thermal motion or strong hydrogen bonding, a lesser degree of refinement is to be expected.

Thanks are due to the Atlas Computer Laboratory, Chilton, near Didcot, Berkshire, England for the use of the ATLAS computer and to the staff of the computing laboratory at the University of Western Australia for advice on computational problems. The receipt of a Nuffield Foundation Travelling Fellowship is very gratefully acknowledged.

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A Phase Refinement of the Crystal Structure of Benzotrifuroxan

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The structure-factor phases for benzotrifuroxan have been refined by a procedure which takes advantage of the molecular but non-crystallographic symmetry. The difference synthesis calculated with the refined phases has been interpreted in terms of the distribution of bonding electrons combined with the effects of disorder in the structure.

The crystal structure of benzotrifuroxan was determined by Cady, Larson & Cromer (1966). The analysis was accurate enough to justify an examination of the final difference synthesis for bonding-electron effects, were it not for the phase errors resulting from the use of isolated atom form factors and the non-centrosymmetric space group of the structure. The structure is closely related to that of 1,3,5-triamino-2,4,6-trinitrobenzene, for which the electron-density distribution has been studied by Cady & Larson (1965) and more closely by O'Connell, Rae & Maslen (1966).

The free benzotrifuroxan molecule contains one threefold axis and a mirror plane of symmetry which are not utilized by the space group of the crystal structure. For the reasons given in the preceding paper (Maslen, 1967*a*) it is expected that the $3/m$ symmetry of the free molecule will be preserved quite closely in the crystal, and if this is valid the structure factor phases may be further refined after the normal refinement has been terminated. The refined phases are then reasonably independent of the theoretical model used to evaluate the atomic form factors, and the systematic nature of the errors in a phase calculation based on an approximate model is destroyed. The examination of the difference synthesis for bonding-electron effects is then justified if the electron-density standard deviation is sufficiently low. In the structural data given by Cady, Larson & Cromer there are no significant differences between chemically equivalent bond lengths and angles. The molecule is also essentially planar although there are some significant deviations from the least-squares mean plane, the largest being 0·096 Å. The method has been shown to be insensitive to small departures from exact symmetry, and since the r.m.s. deviation from planarity (0·049 Å) is less than one tenth of the resolution the phase refinement method should give a satisfactory first order correction to the structure factor phases.

The data of Cady, Larson & Cromer were refined by using the procedure described in the preceding paper. The progress of the refinement is given in Table 1. Sections of the difference density and averaged difference density in the molecular plane at the start and the conclusion of the refinement are shown in Fig. 1(*a*), (*b*), (*c*) and (*d*). The numbering of the atoms in the molecule is given in Fig. 1(*e*).

Table 1. *Refinement progress**

Cycle number	$\frac{\sum^{N} \lvert F_{no}-F'\rvert}{\sum^{N} F_n^{\circ}}$	$\frac{\sum^{N} \lvert \mathbf{F}_n^{o}-\mathbf{F}_{nc}\rvert}{\sum^{N} F_n^{\circ}}$	$\sigma_1(\varrho)$ (e.Å^{-3})	$\sigma_2(\varrho)$ (e.Å^{-3})
0	—	0·0375	0·036	0·068
1	0·0279	0·0412	0·034	0·048
2	0·0271	0·0461	0·034	0·046
3	0·0278	0·0498	—	0·046

* Symbols are defined as in Maslen (1968*a*).

The standard deviation in the refined electron-difference density, estimated as described in the following paper (Maslen, 1968*b*), is 0·046 e.Å^{-3}. The standard deviations in the averaged difference density in and

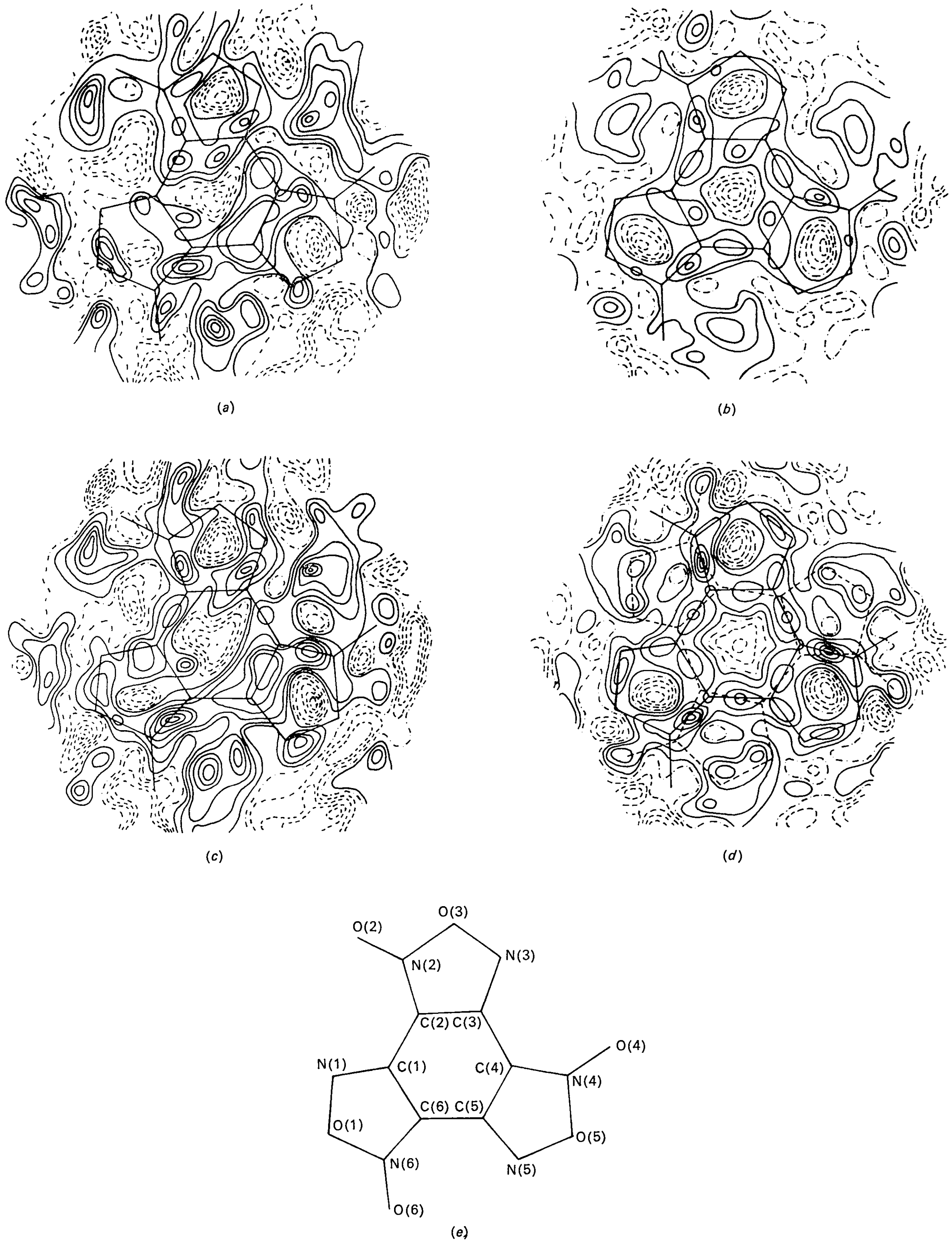

Fig. 1. (*a*) Section through the molecular plane in the difference synthesis prior to refinement. (*b*) Section of the averaged synthesis corresponding to (*a*). (*c*) Section through the molecular plane in the difference synthesis after refinement. (*d*) Section of the averaged synthesis corresponding to (*c*) showing (dotted) the orientation of disordered molecules which appear to contribute to the difference synthesis. Contour interval 0·02 e.Å^{-3}. (*e*) Numbering of atoms in the molecule.

away from the molecular plane are 0·027 and 0·020 e.Å^{-3} respectively. A search for bonding-electron effects, which may be of the order of 0·1 e.Å^{-3}, was thus amply justified.

Within the framework of the molecule the most significant peaks are at the bond centres, and are distributed roughly as expected from the work of O'Connell, Rae & Maslen (1966). However, the resolution is not as good, and the maximum densities, with the possible exception of the C(2)–N(2) bond, are not quite as high as expected for a well ordered structure. Outside the molecular framework there are significant features between the substituent oxygen O(2) and the nitrogen with two bonds N(1), and another significant peak on the other side of O(2) at the same radial distance as O(2) from the ring centre. It is readily seen that all the significant peaks can be generated by arranging the molecule with the central ring in very nearly the same orientation, but with the molecule as a whole having either opposite sense, and/or an orientation corresponding to a rotation of 60° about the threefold molecular axis. There are no significant features of the synthesis which cannot be explained on this basis, and one must conclude that, notwithstanding the low final R value of 4·0%, the structure is disordered. The amount of disorder is small, but is sufficient to preclude a detailed examination of the effects of the bonding electrons in the structure. It is to be expected that this disorder will have resulted in incorrect thermal parameters, especially for the outer atoms. It had already been noted by Cady, Larson & Cromer (1966) that the thermal parameters are not consistent with a rigid body model for the structure. This was attributed by these authors to flexibility in the furoxan rings, but in the light of the evidence from the difference map the effect of disorder provides a more probable explanation for this inconsistency.

The author wishes to express his thanks to Dr H. H. Cady and the Los Alamos Scientific Laboratories for providing the data for this analysis. Thanks are also due to the Atlas Computer Laboratory, Chilton, near Didcot, Berkshire, England for the use of the ATLAS computer, and to the staff of the Computing Laboratory at the University of Western Australia for advice on computational problems. The receipt of a Nuffield Foundation Travelling Fellowship is very gratefully acknowledged.

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On the Accuracy of Electron-Density Distributions with Particular Reference to Structures with Non-Crystallographic Molecular Symmetry

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The effects of scale and phase angle errors on the accuracy of electron-density distributions are discussed. It is shown that scale factor errors may result in errors in the electron density at the atomic centres which are several times the standard deviations calculated by the normal method. The phase errors have a systematic effect on the difference density, which makes a quantitative analysis of the electron distribution impossible unless the structure is either centrosymmetric or phase-refined.

Introduction

Cruickshank (1949*a*,*b*; 1950*a*,*b*) has derived expressions for the standard deviation of the structural parameters and the electron-density distributions in crystal-structure analysis. In a more recent paper Cruickshank (1960) has used these expressions to determine the conditions necessary to attain certain desirable levels of precision in crystal-structure analysis. The standard deviations are related primarily to errors in the observed structure factors F_o. It is assumed that these errors are random, or may be treated as random for the parameter in question. In general this assumption appears to be satisfactory, although it has been shown on a number of occasions (*e.g.* O'Connell & Maslen, 1967) that the effects of systematic error may in some cases be considerably greater than those of random errors of similar magnitude. This has led some workers (*e.g.* Hamilton, 1965) to suggest the application of a correction factor to the calculated standard deviations in assessing their significance. The correction factor appears to be somewhat arbitrary, however, and a more systematic approach to the problem is to be preferred. Systematic errors invalidate the calcula-