Errors in bond angles. By S. F. DARLOW, *Physics Department, College of Science and Technology, Manchester 1, England*

Whilst calculating the standard deviations for the bond angles in mellitic acid (Darlow, 1960), it was realized that the formula given by Ahmed & Cruickshank (1953) is incorrect. They give (eq. (4·4) in their paper)

$$\sigma^2(\theta) = (1/lm \sin \theta)^2$$
$$\times [(x_2 - x_3)^2\sigma^2(x_1) + (x_1 - 2x_2 + x_3)^2\sigma^2(x_2) + (x_2 - x_1)^2\sigma^2(x_3)$$
$$+ \text{similar terms in } y \text{ and } z], \qquad (1)$$

where θ is the angle subtended at atom 2 by the bonds (lengths l and m) from atoms 1 and 3, and x, y, z are coordinates referred to orthogonal axes. The derivation of the new result is given below.

Let the bond between atom 2 and atom 1 have length l_1 and direction cosines $\cos\alpha_1$, $\cos\beta_1$, $\cos\gamma_1$, and the bond between atom 2 and atom 3 have length l_3 and direction cosines $\cos\alpha_3$, $\cos\beta_3$, $\cos\gamma_3$.

Then

$$\cos\theta = \cos\alpha_1 \cos\alpha_3 + \cos\beta_1 \cos\beta_3 + \cos\gamma_1 \cos\gamma_3, \qquad (2)$$

where

$$\cos\alpha_1 = (x_2 - x_1)/l_1, \quad \cos\alpha_3 = (x_2 - x_3)/l_3, \qquad (3)$$

with similar expressions for the other direction cosines, and

$$l_1^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \Big\}$$
$$l_3^2 = (x_2 - x_3)^2 + (y_2 - y_3)^2 + (z_2 - z_3)^2 \Big\} . \qquad (4)$$

Differentiating (2), and using (3) and (4) to eliminate dl_1 and dl_3 terms, leads to

$$d\theta = (1/l_1l_3 \sin\theta) \begin{bmatrix} l_3 (\cos\alpha_3 - \cos\theta\cos\alpha_1)dx_1 \\ -\{l_3 (\cos\alpha_3 - \cos\theta\cos\alpha_1) \\ +l_1 (\cos\alpha_1 - \cos\theta\cos\alpha_3)\}dx_2 \\ +l_1 (\cos\alpha_1 - \cos\theta\cos\alpha_3)dx_3 \\ +\text{similar terms for } y, z \end{bmatrix} . \qquad (5)$$

If the atomic coordinates are independent, this may be put in terms of standard deviations as

$$\sigma^2(\theta) = (1/l_1l_3 \sin\theta)^2$$
$$\times \begin{bmatrix} A_3^2\sigma^2(x_1) + (A_1 + A_3)^2\sigma^2(x_2) + A_1^2\sigma^2(x_3) \\ + \text{ similar terms in } y \text{ and } z \end{bmatrix}, \qquad (6)$$

where

$$\begin{aligned} A_1 &= l_1 (\cos\alpha_1 - \cos\theta\cos\alpha_3) \\ A_3 &= l_3 (\cos\alpha_3 - \cos\theta\cos\alpha_1) \\ B_1 &= l_1 (\cos\beta_1 - \cos\theta\cos\beta_3) \\ &\quad\text{etc.} \end{aligned} \Bigg\} . \qquad (7)$$

Alternatively, (7) may be written as

$$\begin{aligned} A_1 &= (x_2 - x_1) - (l_1/l_3) \cos\theta \ (x_2 - x_3) \\ A_3 &= (x_2 - x_3) - (l_3/l_1) \cos\theta \ (x_2 - x_1) \\ B_1 &= (y_2 - y_1) - (l_1/l_3) \cos\theta \ (y_2 - y_3) \\ &\quad\text{etc.} \end{aligned} \Bigg\} . \qquad (8)$$

Ahmed & Cruickshank's equation ((1) in this note) does not include the $\cos\theta$ terms in (7) or (8), which is equivalent to omitting the dl_1 and dl_3 terms in the differentiation, and results in too small a value for $\sigma(\theta)$. In the case of mellitic acid, with values of θ around 120°, (6) gave an increase of about 8% in $\sigma(\theta)$ compared with (1).

The main difference between the two formulae occurs, however, when some of the coordinates are either fixed by symmetry or are not independent. In the latter case the factors in (5) multiplying the differentials which are not independent of each other must be grouped together before squaring in (6). When some of the coordinates are fixed by symmetry, as for instance when one of the bonds lies along a symmetry axis, (1) gives an expression of the wrong form completely.

The formula of Ahmed & Cruickshank is in fact inconsistent with the formula

$$\sigma^2(\beta) = \frac{\sigma^2(A)}{AB^2} + \sigma^2(B)\left(\frac{1}{AB^2} - \frac{2\cos\beta}{AB \cdot BC} + \frac{1}{BC^2}\right) + \frac{\sigma^2(C)}{BC^2} \qquad (9)$$

given by Cruickshank & Robertson (1953, eq. (5·4)) and by Cruickshank in the *International Tables*, Vol. II (p. 331, eq. (17)). In (9), β, A, B, C, AB, BC correspond to θ, 1, 2, 3, l_1, l_3, respectively, $\sigma(A)$ and $\sigma(C)$ are the standard deviations of A and C in directions at right angles to AB and BC respectively (and in the plane ABC), and $\sigma(B)$ is the standard deviation of B in the direction of the centre of the circle passing through A, B, and C. It can be shown that (6) and (9) are equivalent. The proof will not be given, but may be obtained from the author.

Dr. Cruickshank (private communication) has observed that with isotropic standard deviations for each atom, both (6) and (9) reduce to the simple form

$$\sigma^2(\theta) = \frac{\sigma^2(1)}{l_1^2} + \frac{l_{13}^2}{l_1^2 l_3^2}\sigma^2(2) + \frac{\sigma^2(3)}{l_3^2}, \qquad (10)$$

where $\sigma(1)$, $\sigma(2)$, and $\sigma(3)$ are the standard deviations of any coordinate for atoms 1, 2 and 3, and l_{12} is the distance between atoms 1 and 3.

For actual calculation, (10) seems the simplest formula to use in the isotropic case, with (6) the easiest in the anisotropic case. It must be remembered that x, y, z refer to orthogonal axes.

The author wishes to thank Dr Cruickshank for his helpful comments.

References

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