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References

GEISE, H. J., ROMERS, C. & RUTTEN, E. W. M. (1966). *Acta Cryst.* **20**, 249.

GROTH, P. & HASSEL, O. (1962). *Acta Chem. Scand.* **16**, 2311.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

RUTTEN-KEULEMANS, E. W. M. (1966), *Acta Cryst.* **21**, A293.

SECRET, J. H. & BROCKWAY, L. O. (1944). *J. Amer. Chem. Soc.* **66**, 1941.

SMITSKAMP, C. C., OLIE, K. & GERDING, H. (1968). *Z. anorg. allg. Chem.* **359**, (5-6), 318.

Acta Cryst. (1969). **B25**, 977

Least-squares Weighting Schemes for Diffractometer-Collected Data. III. Optimization Process

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The optimization equations of Shoemaker and Hamilton are critically discussed. The equation due to Hamilton is shown to be invalid as an optimizing equation and experimental limits to the use of the Shoemaker equation are discussed.

Recently Shoemaker (1968) has derived equations for the optimization of counting times in computer-controlled X-ray and neutron single-crystal diffractometry and shown that by making certain simplifying assumptions his derivation leads to the equation presented by Hamilton (1967) that the counting time for the j th structure factor, $|F_j|$, is given by

$$t_j \propto (\text{Lp})^{-1} \left| \frac{\partial |F_j|^2}{\partial \xi_i} \right| \frac{1}{|F_j|^3}, \quad (1)$$

where (Lp) is defined in the usual way and not as the reciprocal, as given by Hamilton.

The total time for the complete diffractometer experiment is

$$T = \varphi + \sum_i t_j \quad (2)$$

where φ is the total time required for setting the circles of the diffractometer. It is claimed that the use of (1) leads to a minimizing of the variances of the ξ_i . The importance of this claim is such that it requires careful investigation.

Let I_j be the integrated peak counts. Then

$$|F_j|^2 = \frac{KI_j}{\text{Lp } t_j}$$

and, following Hamilton, assuming a negligible background count

$$\sigma_1\{|F_j|\} = \frac{|F_j|}{2I_j^{1/2}}$$

where $\sigma_1\{|F_j|\}$ is due to counting statistics alone.

Hamilton also assumes that

$$\sigma_2\{|F_j|\} = C|F_j|$$

is the remaining contribution to the variance of a structure factor. This assumption has been shown to be a good approximation in practice (Grant, Killean & Lawrence, 1969). Consequently the weight of a structure factor is

$$\begin{aligned} \omega_j &= \frac{1}{\sigma_1^2\{|F_j|\} + \sigma_2^2\{|F_j|\}} \\ &= \frac{1}{\left\{ \frac{F_j}{2I_j^{1/2}} \right\}^2 + C^2|F_j|^2} \\ \omega_j &= \frac{1}{|F_j|^2} \cdot \frac{4I_j}{1 + 4C^2I_j}. \end{aligned} \quad (3)$$

Minimizing the variance of ξ_i subject to the linear constraint of equation (2) leads to (1) provided the approximation

$$4C^2I_j \gg 1 \quad (4)$$

is made. Under this condition equation (3) reduces to

$$\omega_j = \frac{1}{C^2|F_j|^2} = \frac{1}{\sigma_2^2\{|F_j|\}}$$

and no optimization of counting time with respect to minimizing the variance of ξ_i exists. If inequality (4) is true then the variance of the structure factor is only

given a very small perturbation with variation of counting time and any optimization produced by the use of (1) will be minimal. Table 1 gives the limiting values of I_j for various values of C .

Table 1. Limiting values of I_j for various values of C

C	0.10	0.08	0.06	0.04	0.02	0.01
$10^4 C^2$	100	64	36	16	4	1
I_j	25	39	69	156	625	2500

It is of interest to compute the order of magnitude of I_j in inequality (4). The G index for a structure is defined as

$$G^2 = \frac{\sum_j \{|F_{0,j}| - |F_{C,j}|\}^2}{\sum_j |F_{0,j}|^2}$$

which, assuming normal distribution with the variance of $|F_{0,j}|$ as

$$\begin{aligned} \sigma^2\{|F_{0,j}|\} &= \sigma_1^2\{|F_{0,j}|\} + \sigma_2^2\{|F_{0,j}|\} \\ &\doteq \sigma_2^2\{|F_{0,j}|\} \text{ if } \sigma_1^2\{|F_{0,j}|\} \ll \sigma_2^2\{|F_{0,j}|\}, \end{aligned}$$

leads to

$$G^2 = C^2$$

or

$$G = C.$$

The G index and R index are numerically very similar and for a completed structure, using high values of I_j , might be of the order of 0.04.

It follows for this case that the analysis of Shoemaker (1968) is important for counts of less than about 150, if negligible background counts are assumed. If the background counts are not negligible then it is easy to compute the effect on I_j . However, it should be noted that there is something suspect in limiting the counts in order to minimize the variances of the parameters. It would be better virtually to eliminate the $\sigma_1^2\{|F_{0,j}|\}$ term by increasing the counts, particularly as with $I_j = 150$ most of the time on the X-ray diffractometer would be spent setting the circles rather than measuring reflexions. This might not be so for a neutron diffractometer. It is extremely unlikely, however, that the optimization process described by Shoemaker will have any use in X-ray diffractometry aimed at normal stereochemical work ($R \approx 0.05$, $I \approx 150$), but may well be of practical use when it is possible to obtain diffractometers and crystals capable of producing much lower reliability indices ($R \approx 0.01$, $I \approx 2500$).

References

- GRANT, D. F., KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* B25, 374.
 HAMILTON, W. C. (1967). Abstract E6, ACA Summer Meeting, Minneapolis, Minnesota, U.S.A.
 SHOEMAKER, D. P. (1968). *Acta Cryst.* A24, 136.

Acta Cryst. (1969). B25, 978

The Crystal Structure of Benzo[1,2:4,5]dicyclobutene

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The structure of benzo[1,2:4,5]dicyclobutene, $C_{10}H_6$, has been determined by interpretation of the Patterson projections and refined by least-squares techniques in three dimensions. The molecule is planar and the benzene ring has been distorted from its usual geometry.

Introduction

The chemical structure of benzo[1,2:4,5]dicyclobutene is shown in Fig. 1. The benzenoid system must be highly strained as a result of fusion on opposite sides to cyclobutene rings and this strain is clearly manifested in its ultraviolet spectrum which shows both bathochromic shift and greatly enhanced extinction relative to its open analogue durene (Cava, Deana & Muth, 1960). An X-ray crystallographic investigation was undertaken to give a detailed picture of the type of strain present in the molecule.

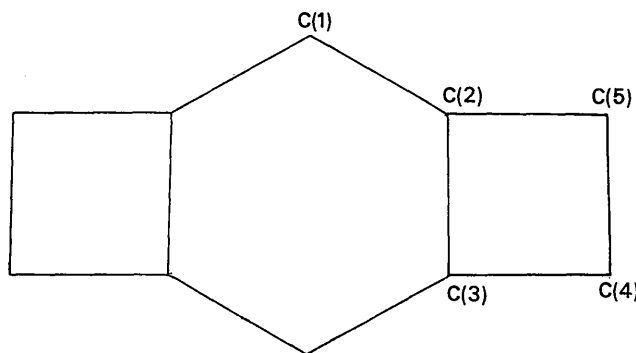


Fig. 1. The chemical structure of benzo[1,2:4,5]dicyclobutene showing the numbering of the atoms.

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