

The C(6) methylenic group is exposed to the —C(33)—C(32)—N(45)—C(42) moiety and is confirmed as a potentially reactive site, whereas the C(19) methyl groups, belonging to a pair of DCA related by the 2_1 axis, each interact with a different phenyl ring. The outer H atoms of DAB point towards the side chains of DCA and form good contacts with all the atoms except that with the terminal methylenic and carboxyl groups. In this connection we should remember the ability of DCA to change by about 80° the orientation of the guest molecular plane with respect to the *A* rings and to the side chains, as in the case of the phenanthrene and *p*-diiodobenzene choleic acids (Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972) populating the *B* minimum region of Fig. 6. Thus, the most probable candidates as photoaddition sites may become C(15) and C(16).

The Central Services of the CNR Research Area of Rome are thanked for the NMR spectra. Two of the authors (EG and GP) acknowledge financial support from the Consiglio Nazionale delle Ricerche.

References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701–704.
- BROWN, C. J. (1966a). *Acta Cryst.* **21**, 146–152.
- BROWN, C. J. (1966b). *Acta Cryst.* **21**, 153–158.
- CANDELORO DE SANCTIS, M. S. (1982). *Acta Cryst.* In preparation.
- CANDELORO DE SANCTIS, M. S. & GIGLIO, E. (1979). *Acta Cryst.* **B35**, 2650–2655.
- CANDELORO DE SANCTIS, S., GIGLIO, E., PAVEL, V. & QUAGLIATA, C. (1972). *Acta Cryst.* **B28**, 3656–3661.
- CILENTO, G. (1951). *J. Am. Chem. Soc.* **73**, 1355–1357.
- CILENTO, G. (1952). *J. Am. Chem. Soc.* **74**, 968–970.
- COIRO, V. M., D'ANDREA, A. & GIGLIO, E. (1979). *Acta Cryst.* **B35**, 2941–2944.
- COIRO, V. M., D'ANDREA, A. & GIGLIO, E. (1980). *Acta Cryst.* **B36**, 848–852.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- D'ANDREA, A., FEDELI, W., GIGLIO, E., MAZZA, F. & PAVEL, N. V. (1981). *Acta Cryst.* **B37**, 368–372.
- FERRO, D., QUAGLIATA, C., GIGLIO, E. & PIACENTE, V. (1981). *J. Chem. Eng. Data*, **26**, 192–195.
- GIGLIO, E. (1981). *J. Mol. Struct.* **75**, 39–50.
- GIGLIO, E. & QUAGLIATA, C. (1975). *Acta Cryst.* **B31**, 743–746.
- HANSON, A. W. (1973). *Acta Cryst.* **B29**, 454–460.
- HOPE, H. & VICTOR, D. (1969). *Acta Cryst.* **B25**, 1849–1853.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- KUROSAKI, S., KASHINO, S. & HAISA, M. (1976). *Acta Cryst.* **B32**, 3160–3163.
- PAVEL, N. V., QUAGLIATA, C. & SCARCELLI, N. (1976). *Z. Kristallogr.* **144**, 64–75.
- POPOVITZ-BIRO, R., CHANG, H. C., TANG, C. P., SHOCHET, N. R., LAHAV, M. & LEISEROWITZ, L. (1980). *Pure Appl. Chem.* **52**, 2693–2704.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- TANG, C. P. (1979). PhD Thesis, The Feinberg Graduate School, The Weizmann Institute of Science, Rehovot, Israel.

Acta Cryst. (1982). **B38**, 2620–2625

Electron Density Distribution in Thiourea. Comparison with the Urea Molecule

BY D. MULLEN

Fachrichtung Kristallographie, Universität des Saarlandes, D-6600 Saarbrücken, Federal Republic of Germany

(Received 30 January 1981; accepted 21 September 1981)

Abstract

The electron density distribution in thiourea has been refined using a multipolar expansion, and a comparison is made with the urea molecule [Mullen (1980), *Acta Cryst.* **B36**, 1610–1615]. An analysis is made of the errors arising from attributing phases from $F_{c,n}$ to the observed structure amplitudes and the model-dependency of these errors is discussed.

Introduction

Initial work on thiourea has been reported by Mullen & Hellner (1978). X-ray data were measured at 123 K and full experimental details are reported in the above reference.

Previous work on urea has already been reported. Scheringer, Mullen, Hellner, Hase, Schulte & Schweig (1978) have carried out a study of urea in which the

electron density was refined on the basis of a pseudo-atom model. In the same paper, a theoretical charge-density distribution was reported. Mullen (1980) has recently carried out multipole refinements for urea and analysed the errors in the structure factor phases arising from the assumption of spherically symmetric atoms.

An important feature of the present paper is a comparison of the urea and thiourea molecules. Throughout the paper the numbering scheme of Elcombe & Taylor (1968) is used for the two independent thiourea molecules.

Multipole refinement of thiourea

For data given in the present paper an isotropic extinction correction has been carried out using the program *LINEX*. In the paper of Mullen & Hellner (1978) the extinction correction is inadequate because corrections were only applied to the strongest reflections.*

An anomalous-dispersion correction has been included for the S atoms. All scattering factors and the anomalous-dispersion correction have been taken from *International Tables for X-ray Crystallography* (1974). The treatment of the anomalous-dispersion correction for non-centrosymmetric structures in application to charge-density studies has been discussed by Ngo Thong & Schwarzenbach (1979). If the correction is small ($f' = 0.110$, $f'' = 0.129$ for S), averaging the reflections F_{hkl}^2 and $F_{\bar{h}\bar{k}\bar{l}}^2$ leads to a negligibly small imaginary part and the averaged data may be used with application of the real term, f' , of the anomalous-dispersion correction only. This may be checked by model calculations as suggested by Ngo Thong & Schwarzenbach (1979).

The effect on the charge-density distribution of neglecting the anomalous-dispersion correction is discussed in a later section.

A high-order refinement ($\sin \theta/\lambda \geq 0.8 \text{ \AA}^{-1}$) was carried out (van der Wal, de Boer & Vos, 1979). The scale factor was refined using the complete data set, while positional parameters and temperature factors were refined using only the high-order data. In the scale-factor cycles the atomic parameters were kept constant and in the high-order cycles the scale factor was fixed. These cycles were calculated iteratively to convergence.

The multipolar expansion of the charge density in the stationary molecule has been described by Hirshfeld (1971). The refinement for thiourea parallels that for urea (Mullen, 1980).

* The corrected data (structure factors) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36435 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The multipole refinement was carried out with functions up to hexadecapole ($n = 4$) on S, up to octopole ($n = 3$) on C and N, and with rotational symmetry assumed for the H atoms (functions up to $n = 2$). Starting parameters for the multipole refinement came from a high-order refinement for S, C and N ($\sin \theta/\lambda > 0.8 \text{ \AA}^{-1}$), and from the neutron diffraction results of Elcombe & Taylor (1968) for H.

The weighting scheme used was $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o) = \sigma_c^2(F_o) + (0.01F_o)^2$, and $\sigma_c(F_o)$ is the standard deviation from counting statistics.

Agreement factors for conventional, high-order and multipole refinements are summarized in Table 1. Hamilton's (1965) *R*-factor test shows that the multipole refinement with its 63 extra parameters brings a significant improvement at the 0.005 level. Normal probability plots of the residual structure factors ΔF (Abrahams & Keve, 1971) are fairly linear with unit slope.

The $(F_o - F_c)$ maps for the two molecules (Fig. 1*a,b*) are reasonably flat with the highest residual peaks of the order of 0.1 e \AA^{-3} . These occur close to the lone pair on S for molecule 2, but away from regions of bonding density for molecule 1.

Table 1. *Thiourea: agreement factors for refinements*

	Multipole	Spherical atom	
		Full data	High angle ($\sin \theta/\lambda \geq 0.8 \text{ \AA}^{-1}$)
Number of deformation functions	63	—	—
<i>R</i> (%)	1.28	1.82	1.83
<i>R_w</i> (%)	1.46	2.63	1.73
Goodness-of-fit	0.95	1.68	0.71

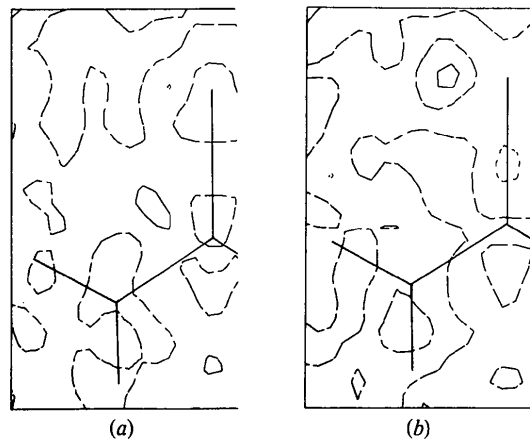


Fig. 1. $(F_o - F_c)$ maps for (a) molecule 1 and (b) molecule 2. Contour intervals are 0.1 e \AA^{-3} . Positive contours solid lines, negative contours dashed, zero contour broken line (long dashes).

Table 2. Comparison of atomic parameters from (a) high-order and (b) multipole refinements (U_{ij} in \AA^2)
$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	a	0.0062 (3)	0.0	0.34557 (7)	0.0245 (2)	0.0147 (1)	0.00983 (9)	0.0	0.0007 (1)	0.0
	b	0.00584 (4)	0.0	0.34567 (4)	0.02458 (9)	0.01454 (7)	0.00975 (6)	0.0	0.00055 (7)	0.0
C(1)	a	0.0740 (3)	0.0	0.0465 (3)	0.0194 (5)	0.0127 (4)	0.0128 (4)	0.0	0.0034 (4)	0.0
	b	0.0734 (1)	0.0	0.0468 (2)	0.0186 (3)	0.0128 (3)	0.0127 (3)	0.0	0.0033 (3)	0.0
N(1)	a	0.1000†	0.1338 (1)	-0.0742 (2)	0.0361 (6)	0.0139 (4)	0.0130 (3)	-0.0006 (3)	0.0089 (4)	0.0007 (3)
	b	0.1000	0.13383 (7)	-0.0739 (1)	0.0357 (3)	0.0141 (2)	0.0162 (2)	-0.0004 (2)	0.0091 (2)	0.0012 (2)
H(1)	*	0.1365	0.1305	-0.2506	0.0687	0.0258	0.0229	-0.0010	0.0195	0.0033
H(2)	*	0.0772	0.2378	0.0052	0.0520	0.0185	0.0301	0.0045	0.0071	-0.0017
S(2)	a	0.0259 (2)	0.5	0.12299 (7)	0.0205 (2)	0.0133 (1)	0.01234 (9)	0.0	0.0010 (1)	0.0
	b	0.02543 (4)	0.5	0.12297 (4)	0.02038 (9)	0.01319 (7)	0.01226 (6)	0.0	0.00107 (7)	0.0
C(2)	a	-0.0978 (3)	0.5	0.3869 (3)	0.0147 (4)	0.0135 (4)	0.0153 (4)	0.0	0.0006 (3)	0.0
	b	-0.0980 (1)	0.5	0.3869 (2)	0.0149 (3)	0.0134 (3)	0.0152 (3)	0.0	0.0018 (3)	0.0
N(2)	a	-0.1473 (3)	0.3659 (1)	0.4919 (3)	0.0258 (4)	0.0145 (3)	0.0228 (4)	-0.0004 (3)	0.0087 (3)	0.0011 (3)
	b	-0.1477 (1)	0.36580 (7)	0.4921 (1)	0.0257 (3)	0.0145 (2)	0.0230 (2)	-0.0001 (2)	0.0091 (2)	0.0016 (2)
H(3)	*	-0.2169	0.3698	0.6506	0.0494	0.0314	0.0287	-0.0029	0.0245	0.0036
H(4)	*	-0.1028	0.2614	0.4271	0.0378	0.0244	0.0329	-0.0016	0.0083	0.0050

* Parameters fixed at neutron diffraction values (Elcombe & Taylor, 1968).

† Parameter fixed to define origin.

A comparison of atomic parameters from high-order ($\sin \theta/\lambda > 0.8 \text{ \AA}^{-1}$) and multipole refinements is given in Table 2. Positional parameters from the two refinements agree within 1σ . For the thermal parameters, all U_{ii} agree within 1.2σ and U_{ij} within 2.5σ .

Dynamic and static deformation density maps in the planes of the molecules are given in Fig. 2(a,b) and Fig. 3(a,b) respectively. Peak heights are summarized in Table 3. The average standard deviation of the dynamic maps, $\sigma(\Delta\rho)$, is 0.037 e \AA^{-3} .

As can be seen from the Figs. 1–3 and Table 1, the two molecules show closely similar deformation-density distributions. Since the deformation functions on both molecules were constrained to be the same, any differences in the deformation density must arise from differences in the relative atomic coordinates and temperature factors. These parameters were allowed to refine independently for the two molecules. As the ($F_o - F_c$) maps for the two molecules (Fig. 1a,b) from the constrained refinement show no residual features, an unconstrained refinement was not considered worth the extra computations which would be required.

The S-atom lone-pair peaks are low and fairly diffuse (0.17 e \AA^{-3}) (Fig. 2). From the ($F_o - F_c$) maps (Fig. 1a,b) it can be seen that the largest residual peak (0.13 e \AA^{-3}) occurs at the lone-pair position for S(2) (cf. Fig. 2). This is of the order of 3.5σ . In the hydrogen-bonding system between the two molecules S(2)···H(2)–N(1), with a length of $3.353(1) \text{ \AA}$ and an S–H–N angle of 170.1° , is the strongest hydrogen bond. The corresponding bond S(1)···H(4)–N(2) with a length of $3.422(1) \text{ \AA}$ (S–H–N angle 170°) is considerably longer. Such differences cannot be properly accounted for in a treatment which constrains the

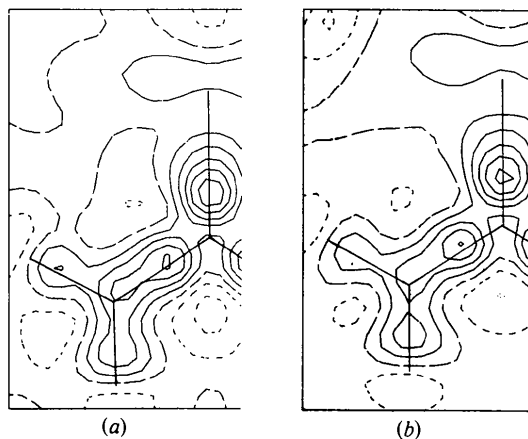


Fig. 2. Dynamic deformation densities for (a) molecule 1 and (b) molecule 2. Contours as for Fig. 1.

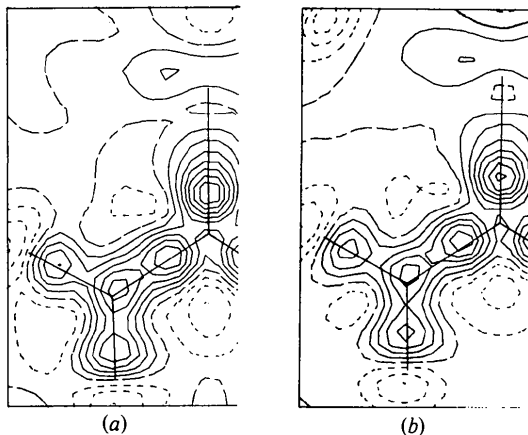


Fig. 3. Static deformation densities for (a) molecule 1 and (b) molecule 2. Contours as for Fig. 1.

deformation function on both molecules to be identical, so that the residual peak at the S(2) lone pair may indicate a build-up of charge corresponding to the formation of this shortest hydrogen bond.

Sections through the C–S bond and S lone pair perpendicular to the C–S bond are given in Figs. 4 and 5 respectively. The C–S bond peaks are only slightly extended into the π regions.

Table 3. *Thiourea: peak heights* ($e \text{ \AA}^{-3}$)

(a) Dynamic densities

	Molecule 1	Molecule 2
C=S	0.58	0.54
C–N	0.41	0.41
N–H(1,3)	0.28	0.26
N–H(2,4)	0.21	0.17
S (lone pair)	0.17	0.17

(b) Static densities

	Molecule 1	Molecule 2
C=S	0.78	0.74
C–N	0.59	0.60
N–H(1,3)	0.50	0.45
N–H(2,4)	0.42	0.36
S (lone pair)	0.21	0.21

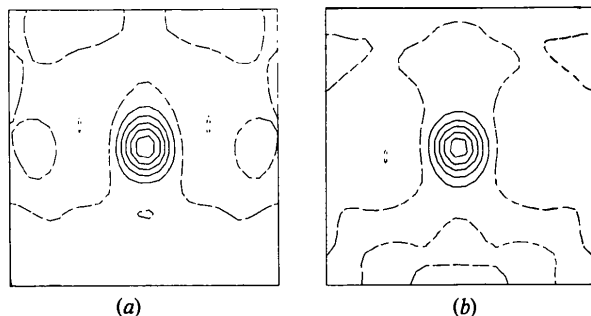


Fig. 4. Sections through C–S bond peaks perpendicular to C–S bonds for (a) molecule 1 and (b) molecule 2. Contours as for Fig. 1.

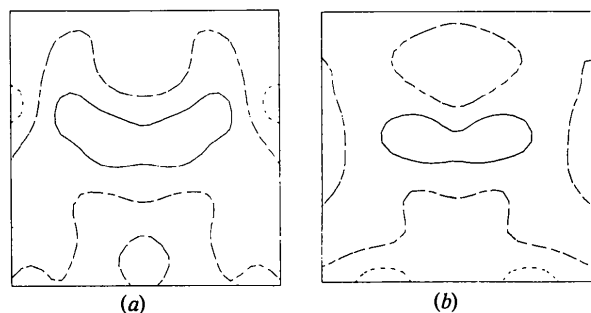


Fig. 5. Sections through S lone pairs perpendicular to C–S bonds for (a) molecule 1 and (b) molecule 2. Contours as for Fig. 1.

Discussion

(a) Comparison of the urea and thiourea molecules

The effect on the electron density distribution of replacing the O atom in the urea molecule by S may be examined by comparing the results for urea (Mullen, 1980) with the present calculations for thiourea. Table 4 gives a summary of the deformation density in urea and thiourea. Results for thiourea are averaged over the two molecules. Values for urea are taken from a refinement with deformation terms up to hexadecapole level.

It can be seen from Table 4 that the molecular moiety common to both compounds shows a striking agreement in the deformation-density peak heights. This portion includes the C–N bond and the N–H bonds. The individual N–H bonds are listed only to show the variation over individual N–H bonds. A comparison for the two molecules is only intended for the mean N–H bond, since the hydrogen-bonding schemes in urea and thiourea do not allow direct comparison between individual N–H bonds. A comparison of the mean N–H bonds neglects hydrogen-bonding effects. However, the mean peak heights agree within 1σ .

On the other hand, the C=S bond has a much higher bond peak ($0.76 e \text{ \AA}^{-3}$) compared with urea ($0.45 e \text{ \AA}^{-3}$), while for the lone pairs on S and O the opposite is the case. The S atom has a low, diffuse lone-pair peak ($0.21 e \text{ \AA}^{-3}$) while O has a sharper, higher peak ($0.67 e \text{ \AA}^{-3}$).

Further comparison may be made between the urea and thiourea molecules by considering the exponents α of the radial functions $r^n \exp(-\alpha r)$ in the multipolar expansion. These parameters are listed in Table 5. The

Table 4. *Comparison of static density peak heights in urea and thiourea* ($e \text{ \AA}^{-3}$)

	Urea	Thiourea*
C=O/C=S	0.45	0.76
Lone pair (O, S)	0.67	0.21
C–N	0.58	0.60
Mean N–H	0.47	0.43
N–H(1)	0.52	0.48
N–H(2)	0.41	0.39

* Average for two molecules.

Table 5. *Comparison of exponents α of radial functions for urea and thiourea (multipole refinements)*

	Urea		Thiourea
	Hexadecapole	Octopole	
O, S	8.54 (2.07)	8.13 (0.68)	4.17 (0.22)
C	5.30 (0.61)	5.07 (0.27)	6.32 (0.31)
N	4.14 (0.25)	4.22 (0.13)	4.38 (0.09)
H	2.94 (0.30)	3.60 (0.16)	3.40 (0.11)

two values for urea are from refinements including terms up to octopole level and up to hexadecapole level on O. For the H atom the values for urea lie on either side of the thiourea value. C and N atom values agree within 2σ . The O-atom α value is twice that for S, showing the relative diffuseness of the S-atom functions.

(b) Effects of anomalous-dispersion corrections

The multipole refinement has also been carried out omitting the anomalous-dispersion correction. R factors and goodness-of-fit parameter are $R = 1.27\%$, $R_w = 1.42\%$ and $S = 1.07$ (cf. Table 1).

The deformation functions differ by a maximum of 2.8σ for $\alpha[\alpha(S) = 3.23$ (22), $\alpha(C) = 5.43$ (22), $\alpha(N) = 4.77$ (10), $\alpha(H) = 3.64$ (14); cf. Table 5]. The population parameters agree within 3σ . Atomic positional parameters differ by not more than 1.5σ and thermal parameters, U_{ij} , by not more than 2.5σ .

The effect on the charge-density distribution of neglecting the anomalous-dispersion correction may be judged by comparing Fig. 2 with Fig. 6. In Fig. 6 the dynamic deformation densities have been calculated without an anomalous-dispersion correction. The peak heights for these maps are for molecules 1 and 2 respectively: $\rho(S-C) = 0.55, 0.50$; $\rho(C-N) = 0.39, 0.37$; $\rho[N-H(1,3)] = 0.27, 0.25$; $\rho[N-H(2,4)] = 0.21, 0.17$; $\rho(\text{lone pair}) = 0.12, 0.11 \text{ e } \text{\AA}^{-3}$. All bond peaks agree within about 1σ [average $\sigma(\Delta\rho) = 0.037 \text{ e } \text{\AA}^{-3}$] with corresponding peaks in Fig. 2. The S-atom lone-pair peaks agree within 1.7σ . Thus, with small anomalous-dispersion corrections omission of the correction has negligible effects on the dynamic deformation-density distribution, causing a systematic but insignificant lowering of all peak heights.

(c) Phase differences for $F_{o,x}$ and $F_{c,N}$

The magnitudes of the mean phase differences $|\overline{\Delta\phi}|$ between $F_{o,x}$ and $F_{c,N}$ for ranges of $\sin \theta/\lambda$ are shown in Fig. 7. A similar analysis of phase effects was given for urea (Mullen, 1980). In the present case, the analysis has been extended to consider both a conventional refinement ($|\overline{\Delta\phi_2}|$) as well as a multipole model ($|\overline{\Delta\phi_1}|$) (Thomas, 1978). $F_{c,N}$ are considered to be based on the 'true' nuclear parameters obtained from neutron or high-order X-ray refinements or by fitting some model to the data. In this case, the nuclear parameters were taken from the multipole model and agree closely with those from a high-order refinement. $F_{o,x}$ are attributed in one case the phases from a multipole refinement ($|\overline{\Delta\phi_1}|$) and, in the other case, phases from a conventional refinement ($|\overline{\Delta\phi_2}|$).

Thiourea may be compared with urea in terms of the distribution of $|\overline{\Delta\phi}|$ (multipole model). Additionally, the distributions of $|\overline{\Delta\phi_1}|$ and $|\overline{\Delta\phi_2}|$ for thiourea may be examined.

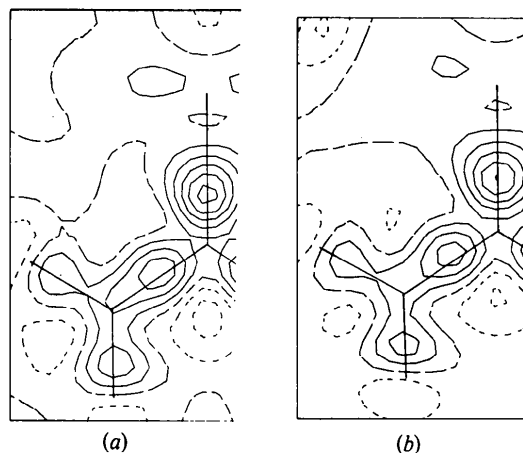


Fig. 6. Dynamic deformation densities for (a) molecule 1 and (b) molecule 2, omitting anomalous-dispersion correction.

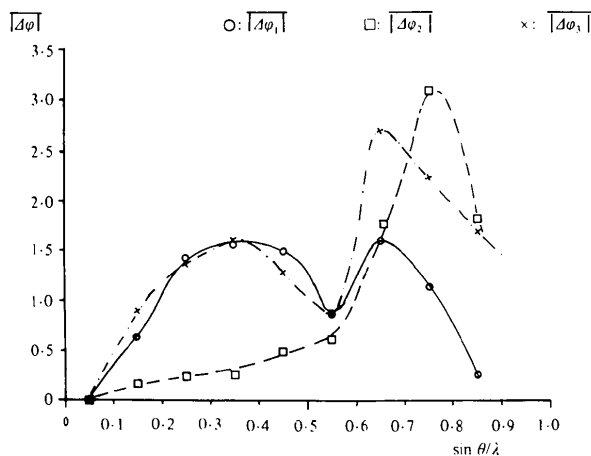


Fig. 7. Variation of $|\Delta\phi|$ (in degrees) with $\sin \theta/\lambda$ for phases for $F_{o,x}$ from multipole refinement ($|\overline{\Delta\phi_1}|$) and from conventional refinement ($|\overline{\Delta\phi_2}|$). Phases for $F_{c,N}$ from spherical-atom model. $|\overline{\Delta\phi_3}|$ gives the 'errors' in attributing phases from the conventional refinement to $F_{o,x}$, assuming 'true' phases from the multipole model.

For urea the $|\overline{\Delta\phi}|$ values rise to a peak at about 0.5 \AA^{-1} in $\sin \theta/\lambda$ and then fall again. For thiourea, the structure of the distribution is somewhat more complicated in that a first peak appears at about 0.35 \AA^{-1} in $\sin \theta/\lambda$ (1.5°) and a second peak of about the same height (1.6°) at about 0.7 \AA^{-1} . In between (at about 0.6 \AA^{-1} in $\sin \theta/\lambda$) is a shallow minimum (0.87°). Above 0.8 \AA^{-1} in $\sin \theta/\lambda$ $|\overline{\Delta\phi_1}|$ falls to 0.28° .

A comparison of $|\overline{\Delta\phi_1}|$ (multipole) and $|\overline{\Delta\phi_2}|$ (conventional refinement) for thiourea shows that the peak for the conventional refinement occurs at $0.7-0.8 \text{ \AA}^{-1}$ in $\sin \theta/\lambda$ and $|\overline{\Delta\phi_2}|$ values even at 0.9 \AA^{-1} in $\sin \theta/\lambda$ are still substantial (see Fig. 7). Values of $|\overline{\Delta\phi}|$ below 0.6 \AA^{-1} in $\sin \theta/\lambda$ are much lower for the conventional refinement.

In the conventional refinement, the atomic positions and U_{ij} are shifted from the nuclear positions as determined by a neutron diffraction experiment, since the refinement attempts to fit the aspherical part of the density. This leads to a poorer description of the high-angle region than for the multipole case which yields atom parameters corresponding well to the 'true' nuclear positions (Coppens & Stevens, 1977). Thus the high-angle region has higher $|\Delta\varphi|$ values for the conventional refinement (*cf.* values of $|\Delta\varphi_1|$ and $|\Delta\varphi_2|$ at $0.8\text{--}0.9 \text{ \AA}^{-1}$ in $\sin \theta/\lambda$).

In the low-angle region ($<0.6 \text{ \AA}^{-1}$ in $\sin \theta/\lambda$) the $|\Delta\varphi|$ values are much lower for the conventional refinement than for the multipole model because in this region an important contribution comes from the deformation functions. In the conventional refinement with spherical atoms, smaller discrepancies (less than about 0.5°) are found in this region, brought about by small shifts of the spherical atoms and changes in U_{ij} . The large differences between $|\Delta\varphi_1|$ and $|\Delta\varphi_2|$ (and the small $|\Delta\varphi_2|$ values) in this low-angle region are thus a measure of the poorness of fit of the conventional spherical-atom refinement to the aspherical part of the density.

$|\Delta\varphi_3|$ represents the 'errors' introduced in attributing phases from a conventional spherical-atom refinement to $F_{o,x}$ compared with the 'true' phases which are here assumed to be given by the multipole model. The $|\Delta\varphi_3|$ distribution supports the conclusions from analysis of the distributions of $|\Delta\varphi_1|$ and $|\Delta\varphi_2|$. Below 0.6 \AA^{-1} in $\sin \theta/\lambda$, the $|\Delta\varphi_3|$ distribution is closely similar to that of $|\Delta\varphi_1|$, *i.e.* the conventional refinement does not fit low-angle data very much better than a model based on $F_{c,N}$. Above 0.6 \AA^{-1} the $|\Delta\varphi_3|$ values reach a peak, and even above 0.8 \AA^{-1} where little contribution from deformation terms is found ($|\Delta\varphi_1| = 0.28^\circ$), the conventional refinement yields phases substantially different from those of the multipole model ($|\Delta\varphi_3| = 1.70^\circ$), revealing the inadequacy of the conventional refinement in this region of

reciprocal space for the reasons already discussed above.

The author thanks Mr K. Eichhorn who has adapted the multipole refinement program for use on the TR 440 computer at Saarbrücken. Financial support from the Deutsche Forschungsgemeinschaft is also gratefully acknowledged.

**Note added in proof:* The following paper (Kutoglu, Scheringer, Meyer & Schweig, 1982) reports the results of a theoretical calculation of the static and dynamic deformation densities for thiourea, and a comparison with the experimental data.

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- COPPENS, P. & STEVENS, E. D. (1977). *Adv. Quantum Chem.* **10**, 79–85.
- ELCOMBE, M. M. & TAYLOR, J. C. (1968). *Acta Cryst.* **A24**, 410–420.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- HIRSHFELD, F. L. (1971). *Acta Cryst.* **B27**, 769–781.
- KUTOGLU, A., SCHERINGER, C., MEYER, H. & SCHWEIG, A. (1982). *Acta Cryst.* **B38**, 2626–2632.
- MULLEN, D. (1980). *Acta Cryst.* **B36**, 1610–1615.
- MULLEN, D. & HELLNER, E. (1978). *Acta Cryst.* **B34**, 2789–2794.
- NGO THONG & SCHWARZENBACH, D. (1979). *Acta Cryst.* **A35**, 658–664.
- SCHERINGER, C., MULLEN, D., HELLNER, E., HASE, H. L., SCHULTE, K.-W. & SCHWEIG, A. (1978). *Acta Cryst.* **B34**, 2241–2243.
- THOMAS, J. O. (1978). *Acta Cryst.* **A34**, 819–823.
- WAL, H. R. VAN DER, DE BOER, J. L. & VOS, A. (1979). *Acta Cryst.* **A35**, 685–688.