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The Influence of Valence Electron Scattering on the Results of X-ray Structure Analyses

By A. M. O'CONNELL

Crystallography Group, Medical Research Council Unit for Molecular Structure Analysis, University of Göteborg, Göteborg, Sweden

(Received 13 March 1968 and in revised form 1 July 1968).

The influence of valence electron scattering on the results derived from the least-squares refinement of single-crystal X-ray diffraction data has been examined for the structure of taurine, 2-aminoethylsulfonic acid. The parameters derived from a refinement including only high order reflexions ($\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$), which are relatively unaffected by valence electron scattering, are compared with those from a low order ($\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$) refinement. An analysis of the difference Fourier syntheses indicates that features attributable to the valence electrons are systematically modified in the low-order treatment.

Introduction

Current X-ray refinement techniques are based on spherically averaged form-factor curves and thus the redistribution of valence electrons in bonded atoms is ignored. In the least-squares procedure, aspherical scattering effects can be absorbed by both the anisotropic temperature factors and by movement of the atomic centre. This may lead to significant errors in the structural parameters and may also result in the

loss of important information about the valence electron distribution.

Dawson (1964) has examined a hypothetical structure consisting of two sp^3 'prepared' state nitrogen atoms and found that least-squares positional parameters are in error by about 0.02 \AA when conventional atomic scattering factors are used. O'Connell, Rae & Maslen (1966) have extended Cochran's (1956) calculations of the electron distribution in benzene. They have shown that the asymmetric environment of the

carbon atoms results in radial shifts of 0.007 Å towards the ring centre for these atoms when the structure is subject to least-squares refinement using spherically symmetric scattering curves. Coppens & Coulson (1967) have examined the case of terminal oxygen atoms in a nitro group and their calculations indicate that the direction and magnitude of positional shifts are dependent on the hybridization of the oxygen atoms.

Experimental evidence of these effects may be obtained by (i) the comparison of accurate X-ray and neutron parameters or (ii) the comparison of X-ray refinements based on low order and high order reflexion data (Cruickshank, 1960). Coppens & Bednowitz (1967) have employed the first method in the accurate analysis of *s*-triazine. The second technique has been used by Stewart & Jensen (1967) and Stewart (1967*b*) in the study of the structure of uracil, the high order least-squares refinement being carried out on the non-hydrogen atoms anisotropic thermal parameters.

The present study was undertaken to extend the available experimental information regarding these effects. The method followed was similar to the one employed by Stewart & Jensen; however the high order refinement included both positional and thermal parameters of the non-hydrogen atoms. This was considered necessary, since positional errors are likely to be quite serious, particularly for atoms in a markedly asymmetric environment (Dawson, 1964). Parameters from low order (including reflection data with $\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$) and high order ($\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$) least-squares refinements were compared. The former results correspond to those most usually obtained in X-ray structure analyses, while the latter correspond more closely to the 'correct values' since the high order scattering is predominately from the spherically symmetric core electrons.

Refinement

Okaya's (1966) published reflexion data and parameters for taurine (Fig. 1) were used for the present analysis. The advantages of the choice of this structure are (a) the space group is centric, $P2_1/c$; (b) the data have been accurately measured using a diffractometer and appear to be largely free from systematic errors; (c) the intensity measurements were made using one small crystal with Mo $K\alpha$ radiation, therefore absorption errors are negligible small; (d) the observed data extend fairly uniformly through a large volume of reciprocal space ($\sin \theta/\lambda < 0.91 \text{ \AA}^{-1}$); (e) the zwitterion character of the molecule provides an interesting example of the influence of charge movements (predominantly a low angle effect) on the least-squares refinement [see *Discussion*, § (ii)]. The disadvantages of this choice are (a) the structure contains the relatively heavy sulphur atom and (b) the intensity measurements were not made at low temperatures. The latter objection is offset to some degree since the thermal vibration of most of the atoms is relatively small (Table 5, below), presumably

because the molecules are held rather rigidly in the crystal lattice by the extensive three-dimensional hydrogen bond network.

Only the observed reflexion data were considered; of these 11 of the strongest were rejected since they appeared to suffer from extinction effects and 75 of the very weak reflexions were omitted because it was thought that the counting statistics for these were unreliable. Thus 2547 independent observed structure factors were available for the analysis.

Four different refinement conditions were examined.

- (1) A full angle refinement using the complete data set. Hereafter referred to as the FA refinement.
- (2) A high angle refinement using data restricted to the range $\sin \theta/\lambda \geq 0.65 \text{ \AA}^{-1}$. Hereafter the HA refinement.
- (3) A low angle refinement using data restricted to the range $\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$. Hereafter the LA refinement.
- (4) A refinement using the complete data set, but with unit weights applied to all reflexions. Hereafter the W1 refinement.

In all cases full matrix least-squares techniques were used for the parameter refinement and standard de-

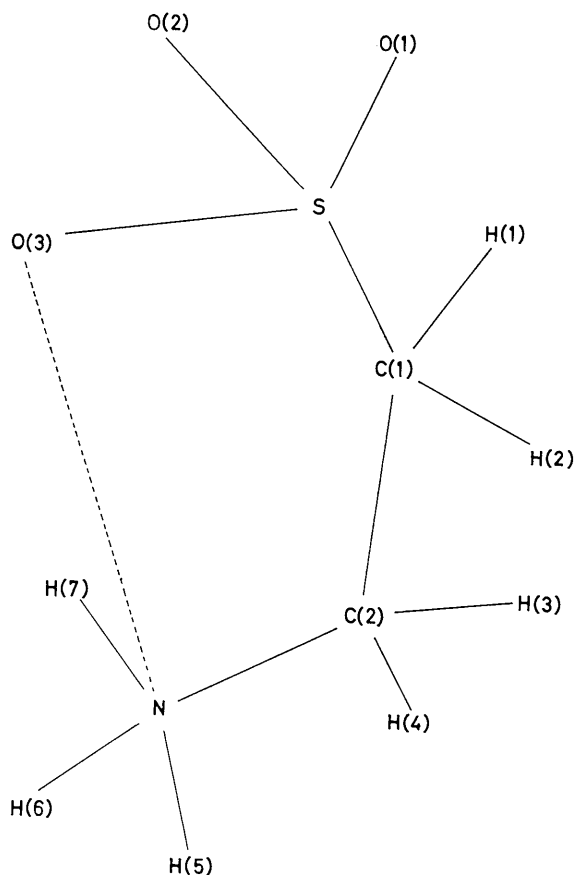


Fig. 1. Taurine atom numbering.

viation calculations. In (1), (3), and (4) the sulphur, carbon, nitrogen and oxygen positional and anisotropic thermal parameters and the hydrogen positional and isotropic thermal parameters were refined. In the HA refinement the hydrogen parameters were included as defined by the FA results and were not varied in the least-squares procedure. In the first three cases weights were applied according to the system:

$$w = 1.0 \quad \text{for } |F_{\text{obs}}| \leq 7$$

$$w = 7/|F_{\text{obs}}| \quad \text{for } |F_{\text{obs}}| > 7$$

This differs from the procedure adopted by Okaya ($w = 1.0$ for $|F_{\text{obs}}| \leq 20$, $w = 20/|F_{\text{obs}}|$ for $|F_{\text{obs}}| > 20$) however, the present weighting scheme was preferred since it gave a more even distribution of the average weighted differences as a function of $|F_{\text{obs}}|$. Furthermore, the influence of the very strong reflexions, which may be subject to secondary extinction, is reduced. The scattering factors for sulphur (corrected for the real

part of the anomalous dispersion coefficient), carbon, nitrogen and oxygen were taken from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used (again this differs from Okaya's procedure). A summary of the various refinement conditions and results is given in Table 1.

Fig. 2, which is a histogram plot of the number of reflexions in ranges of $(\sin \theta/\lambda)^3$, illustrates that the data are fairly evenly distributed throughout the range of reciprocal space considered. About 59% of the observed reflexion material lies outside the Cu $K\alpha$ sphere, thus providing a very favourable situation for testing high order refinement procedures. The HA refinement of the 63 non-hydrogen atom parameters plus the scale factor is overdetermined by a factor of 23.5, while the FA refinement of all parameters is overdetermined by a factor of 27.7 [as compared to a factor 5.0 in Stewart & Jensen's (1967) high order refinement of the non-hydrogen atom anisotropic thermal parameters of uracil].

The F_{obs} scale factors derived from the four refinement conditions are listed in Table 1. These values are referred to Okaya's data with unit scale factor. All values are slightly greater than 1.0. This is probably due to (a) the truncation of the data set as described above, (b) the inclusion of the sulphur anomalous dispersion correction which is positive and would tend to increase the F_{obs} scale or (c) the different scattering factor interpolation routines used. [Linear on f_j^2 by Okaya, and according to Vand, Eiland & Pepinsky (1957) in the present work]. The mean F_{obs} scale is 1.008 and none of the individual values differ from this by more than 0.5%. This is encouraging evidence of the absence of systematic errors in the reflexion data.

Discussion

(i) Atomic positions

The positional differences HA-FA, HA-LA and FA-W1 are listed in Table 2. The HA-LA results indicate the magnitude of the positional errors which are likely to occur if only data within the Cu $K\alpha$ sphere of reflexion are used in the least-squares refinement. Two of these differences exceed 3σ ; 4.5σ and 3.5σ for O(1) and C(1) respectively. In the HA-FA results only one difference is significant at the 3σ level: 3.6σ for O(1).

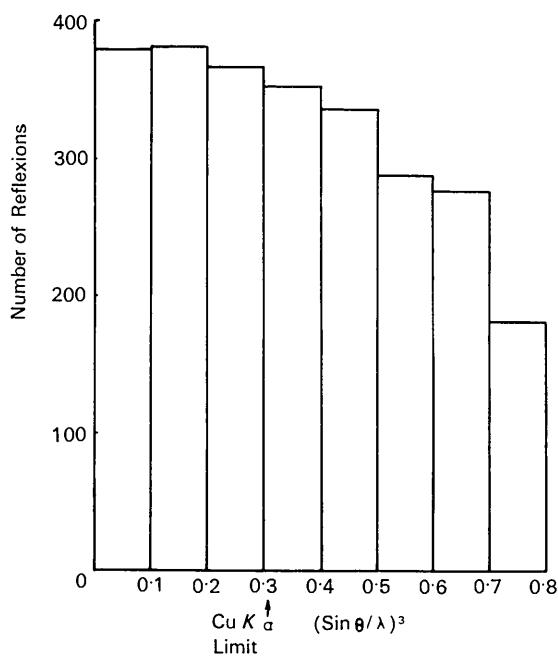


Fig. 2. The distribution of the observed reflexion data as a function of $(\sin \theta/\lambda)^3$.

Table 1. *Details of refinement*

Refinement	Number of reflexions	Number of parameters	Parameters Reflexions	Least squares F_{obs} scale*	$\Sigma F_c /\Sigma F_o $	R
FA	2547	92	27.7	1.005	0.999	0.038
HA	1507	64	23.6	1.010	0.996	0.041
					0.997	0.038‡
LA	1040	92	11.3	1.003	1.000	0.035
W(1)	2547	92	27.7	1.013	0.995	0.038

* Referred to Okaya's listed data with scale 1.000.

‡ Calculated using all the reflexion material.

Table 2. *Positional differences resulting from the four refinement conditions*The standard deviations have been multiplied by 10⁴.

	HA-FA	HA-LA	FA-W1
S	0.0006 (4) Å	0.0010 (5) Å	0.0006 (4) Å
O(1)	0.0087 (24)*	0.0112 (25)*	0.0021 (16)
O(2)	0.0052 (22)	0.0065 (23)	0.0036 (15)
O(3)	0.0016 (17)	0.0020 (20)	0.0015 (15)
C(1)	0.0046 (19)	0.0084 (24)*	0.0019 (19)
C(2)	0.0014 (20)	0.0018 (25)	0.0010 (18)
N	0.0011 (15)	0.0036 (20)	0.0042 (15)

* Indicates differences which exceed 3 σ

The influence of these shifts on the bond lengths is shown in Table 3. The three S-O distances from the LA refinement are all shorter than those from the HA results. The mean decrease in these bond lengths is 0.0027 Å. This is in good agreement with the mean difference (0.004 Å) between the S-O bond lengths determined by neutron and X-ray diffraction for β -sulphanilamide and orthonilic acid (Lum & Maslen, 1967*a, b*). The shortening is apparently due to a partial compensation for the S-O bond residual electron density by the LA least-squares refinement. There is a similar decrease in the S-O distances of the FA refinement. However, in this case the effect is smaller, the mean bond shortening being 0.0016 Å, *i.e.* about half that of the LA results.

A large component of the shift in the oxygen atom O(1) is at right angles to the S-O(1) bond. To a much smaller degree this is also true for O(2). Difference syntheses based on the HA parameters, in planes perpendicular to the S-O bonds and through the oxygen atoms showed, in the case of O(1) and O(2), positive residual electron density features (peak height ~ 0.35 e.Å⁻³) at distances 0.6 Å from the oxygen positions with negative features symmetrically situated on opposite sides of the atomic sites. The plane through O(3) showed two positive peaks (~ 0.30 e.Å⁻³) symmetrically situated about the oxygen position. The origin of these features is not clear and since the electron density near the oxygen atoms is probably nearly cylindrically symmetrical (Cruickshank, D. W. J., private communication) it is unlikely that they result from valence electron effects. A neutron diffraction analysis which is currently being planned may provide further information about these features.

The S-C(1) distance of the LA refinement is 0.008 Å shorter than obtained from the HA parameters (0.005 Å shorter in the FA case). This results almost wholly from a shift in the position of C(1) (see Table 2). The shortening is not directly analogous to that described above for the S-O bonds since C(1) is not a terminal atom. It is, however, situated in an asymmetric environment as can be seen from Fig. 3. The S-C(1) σ -bond residual density peak apparently has more influence on the LA least-squares refinement than the C(1)-C(2) peak since the shift in C(1) is directed approximately toward the sulphur atom.

The FA bond lengths are almost identical with those reported by Okaya. For the four bonds associated with the sulphur atom, the FA results lie about midway between those obtained in the HA and LA refinements. The C(1)-C(2) and C(2)-N distances are similar in all three cases.

A comparison of the FA results with those derived from the W1 refinement gives some indication of the effect of the weighting function on the least-squares refinement. Since there are systematic discrepancies between the observed and calculated structure factors arising from the assumption of spherically symmetric electron densities, it might be expected that weighting schemes which give bias to different regions of the data would result in different atomic parameters. A comparison of the FA and W1 results in Table 2 indicates some differences, but these are not significant at the 3 σ level. The maximum positional shifts are 0.0042 Å (2.8 σ) for the nitrogen atom and 0.0036 Å (2.4 σ) for O(2). None of the other shifts exceed 1.8 σ .

The hydrogen atom positional differences FA-LA and FA-W1 are listed in Table 4. None of the FA-LA results exceed 1 σ . The FA-W1 differences are larger [maximum 3.9 σ for H(5)] indicating that the choice of

Table 4. *Differences in the hydrogen atom positions obtained from the FA, LA and W1 refinements*The standard deviations have been multiplied by 10³.

	FA-LA	FA-W1
H(1)	0.011 (33) Å	0.020 (30) Å
H(2)	0.045 (44)	0.081 (37)
H(3)	0.014 (33)	0.079 (29)
H(4)	0.017 (43)	0.073 (35)
H(5)	0.018 (47)	0.141 (36)*
H(6)	0.022 (34)	0.066 (31)
H(7)	0.009 (44)	0.046 (35)

* Indicates difference which exceeds 3 σ .Table 3. *Bond lengths derived from the various refinement conditions*The standard deviations have been multiplied by 10⁴.

	HA	FA	LA	OKAYA	W1
S—O(1)	1.4627 (14) Å	1.4606 (9) Å	1.4593 (15) Å	1.461 (20) Å	1.4608 (11) Å
S—O(2)	1.4498 (16)	1.4480 (10)	1.4466 (14)	1.448 (20)	1.4506 (12)
S—O(3)	1.4656 (14)	1.4647 (9)	1.4642 (14)	1.465 (20)	1.4633 (11)
S—C(1)	1.7838 (15)	1.7792 (12)	1.7760 (19)	1.780 (20)	1.7764 (14)
C(1)—C(2)	1.5187 (20)	1.5186 (16)	1.5195 (26)	1.520 (30)	1.5176 (19)
C(2)—N	1.4829 (20)	1.4843 (15)	1.4826 (25)	1.484 (20)	1.4799 (18)

weighting constants may be important in hydrogen atom refinement.

(ii) *Thermal parameters*

An analysis of the thermal parameters derived from the LA, HA and FA refinements is given in Tables 5 and 6 in terms of the magnitudes and angles (relative to the crystallographic axes) of the principal axes of the vibrational ellipsoids. The calculations were performed using a FORTRAN program devised by Larson, Roof & Cromer (1965). The differences ΔB_i , corresponding to B_i (HA-LA) and B_i (HA-FA) are listed in columns 4, 6 and 8 of Table 5. The equivalent isotropic temperature factors, $B_{\text{iso}} = \frac{1}{3}B_1B_2B_3$, are given in column 9. The mean difference between the magnitudes of the B_i 's derived from the HA and LA refinements is 0.050 \AA^2 ($\sim 0.8\sigma$) and none of the differences exceed 2.4σ . The corresponding figures for the HA and FA refinements are 0.024 \AA^2 ($\sim 0.5\sigma$) and 2.3σ . The differences for the direction angles are somewhat larger, but generally these do not exceed 2.5σ . The

equivalent isotropic thermal parameters are lower in the HA treatment for all atoms except O(1). The mean differences $B(|\text{LA-HA}|)$ and $B(|\text{FA-HA}|)$ are 0.035 \AA^2 and 0.013 \AA^2 . This may possibly result from some accommodation of the bonding electron asphericity by the temperature factor coefficients. The differences are small, however, and are not significant in comparison with the estimated standard deviations.

The good agreement between vibrational parameters derived from the three refinement conditions indicates that, in this case, the aspherical components of the valence electron density have little influence on the temperature factor refinement. Accommodation of the valence structure by thermal parameter changes has been reported in several recent publications. In the high order refinement of uracil, Stewart & Jensen (1967) have noted changes in the B_i values from the parameters derived using the full data. Similar results have been obtained by Verschoor (1967) in the low order ($\sin \theta/\lambda \leq 0.63 \text{ \AA}^{-1}$) and full data ($\sin \theta/\lambda < 0.8 \text{ \AA}^{-1}$) refinements of cyanuric acid. The introduction of non-

Table 5. *The magnitudes of the principal axes (\AA^2) of the vibrational ellipsoids for the LA, HA and FA refinements*
The ΔB_i 's refer to the differences B_i (HA-LA) and B_i (HA-FA). Standard deviations are multiplied by 10^3 .

Refinement	B_1	ΔB_1	B_2	ΔB_2	B_3	ΔB_3	B_{iso}
S	LA	1.454 (22)		1.243 (22)		2.296 (23)	1.607
	HA	1.447 (12)	-0.007 (25)	1.183 (11)	-0.060 (25)	2.267 (15)	1.571
	FA	1.454 (8)	-0.007 (15)	1.192 (8)	-0.009 (14)	2.284 (10)	1.582
O(1)	LA	1.226 (49)		2.470 (61)		4.635 (80)	2.412
	HA	1.280 (27)	0.054 (56)	2.384 (39)	-0.086 (73)	4.717 (74)	2.433
	FA	1.284 (27)	-0.004 (38)	2.394 (33)	-0.010 (51)	4.642 (54)	2.425
O(2)	LA	2.931 (62)		1.256 (50)		4.419 (74)	2.534
	HA	2.925 (46)	-0.006 (77)	1.184 (26)	-0.072 (56)	4.377 (67)	2.475
	FA	2.896 (36)	0.029 (60)	1.213 (23)	-0.029 (35)	4.439 (49)	2.498
O(3)	LA	2.557 (43)		2.358 (101)		1.874 (50)	2.244
	HA	2.516 (44)	-0.041 (61)	2.270 (42)	-0.088 (109)	1.852 (29)	2.195
	FA	2.503 (29)	0.013 (53)	2.388 (29)	-0.118 (51)	1.854 (25)	2.229
C(1)	LA	1.636 (67)		1.949 (60)		2.296 (69)	1.942
	HA	1.616 (27)	-0.020 (72)	1.855 (42)	-0.094 (73)	2.304 (51)	1.904
	FA	1.637 (27)	-0.021 (38)	1.857 (32)	-0.002 (53)	2.310 (39)	1.915
C(2)	LA	2.691 (74)		1.655 (61)		1.992 (61)	2.070
	HA	2.617 (41)	-0.074 (85)	1.618 (31)	-0.037 (68)	2.004 (39)	2.040
	FA	2.614 (37)	0.003 (55)	1.615 (31)	0.003 (44)	1.995 (34)	2.035
N	LA	1.798 (62)		1.544 (64)		2.482 (66)	1.903
	HA	1.816 (29)	0.018 (68)	1.512 (28)	-0.032 (70)	2.325 (35)	1.855
	FA	1.802 (26)	0.014 (39)	1.524 (25)	-0.012 (38)	2.386 (41)	1.871

spherical scattering curves into the analysis of 1,3,5-triamino-2, 4, 6-trinitrobenzene (Cady & Larson, 1965) and 2,5-dimethyl-7,7-dicyanonorcaradiene (Fritchie, 1966) has also led to significant changes in the temperature parameters, accompanied in the latter case by a 3% increase in the F_{obs} scale factor.

The lack of significant interaction between the valence electron asphericity and the vibrational parameters in the present case can probably be attributed to the molecular configuration. The four structures mentioned above are all essentially planar molecules with extensive π -bond systems. The sulphur, carbon and nitrogen atoms in taurine have tetrahedral environments and the only π -bond system is that associated with the S-O bonds.

The zwitterion configuration of the molecule does not have any significant influence on the magnitude of the B_i values in the LA refinement. Although the largest individual B_i change is associated with the nitrogen atom [$B_3(\text{HA-LA}) = -0.16 \text{ \AA}^2$], this difference corresponds only to approximately 2σ . The equivalent isotropic B value for O(1) is the only one to increase in the HA treatment (by 0.02 \AA^2) but again this change is not significant in comparison with the estimated standard deviation.

(iii) Residual electron density

Qualitative studies of electron density features have been carried out in a number of recently reported X-ray structure analyses. Since quantitative analyses are highly desirable it is important to know how the electron density distributions are affected by different re-

finement procedures. In particular it is of interest to study the difference between the LA and HA refinements since most of the qualitative studies reported have used data restricted to the reflexion sphere of Cu $K\alpha$ radiation.

Figs. 3(a)-(d) show Fourier difference syntheses calculated in the C-S-O and C-C-N bond planes using (a) the HA parameters with all data; (b) the FA parameters with all data; (c) the LA parameters with all data and (d) the LA parameters with the low order data. The root mean square value of the residual electron density throughout the unit cell is 0.09 e\AA^{-3} . It should be noted that the residual densities do not represent the valence electron distributions since they are derived from the difference between the observed structure factors and calculated structure factors based on spherically averaged treatments of the atomic scattering power. Nevertheless the results presented here do give an indication of how electron densities are modified when the structural parameters are obtained from restricted data sets.

The general features of the syntheses calculated from the different refinement conditions are quite similar. The central region of each bond contains a positive residual density peak, while most of the atomic positions lie close to zero contours. There are, however, some important differences in the fine detail of the maps, particularly between HA and LA results. These differences arise from two sources:

(1) The partial accommodation of valence electron features by the LA refinement. This results in the re-

Table 6. *The directions of the principal axes of the vibrational ellipsoids with respect to the crystallographic axes*
The angles are given in degrees.

Refinement	Angle between B_1 and			Angle between B_2 and			Angle between B_3 and			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	
S	LA	34 (3)	56 (4)	97 (1)	124 (3)	34 (4)	82 (1)	84 (1)	93 (1)	11 (1)
	HA	27 (2)	63 (2)	99 (1)	116 (2)	27 (2)	82 (1)	83 (1)	93 (1)	12 (1)
	FA	29 (1)	62 (1)	98 (1)	118 (1)	28 (1)	82 (1)	83 (1)	93 (1)	12 (1)
O(1)	LA	33 (2)	60 (2)	82 (1)	122 (2)	32 (2)	85 (1)	98 (1)	99 (1)	10 (1)
	HA	32 (1)	60 (1)	83 (1)	121 (1)	31 (1)	86 (1)	98 (1)	97 (1)	8 (1)
	FA	32 (1)	60 (1)	86 (1)	120 (1)	30 (1)	93 (1)	99 (1)	89 (1)	5 (1)
O(2)	LA	49 (2)	66 (2)	133 (2)	120 (1)	30 (1)	87 (1)	56 (2)	72 (1)	43 (2)
	HA	56 (2)	70 (1)	142 (2)	119 (1)	29 (1)	87 (1)	48 (1)	69 (1)	53 (2)
	FA	50 (1)	68 (1)	135 (1)	120 (1)	30 (1)	88 (1)	55 (1)	71 (1)	45 (1)
O(3)	LA	55 (12)	128 (12)	60 (3)	45 (11)	45 (12)	90 (9)	115 (5)	69 (4)	30 (3)
	HA	35 (5)	102 (6)	62 (3)	70 (6)	23 (4)	101 (4)	117 (3)	71 (3)	31 (2)
	FA	44 (10)	115 (10)	60 (3)	56 (10)	35 (9)	99 (6)	114 (2)	67 (2)	31 (2)
C(1)	LA	51 (6)	115 (9)	134 (5)	66 (9)	27 (9)	102 (9)	49 (6)	99 (8)	47 (5)
	HA	46 (4)	109 (5)	133 (3)	68 (5)	22 (5)	95 (4)	52 (3)	101 (3)	44 (3)
	FA	46 (3)	106 (5)	135 (2)	72 (5)	19 (5)	95 (4)	50 (2)	100 (3)	46 (2)
C(2)	LA	49 (5)	111 (4)	135 (4)	100 (7)	39 (7)	126 (5)	43 (5)	60 (8)	67 (6)
	HA	46 (3)	110 (2)	133 (2)	104 (3)	45 (4)	130 (3)	47 (3)	52 (4)	69 (4)
	FA	45 (2)	108 (2)	133 (2)	102 (3)	40 (3)	126 (2)	47 (3)	56 (4)	65 (3)
N	LA	28 (10)	69 (11)	111 (4)	115 (11)	26 (9)	96 (5)	78 (4)	76 (3)	22 (4)
	HA	26 (3)	79 (4)	118 (3)	104 (4)	14 (3)	93 (2)	68 (3)	81 (2)	28 (3)
	FA	20 (5)	86 (11)	114 (7)	98 (9)	14 (4)	100 (3)	72 (9)	77 (2)	26 (8)

sidual density features being refined away to some extent in the LA maps.

(2) The exclusion of the high order terms in Fig. 3(d) causes a general reduction in the residual density peak heights since the contribution of the valence electrons to these terms is not negligible. There is also some rounding-off of the residual density features because of the reduced resolution of the restricted data.

The difference between the LA and HA results is most evident for the S-C bond, where the shape of the peak due to the σ -bond scattering has been considerably modified. Apparently this is due to the rather large shift in C(1) towards the sulphur atom (0.008 Å) in the LA refinement. Similar shifts in the three oxygen atoms cause modifications of the same type in the residual density in the S-O bonds. In the maps based on the LA refinement and low order data both the extension of the residual maxima along the S-O bonds and peak heights at the bond centres have been reduced. The lower part of Fig. 3 shows difference maps calculated in the C(1)-C(2)-N plane. For the C-C bond the results of the HA and LA refinements are quite similar. The C-N σ -bonding peak is more compressed in the LA syntheses and in the map based on the low order terms the peak height is reduced by about $0.10 \text{ e}\text{\AA}^{-3}$.

The discrepancy between the LA maps based on the low order data and the HA results is shown more clearly in Fig. 3(e). These are double difference syntheses defined as

$$\Delta\rho = \Delta\rho(\text{HA}) - \Delta\rho(\text{LA})$$

where $\Delta\rho(\text{HA})$ has been calculated using the HA parameters and all data, and $\Delta\rho(\text{LA})$ with the LA parameters and the low order data. The zero contour has been omitted for clarity.

The results of the FA refinement correspond well with those of the HA data. The density maxima near the bond centres agree almost exactly in the two cases, however the extension of the residual peaks along the bonds is somewhat greater in the HA case. Again, this is apparently due to a slight compensation for the non-spherically symmetric electron distributions by the least-squares procedure in the FA refinement.

Structure factors for which $\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$ make only a small contribution to the total electron density associated with bonding. This was illustrated by evaluating the difference density using structure factors from successive shells of equal volume in reciprocal space (intervals of 0.1 \AA^{-3} in $[\sin \theta/\lambda]^3$). The residual density in a region 1.2 \AA in diameter and 0.8 \AA long, with its axis centred on the C(1)-C(2) σ -bond was examined (Fig. 4). A negligible density was contributed by structure factors for which $[\sin \theta/\lambda]^3 > 0.2 \text{ \AA}^{-3}$, 90% of the density was contributed by those within 0.1 \AA^{-3} of the origin. It can however, be seen from Fig. 3(e) that bonding electrons associated with sulphur, oxygen and nitrogen atoms make a somewhat greater contribution to structure factors outside this range.

Examination of Fig. 1 of Stewart (1967a) shows that the above results are in good agreement with the partitioned scattering curve for carbon. For $\sin \theta/\lambda > 0.54 \text{ \AA}^{-1}$ the total scattering curve and the curve corresponding to the $1s^2$ core electrons agree very well.

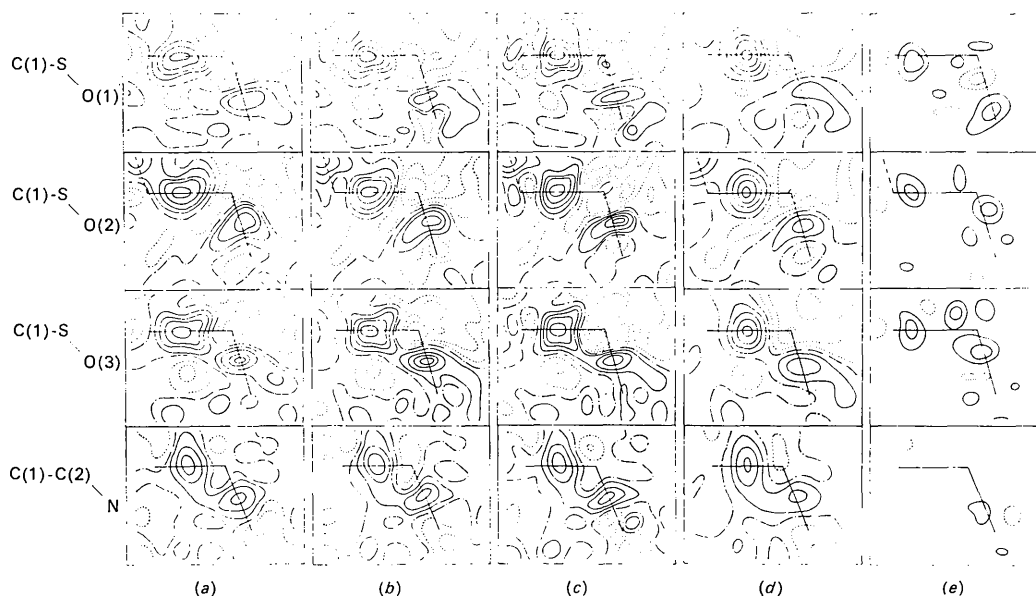


Fig. 3. The residual electron density in the C-S-O and C-C-N planes calculated with (a) the HA parameters and all data; (b) the FA parameters and all data; (c) the LA parameters and all data; (d) the LA parameters and low order ($\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$) data; (e) [HA parameters and all data] - [LA parameters and low order data] *i.e.* (a)-(d). Contours at $0.1 \text{ e}\text{\AA}^{-3}$. Zero contour chain dotted, negative contours dashed, positive contours full lines. The zero contour has been omitted from 3(e).

However, these results differ from those obtained by O'Connell, Rae & Maslen (1966) in their study of the triaminotrinitrobenzene molecule. An analysis of the residual density in the C-C and C-N bonds of the low angle ($\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$) difference synthesis of this structure indicated that the non-spherically symmetric component of the electron density predominantly affected the X-ray scattering at higher Bragg angles. The reason for the apparently conflicting results of these two analyses is difficult to understand and clearly requires further study. The implication is, however, that the σ -bonding electrons of the aromatic molecule are more contracted than those of the sp^3 - sp^3 methylene linkage in taurine, and thus the valence electron scattering curve does not decrease so rapidly with increasing $\sin \theta/\lambda$ values.

The author wishes to thank Drs P. Coppens, R. F. Stewart and E. N. Maslen who kindly provided results ahead of publication, Dr Y. Okaya for information regarding the taurine analysis and Professor D. W. J. Cruickshank for advice and critical comments. The thermal parameter calculations were made on the University of Göteborg's IBM 360/50 computer. The assistance of Dr K. Larsson is acknowledged. The remainder of the computations were performed on a Datsaab D21 computer using programs written by Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdaahl (1965) and additional routines written by the author. Financial support was obtained from the Swedish Medical Research Council, the Swedish National Science Research Council and the U.S. Public Health Service (G.M.-11653).

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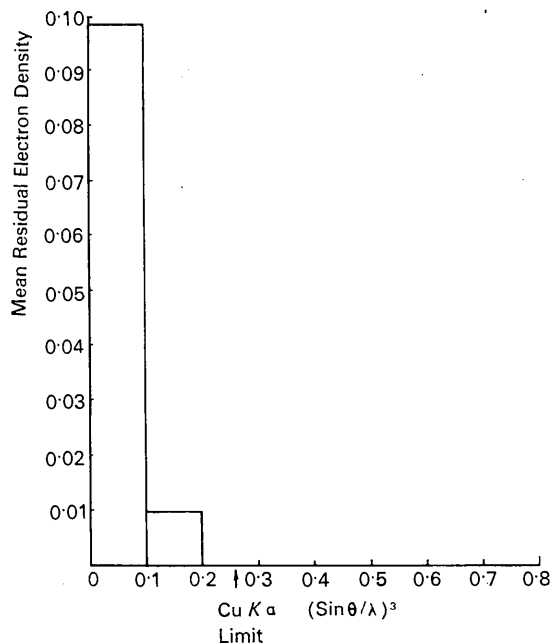


Fig. 4. The total mean residual density in a cylinder 1.2 Å in diameter and 0.8 Å long, centred on the C(1)-C(2) σ -bond peak, plotted as a function of $(\sin \theta/\lambda)^3$.

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