Acta Cryst. (1978). A**34**, 481–483

X–N Maps from Room-Temperature Data – a Warning

BY C. SCHERINGER, A. KUTOGLU AND D. MULLEN

Mineralogisches Institut der Universität Marburg, D-3550 Marburg, Federal Republic of Germany

(*Received* 16 *December* 1977; *accepted* 21 *January* 1978)

Inspection of several *X–N* maps from room-temperature data, which were not corrected for thermal diffuse scattering (TDS), shows that often too high maxima at the bonds and too deep minima at the nuclei are found, which do not represent the distribution of the valence density. The cause lies in the fact that the TDS effect is usually larger in the neutron data than in the X-ray data. For tetracyanoethylene and urea the effect of TDS on the neutron data was simulated by a change of the vibration tensors (multiplication by a common factor >1), and the *X–N* maps thus obtained show a more reasonable distribution of the valence density. It is concluded that *X–N* maps should not be calculated from room-temperature data unless both X-ray and neutron data sets are corrected for TDS.

Often *X–N* maps are published which have been calculated from room-temperature data that have not been corrected for thermal diffuse scattering (TDS) (Pryor & Sanger, 1970; Becker, Coppens & Ross, 1973; Stevens & Hope, 1977). Such maps often display high maxima at the bonds and deep minima at the nuclei. Since, normally, the *X–N* map is considered to be a representation of the distribution of the valence electron density, the question arises if such maps describe the valence density distribution appropriately. On the assumption that this is the case, experimentally obtained density distributions which are falsified by systematic errors may be presented to quantum chemists. An example is found in tetracyanoethylene (TCNE). The *X–N* map (Becker *et al.*, 1973) is based on the X-ray data and neutron parameters of these authors. Hase, Schulte & Schweig (1977) have calculated the static density for TCNE with a 4–31 G basis, and made it dynamic with the experimental temperature factors. They find maxima at the bonds of 0·4, 0·3, 0·2 e Å^{-3} for the C≡N, C=C, C–C bonds respectively. These are much lower than those of the *X–N* map, 0·9, 0·4, 0·6 e Å^{-3} respectively. Hase *et al.* reject a possible inaccuracy of their 4–31 G calculation of this order by comparing their results with those of a very accurate calculation for cyanogen. From the results on TCNE Hase *et al.* are led to conclude that the often quoted accuracy of 0·05 e Å^{-3} of the experimentally determined density distributions does not hold in many cases. For TCNE we agree with Hase *et al.*

In this paper we show that the *X–N* maps, calculated from room-temperature data that were not corrected for TDS, as a rule have too high maxima at the bonds and too deep minima at the nuclei. Since for neutron diffractometers the experimental resolution is smaller (larger crystals and beam cross sections) than for X-ray diffractometers, the TDS correction for the neutron data will usually be the larger one (Scheringer, 1973). Since the vibration tensors become smaller the larger the TDS contribution to the Bragg intensities (Göttlicher, 1968; Helmholdt & Vos, 1977), the vibration tensors obtained from the neutron data are usually smaller than those determined from the X-ray data (other sources of error being neglected). This conclusion is in agreement with experience. Some examples are given by Bats (1976), and for NaN_3 by Stevens & Hope (1977). It is the *difference* between the vibration tensors from the two sets of data that leads to a marked systematic error in the *X–N* map. For vibration tensors which are too small, $\rho_c(N)$ has maxima which are too sharp at the nuclei and too little density between the nuclei, so that $\rho_o(X) - \rho_c(N)$ displays the reverse effect. Only if the vibration tensors from the two data sets can be regarded as identical, is the structural contribution to $\rho(X)$ and $\rho(N)$ the same; and the difference $\rho_o(X) - \rho_c(N)$ can then be exclusively attributed to the valence density distribution.

We demonstrate the effect described with TCNE and urea by simulating a TDS correction of the neutron data on to the level of the X-ray data. For TCNE we take the X-ray data and the neutron parameters from Becker *et al.* (1973). The *X–N* map of these authors shows the high maxima already mentioned at the bonds but (for a reason which we do not understand) not the deep minima at the nuclei. We have recalculated the *X–N* map with the 355 observed X-ray data and find agreement in the maxima, as well as the expected deep minima at the nuclei (Fig. 1*a*). For urea accurate X-ray data were collected by Mullen & Hellner (1977), and the parameters of the neutron diffraction analysis were taken from Pryor & Sanger (1970).

In order to simulate the (partial) TDS correction to the neutron data we have multiplied all vibration tensors by a common factor >1. From actual investigations of the TDS effect (Göttlicher, 1968; Helmholdt & Vos, 1977) one would expect the factor to lie between 1·05 and 1·15. For TCNE and urea factors of 1·10 and 1·12 respectively were found by trial and error. For calculating the *X–N* map, the scale factor for the X-ray data was recalculated from the model of the isolated atoms with the neutron parameters, since there is high correlation between the scale factor and the vibration tensors.

For TCNE the factor used was 1·10. With this factor applied to the vibration tensors the scale factor (as factor of F_c) increased from 0·9641 to 0·9948 (*i.e.* by 3·1%), and *R* for the 355 observed X-ray data (based on the model of isolated atoms) dropped from 8·38 to 6·84%. The two *X–N* maps are shown in Figs. 1(*a*) and 1(*b*) respectively. Obviously, in Fig. 1(*b*) the bond peaks are somewhat lowered and the minima at the nuclei largely reduced (to a level of $-0{\cdot}2$ e Å^{-3}). The bond peaks have heights of 0·65, 0·25, 0·52 e Å^{-3} for the C≡N, C=C, C–C bonds respectively, and are in better agreement with those of Hase *et al.* (1977) (0·4, 0·3, 0·2 e Å^{-3}). The disagreement that still exists partly arises from the fact that the 4–31 G calculation produces bond peaks that are too small. The most exact calculation for cyanogen gives a C≡N bond peak of 0·65 e Å^{-3} (dynamic density) which is in full agreement with our peak in Fig. 1(*b*). The theoretical C–C bond peak in cyanogen of 0·4 e Å^{-3} approaches our peak in Fig. 1(*b*) of 0·52 e Å^{-3}, and coincides with

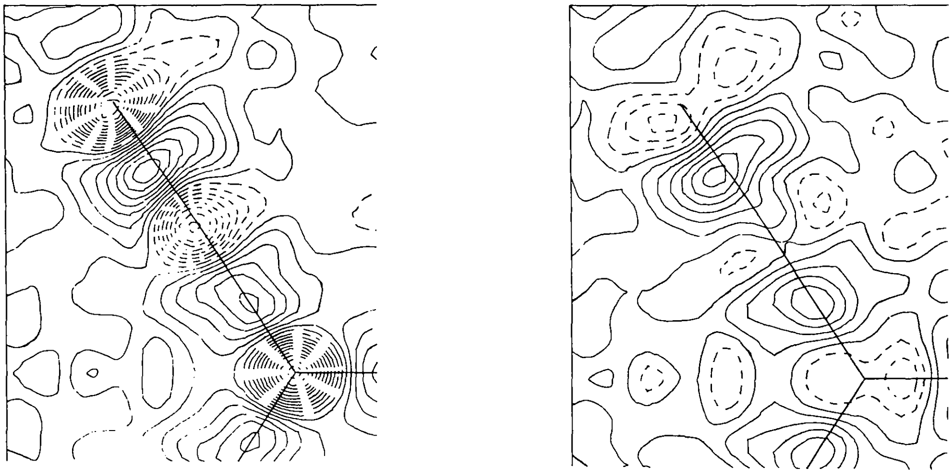
(*a*) (*b*)

Fig. 1. (*a*) *X–N* map for TCNE calculated with Becker, Coppens & Ross's (1973) 355 observed X-ray data and neutron parameters. Scale = 0·9641. (*b*) Like (*a*) with vibration tensors 1·10 **U** for all atoms, and scale = 0·9948. Contour interval: 0·1 e Å^{-3}; positive and zero: full lines, negative: dashed lines.

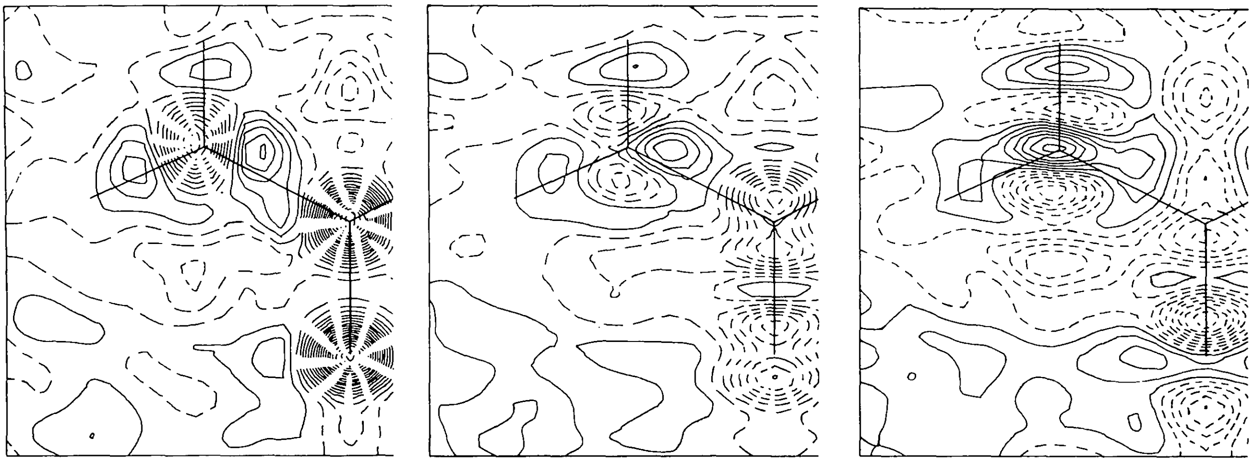
(*a*) (*b*) (*c*)

Fig. 2. (*a*) *X–N* map for urea calculated with 256 observed X-ray data of Mullen & Hellner (1977) and neutron parameters of Pryor & Sanger (1970). Scale = 194·1. (*b*) Like (*a*) with vibration tensors 1·12 **U** for all atoms, and scale = 198·9. (*c*) Low-temperature (123 K) *X–N* map for urea with 288 X-ray data of Mullen & Hellner (1978) and neutron parameters of Heger, Mullen & Treutmann (1977). Contours as in Fig. 1.

it within 3σ. Our C=C bond peak in Fig. 1(*b*) of 0·25 e Å^{-3} also coincides with Hase, Schulte & Schweig's 4–31 G peak of 0·3 e Å^{-3} within 3σ; but it appears that our C=C peak is too low compared to the 0·52 e Å^{-3} peak of the single C–C bond.

For urea the factor used was 1·12. With this factor the scale factor increased from 194·1 to 198·9 (*i.e.* by 2·4%), and *R* for the 256 observed X-ray data dropped from 9·42 to 6·67%. The two *X–N* maps* are shown in Figs. 2(*a*) and 2(*b*) respectively. As with TCNE, the bond peaks are somewhat lowered and the minima at the nuclei largely reduced (Fig. 2*b*). On the other hand, in the C=O bond the zero line appears in Fig. 2(*b*), whereas in Fig. 2(*a*) only a negative density is found which is probably due to the two deep adjacent minima at the nuclei.

By comparison with a low-temperature *X–N* map for urea, where the TDS correction can largely be neglected, it can be shown that the simulated TDS correction yields a reasonable result. X-ray data at 123 K were taken from Mullen & Hellner (1978), and the neutron parameters at 123 K from Heger, Mullen & Treutmann (1977). The 123 K *X–N* map for urea is shown in Fig. 2(*c*). Figs. 2(*b*) and 2(*c*) are in satisfactory agreement.

For the two examples discussed, with room-temperature data, a neglected TDS correction, though only giving rise to errors in the vibration tensors of about 10% and to errors in the scale factor of about 3%, has an effect on the *X–N* maps of the order of 0·5–1·0 e Å^{-3} (errors of 100% and more). This was also found by Helmholdt & Vos (1977) with the example of an oxalate group. In Fig. 3 of these authors the maxima at the nuclei of the C atoms are about 0·8 e Å^{-3} (because of a different definition of this map there are maxima and not minima at the nuclei). As a further example we quote Stevens & Hope's (1977) *X–N* and *X–X*(high-angle data) maps for NaN_3. In the *X–N* map of Stevens & Hope's Fig. 4(*a*), the minima at the nuclei are only black spots so that the contours cannot be distinguished. The *X–X*(high-angle data) map of Stevens & Hope's Fig. 4(*b*), however, shows a more reasonable picture of the valence density distribution in that there are no negative contours at the N nuclei, and only three at the Na nuclei (the contour interval in e Å^{-3} is not given in the paper). Since the high-angle and the full X-ray data were collected from the same crystal, TDS effects largely cancel out and a correction can therefore be neglected.

In contrast to the *X–N* maps, an error in the vibration tensors of 10% only has a small effect ($\pm$0·1 e Å^{-3}) on the dynamic densities obtained from a quantum-chemical static model. The reason is that in calculating the dynamic densities, ρ(molecule) − ρ(isolated atoms), both models are treated with the same temperature factors.

Assuming a constant multiplication factor for all vibration tensors, we have simulated an isotropic TDS correction on the neutron data. In reality the TDS effect will usually be dependent on the direction in reciprocal space. Such anisotropy could also be simulated with the vibration tensors if the anisotropy were known, *e.g.* estimated from the values of the elastic constants. This is usually not the case. However, we do not consider the simulation described as a method for performing the TDS correction, but only as a simple means of demonstrating the effect of neglected TDS correction on the *X–N* maps. We conclude that with room-temperature data, not corrected for TDS, the determination of density distributions is a somewhat hazardous undertaking, and that with low-temperature data for which the TDS correction can largely be neglected, more reliable results can be expected.

References

BATS, J. W. (1976). Thesis, pp. 48–49, Enschede, The Netherlands.

BECKER, P., COPPENS, P. & ROSS, F. K. (1973). *J. Am. Chem. Soc.* **95**, 7604–7609.

GÖTTLICHER, S. (1968). *Acta Cryst.* B**24**, 122–129.

HASE, H. L., SCHULTE, K. W. & SCHWEIG, A. (1977). *Angew. Chem.* **89**, 263–264.

HEGER, G., MULLEN, D. & TREUTMANN, W. (1977). Unpublished.

HELMHOLDT, R. B. & VOS, A. (1977). *Acta Cryst.* A**33**, 38–45.

MULLEN, D. & HELLNER, E. (1977). Unpublished.

MULLEN, D. & HELLNER, E. (1978). *Acta Cryst.* B**34**, 1624–1627.

PRYOR, A. W. & SANGER, P. L. (1970). *Acta Cryst.* A**26**, 543–558.

SCHERINGER, C. (1973). *Acta Cryst.* A**29**, 283–290.

STEVENS, E. D. & HOPE, H. (1977). *Acta Cryst.* A**33**, 723–729.

---

* For urea the *X–N* map is not quite correctly calculated because the phases used for the *X* map were those obtained from the isolated atom model with the *N* parameters. Since urea is not centrosymmetric all phase angles are slightly incorrect. However, this small error in the *X–N* map does not disturb the demonstration of the TDS effect which is much greater.