CRYSTALLOGRAPHY

Electron Density in Long Carbon-Carbon Bonds

THE crystal structures of ammonium oxamate and lithium oxalate have been studied by X-ray diffraction methods. Three-dimensional intensity data were collected with a xenon-filled proportional counter using copper $K\alpha$ -radiation. Refinement of the three positional and six anisotropic vibrational parameters for each atom, including hydrogen, was carried out by the method of least squares; convergence occurred at $R = 0.044$ for ammonium oxamate and $R = 0.060$ for lithium oxalate. At this stage, three-dimensional $F_o - F_c$ Fourier syntheses were computed. These are shown in the form of superimposed sections in Figs. 1a and b. Contours are drawn at intervals of 3σ , where σ is the root mean square deviation of electron density averaged over the whole unit cell.

In each case an approximately spherical region of electron density, of height greater than 9σ , is found at the centre of the carbon-carbon bond; no other peaks higher than 4.5σ or regions lower than minus 5σ are present. Although in the case of lithium oxalate the peak lies on a centre of symmetry, the two determinations together provide strong evidence that a significant region of electron density exists at the centre of these carbon-carbon bonds.

The atomic scattering factors of Berghuis *et al.*¹, which were used (modified for anisotropic vibrations) in the calculation of the structure factors, are apparently insufficient to describe exactly the electron density around the carbon atoms, although the valence state of the atom is considered. An exact fit of the electron density along the bond would be expected only if account were taken of the directional nature of the molecular orbital produced by the combination of the atomic orbitals.

In an attempt to remedy the discrepancy empirically, a correction was included, in the form of a fraction of a hydrogen atom placed at the mid-point of the carbon-carbon bond. The fractions of McWeeny's scattering factor for hydrogen² which were used were one-half for ammonium oxamate (an underestimate because it proved insufficient to account for the whole of the electron density peak) and two-thirds in the case of lithium oxalate. Vibrational parameters were also applied to allow for the anisotropic rigid body motion of the ions. The R factors decreased to 0.043 and 0.057, with corresponding slight improvements in the estimated standard deviations of the atomic co-ordinates.

The lengths of the carbon-carbon bonds found in these structures are considerably greater than the longest value (1.517 Å) which has been postulated³ for a single bond between trigonally hybridized carbon atoms. The lengths of the carbon-carbon bonds in Å, corrected for vibrational motion, before and after allowance for the electron density at the centre of the bond are as follows:

	Ammonium oxamate	Lithium oxalate
Before allowance for electron density in bond	1.561 ± 0.002	1.561 ± 0.004
After allowance for electron density in bond	1.564 ± 0.002	1.561 ± 0.004

Although the bond electron density correction did not affect the bond-length in the case of lithium oxalate, a change occurred in the orientation of the vibration ellipsoid. These results indicate, as would be expected, that the parameters of the neighbouring atoms tend to 'assimilate' the electron density in the bond during the least squares refinement.

The tendency of the atomic parameters to 'assimilate' interatomic electron density will be greater if the atoms are closer together, particularly if the experimental struc-

Fig. 1. $F_o - F_c$ syntheses. (a) ammonium oxamate; (b) lithium oxalate. Zero contours omitted, negative contours dotted

ture factor data are deficient in terms of sufficiently short spacing to give effective resolution. Long bonds between atoms of comparatively low scattering power are therefore favourable situations in which to observe interatomic electrons.

B. BEAGLEY
R. W. H. SMALL

Department of Chemistry,
University of Birmingham.

¹ Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H., and Veenendaal, A. L., *Acta Cryst.*, **8**, 478 (1955).

² McWeeny, R., *Acta Cryst.*, **4**, 513 (1951).

³ Coulson, C. A., and Skancke, P. N., *J. Chem. Soc.*, 2775 (1962).

Crystal Structure of Sinigrin

SINIGRIN is a crystalline thioglucoside, extracted first by Bussy¹ from the seeds of black mustard. It is the potassium salt of the anion $[C_{10}H_{16}O_9NS_2]^-$, also called the myronate ion, and the crystals contain one molecule of water per potassium ion. In 1897 Gadamer² proposed formula (I) for the myronate ion. Schneider and collaborators confirmed the thioglucoside linkage in 1914 (ref. 3) and in 1930 (ref. 4) established that sinigrin and analogous glucosides are 1-β-D-thio-glucosides. Important details of the Gadamer formula I were challenged recently by