Short Communications

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The optimum interval for the minimum residual method of molecular location.

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Is has been proposed by Bhuiya & Stanley (1964) that the position of a molecule whose orientation is known can be determined by calculating the value of the residual as the molecule is moved systematically over the unit cell. In using this method it has been observed that the minimum value of the residual, which should indicate the correct position of the molecule, is very sharp indeed, especially if the model is nearly correct. It is thus necessary to perform the calculation at intervals fine enough to make sure that the minimum is not overlooked. At the same time the calculation should be kept as short as possible.

Suppose the model is correct. Then when the molecule is correctly located the structure factors will be given by

$$F=\sum_j f_j \cos 2\pi \mathbf{r}_j.\mathbf{s}$$

for a centrosymmetric structure. When the molecule is moved, as a whole in, say, the x direction by a small distance $\Delta\mathbf{r}_x$ the structure factors will be given by

$$F'=\sum_j f_j \cos 2\pi(\mathbf{r}_j+\Delta\mathbf{r}_x).\mathbf{s}$$

and the difference between the corresponding structure factor values will be

$$\Delta F=F-F'=2\sum_j f_j \sin 2\pi\left(\mathbf{r}_j+\frac{\Delta\mathbf{r}_x}{2}\right).\mathbf{s} \sin \pi\Delta\mathbf{r}_x.\mathbf{s}\ .$$

Assuming that the number of F values which change sign as a result of the movement is small then

$$|F|-|F'|\simeq|\Delta F|\simeq 2\left|\sum_j f_j \sin 2\pi\left(\mathbf{r}_j+\frac{\Delta\mathbf{r}_x}{2}\right).\mathbf{s} \sin \pi\Delta\mathbf{r}_x.\mathbf{s}\right|$$

and the residual (R),

$$\frac{|\overline{\Delta F}|}{|\overline{F}|}=2\frac{\left|\sum_j f_j \sin\left(\mathbf{r}_j+\frac{\Delta\mathbf{r}_x}{2}\right).\mathbf{s} \sin \pi\Delta\mathbf{r}_x.\mathbf{s}\right|}{|\sum_j f_j \cos 2\pi\mathbf{r}_j.\mathbf{s}|}\ .$$

The first term in the numerator and the denominator has the same mean value $\sqrt{(2\Sigma/\pi)}$ where $\Sigma=\sum_j f_j^2$ (Wilson, 1949).

$$\therefore\ R=2\overline{\sin \pi\Delta\mathbf{r}_x.\mathbf{s}}\ .$$

The value of R will depend on whether one-, two-, or three-dimensional data are being considered.

(*a*) *One dimension.* The average value of $2\sin\pi\Delta\mathbf{r}_x.\mathbf{s}$ is required along a line in reciprocal space of length s_{max} parallel to the displacement in real space.

$$\therefore\ R_1=\frac{2}{s_{max}}\int_0^{s_{max}} \sin \pi\Delta\mathbf{r}_x.\mathbf{s}.d\mathbf{s}$$

$$=\frac{2}{\pi\Delta r_x s_{max}}(1-\cos \pi\Delta r_x.s_{max})$$

If we put

$$\pi\Delta r_x s_{max}=z$$

then

$$R_1=\frac{2}{z}(1-\cos z)$$

(*b*) *Two dimensions.* The average value of $2\sin\pi\Delta\mathbf{r}_x.\mathbf{s}$ is required over the area of a circle of radius s_{max}.

$$R_2=\frac{2}{\pi s_{max}^2}\int_0^{\pi/2} 4s_{max}^2 \sin(\pi\Delta r_x s_{max}\cos\theta)\sin^2\theta d\theta\ .$$

This integral can be written in terms of the Struve functions $H_1(z)$ (Watson, 1922):

$$R_2=\frac{8}{\pi}\frac{\sqrt{(\pi)}\Gamma(1{\cdot}5)}{\pi\Delta r_x s_{max}}H_1(\pi\Delta r_x\, s_{max})=\frac{4}{z}H_1(z)\ .$$

(*c*) *Three dimensions.* The average value of $2\sin\pi\Delta\mathbf{r}_x.\mathbf{s}$ is required over the volume of a sphere of radius s_{max}.

$$R_3=\frac{2}{\frac{4}{3}\pi s_{max}^3}\int_0^{\pi/2} 2\pi s_{max}^3 \sin(\pi\Delta r_x s_{max}\cos\theta)\sin^3\theta d\theta\ .$$

This integral can also be expressed in terms of the Struve function $H_{3/2}(z)$.

$$\therefore R_3=\frac{3\sqrt{(\pi)}\Gamma(2)}{\left(\frac{\pi\Delta r_x s_{max}}{2}\right)^{3/2}}H_{3/2}(\pi\Delta r_x s_{max})=\frac{3\sqrt{(2\pi)}}{z^{3/2}}H_{3/2}(z)$$

The numerical values of R

One dimension:

$$R_1=\frac{2}{z}(1-\cos z)\ .$$

Provided Z is small,

$$R_1\simeq\frac{2}{z}\left(\frac{z^2}{2}+\ldots..\right)=z$$

Two dimensions:

$$R_2=\frac{4}{z}H_1(z)$$

$$\simeq\frac{4}{z}\frac{2}{\pi}\left(\frac{z^2}{3}+\ldots..\right)$$

$$=\frac{8}{3\pi}z$$

$$=0{\cdot}85\ z$$

Three dimensions: Struve functions of odd half integral order can be written in terms of more common functions

$$H_{3/2}=\left(\frac{z}{2\pi}\right)^{1/2}\left(1+\frac{2}{z^2}\right)-\left(\frac{2}{\pi z}\right)^{1/2}\left(\sin z+\frac{\cos z}{z}\right)$$

$$\therefore R_3=\frac{3\sqrt{(2\pi)}}{z^{3/2}}\left\{\left(\frac{z}{2\pi}\right)^{1/2}\left(1+\frac{2}{z^2}\right)-\left(\frac{2}{\pi z}\right)^{1/2}\left(\sin z+\frac{\cos z}{z}\right)\right\}$$

$$=3\left\{\frac{1}{z}\left(1+\frac{2}{z^2}\right)-\frac{2}{z^2}\left(\sin z-\frac{\cos z}{z}\right)\right\}$$

$$=3\left\{\frac{1}{z}+\frac{2}{z^3}-\frac{2}{z^2}\left(z-\frac{z^3}{6}+\ldots\ldots+\frac{1}{z}-\frac{z}{2}+\frac{z^3}{24}-\ldots\right)\right\}\simeq\tfrac{3}{4}z.$$

These values are so nearly the same that it is reasonable to say

$$R\simeq z=\pi\Delta r_x s_{\max}.$$

Since only low order reflexions would normally be used a value of $s_{\max}\sim 0{\cdot}5$ would be reasonable; and since, in a centrosymmetric structure the value of R for a randomly wrong structure is 0·828 (Wilson, 1949) it would be reasonable to take $\sim\frac{1}{4}$ of this value as the maximum change to the tolerated within the interval of calculation.

$$i.e.\qquad R=0{\cdot}20=\pi\Delta r_x s_{\max}$$

$$\Delta r_x=\frac{0{\cdot}2}{\pi s_{\max}}\simeq 0{\cdot}07/s_{\max}$$

If $s_{\max}$ is taken as 0·5 then $\Delta r_x\sim 0{\cdot}13$ Å.

This means that an 8 Å cell edge should bedivided into 60ths which is a much finer interval than might at first be expected at this stage of the crystal structure determiation.

References

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Crystallographic data for some cyclobutene derivatives.

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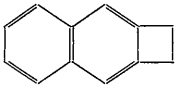
Naphtho[b]cyclobutene: (I) (Cava & Shirley, 1960)

Colourless plates with (100) developed; twinning on (100) is common.



I

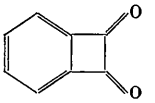
$C_{12}H_{10}$; $M=154{\cdot}2$; m.p. 84·5–86 °C. *Monoclinic*,

$a=18{\cdot}04\pm0{\cdot}02$, $b=5{\cdot}91\pm0{\cdot}01$,
$c=8{\cdot}13\pm0{\cdot}01$ Å; $\beta=92$ °0′ ± 6′.
$U=866{\cdot}3$ Å^3. $D_m=1{\cdot}19$, $Z=4$, $D_x=1{\cdot}18$ g.cm^{-3}.

$F(000)=328$. Absent spectra: hkl when $h+k$ is odd, $h0l$ when l is odd. Space group Cc ($C2/c$ being excluded since it requires the twofold symmetry axis of the molecule (of length ~ 6 Å) to be parallel to b).

Benzocyclobutadienoquinone: (II) (Cava & Napier, 1957)

Yellow prisms bounded by {100}, with {110} also developed.



II

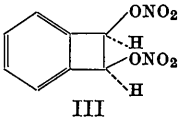
$C_6H_4(CO)_2$; $M=132.1$; m.p. 132·5 °C. *Orthorhombic*,

$a=10{\cdot}72\pm0{\cdot}01$, $b=7{\cdot}94\pm0{\cdot}01$,
$c=7{\cdot}15\pm0{\cdot}01$ Å. $U=608{\cdot}6$ Å^3.
$D_m=1{\cdot}45$, $Z=4$, $D_x=1{\cdot}44$ g.cm^{-3}. $F(000)=272$.

Absent spectra: $h0l$ when h is odd, $0kl$ when l is odd. Space group is $Pca2_1$ or $Pcam$.

cis-1,2-*Benzocyclobutenediol dinitrate*: (III) (Cava & Napier, 1957)

Colourless prisms elongated along a, with (010) and (001) developed.



III

$C_6H_4(CHONO_2)_2$; $M=226{\cdot}1$; m.p. 110 °C. *Monoclinic*,

$a=7{\cdot}41\pm0{\cdot}01$, $b=15{\cdot}71\pm0{\cdot}02$,
$c=8{\cdot}14\pm0{\cdot}01$ Å; $\beta=98$ °2′ ± 5′.
$U=938{\cdot}3$ Å^3. $D_m=1{\cdot}57$, $Z=4$, $D_x=1{\cdot}60$ g.cm^{-3}.

$F(000)=464$. Absent spectra: $h0l$ when $h+l$ is odd, $0k0$ when k is odd. Space group is $P2_1/n$.

No further work on these compounds is planned. The authors are indebted to Dr M. P. Cava for the crystal samples, and to the National Research Council of Canada for financial support and for the award of a studentship (to T.C.W.M.).

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