}663 \pm 0{\cdot}003$, $b = 17{\cdot}031 \pm 0{\cdot}005$, $c = 8{\cdot}247 \pm 0{\cdot}005$ Å. The final structure consists of regular tetrahedral PBr_4^+ ions, within the range of error, and Br^- ions. The average P–Br distance is 2·15 Å.

Independent X-ray studies of PBr_5 by Powell & Clark (1940) and van Driel & MacGillavry (1941) showed this compound to be orthorhombic with space group $Pbcm\,(D_{2h}^{11})$. According to these authors the structure consists of irregular tetrahedral PBr_4^+ ions and Br^- ions. The Raman spectrum of PBr_5 showed however that the deformation of the PBr_4^+ group is small. In order to gain more information we refined the structure. The unit-cell dimensions were determined from Cu $K\alpha$ Weissenberg camera photographs, calibrated with Al: $a = 5{\cdot}663 \pm 0{\cdot}003$, $b = 17{\cdot}031 \pm 0{\cdot}005$, $c = 8{\cdot}247 \pm 0{\cdot}005$ Å; the errors are three times the standard deviations. The intensity data for the refinement were collected on a Nonius diffractometer with Cu $K\alpha$ radiation. The 607 reflexions with an intensity greater than the minimum value were used in the least-squares program of Rutten-Keulemans (1966). The final parameters of van Driel & MacGillavry (1941) were used as a starting point. The atomic scattering factors used were those for P, Br and Br^- from *International Tables for X-ray Crystallography* (1962). With isotropic temperature factors the disagreement index R decreased from 38·5 to 23·3 within 5 cycles. Owing to the size of the crystal (0·50 × 0·58 × 0·25 mm) an absorption correction was necessary (Eikelenboom, 1970). The linear absorption coefficient used was $\mu_{\text{Cu }K\alpha} = 328\ \text{cm}^{-1}$. After this absorption correction R reduced to 18·5 in three cycles

Table 1. *Final parameters of the asymmetric unit in fractions of cell edges*

Standard deviations are given in parentheses.

	x	y	z
P	0·036	0·1340	0·2500
	(0·002)	(0·0006)	0
Br(1)	0·2591	0·1274	0·0384
	(0·0006)	(0·0002)	(0·0005)
Br(2)	−0·2093	0·0390	0·2500
	(0·0009)	(0·0003)	0
Br(3)	−0·1564	0·2440	0·2500
	(0·0009)	(0·0003)	0
Br^-	0·603	0·4050	0·2500
	(0·001)	(0·0003)	0

Table 2. *Vibration parameters of the asymmetric unit* ($Å^{-2}$)

Standard deviations are given in parentheses.

$$T = \exp\left[(-h^2a^{*2}U_{11} - k^2b^{*2}U_{22} - l^2c^{*2}U_{33} - hka^*b^*2U_{12} - klb^*c^*2U_{23} - hla^*c^*2U_{13})2\pi^2\right].$$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P	0·0257	0·0141	0·0480	−0·0005	0	0
	(0·0057)	(0·0044)	(0·0066)	(0·0086)		
Br(1)	0·0392	0·0378	0·0512	0·0024	0·0033	0·0022
	(0·0016)	(0·0015)	(0·0019)	(0·0029)	(0·0031)	(0·0033)
Br(2)	0·0371	0·0397	0·0681	−0·0014	0	0
	(0·0026)	(0·0021)	(0·0036)	(0·0041)		
Br(3)	0·0402	0·0258	0·0593	0·0085	0	0
	(0·0024)	(0·0019)	(0·0031)	(0·0041)		
Br^-	0·0357	0·0320	0·0590	0·0157	0	0
	(0·0030)	(0·0026)	(0·0035)	(0·0048)		