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A Simple Refinement of Density Distributions of Bonding Electrons. IV. The Distribution of Valence Electrons in Cyanuric Acid

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The new proposed refinement for density distributions of bonding electrons has been applied to the crystal structure of cyanuric acid. R becomes 2.62 or 2.52% (LQ1, LQ2). Constrained populations for the bonding electrons (LQ3–LQ5) seem to be less suitable for obtaining agreement with the X-ray data. In these three refinements, fixed population factors ($n = 2$, $n = 3$, and $n = 2$ or 4) for the charge clouds of the bonding electrons have been introduced. A comparison with the atom- and bond-population parameters obtained with atomic-orbital functions, shows that there are differences in the population values. In both cases, however, the difference maps and the bonding electrons outside the spherical arrangement of the core electrons are similar.

Introduction

In the first paper of this series (Hellner, 1977) the refinement procedure is explained. The electron density is split into core electrons (c), bonding electrons (v) and non-bonding electrons (o). For the core electrons the atomic form factors (f_c) and the occupation factors for the first main row elements ($n = 2$) are known, whereas a Gaussian distribution is used for the charge clouds of the bonding and non-bonding electrons. The shape of

the charge clouds is then described by the factors β_{ij} which also include the true temperature factor. At low temperature this part is less than 10% of the total β_{ij} . A correction of the β_{ij} with respect to the temperature factor will be described in a subsequent publication with the aim of transforming the dynamic electron density into a static one. This will be possible even without the knowledge of neutron diffraction data, because it turns out that the xyz and the β_{ij} for the core electrons are very similar to those obtained by neutron diffraction.

Stewart (1970) has shown in a refinement, separated into *K* and *L* shells, that his results for the *K* shells are also similar to those of neutron diffraction experiments.

Experimental data and previous work

In recent years, cyanuric acid ($C_3H_3N_3O_3$), along with a few other substances, has been used as a model compound for the study of bonding electron density. Room- and low-temperature (100 K) X-ray data were collected by Verschoor & Keulen (1971). A neutron diffraction study was published by Coppens & Vos (1971). An application of the least-squares formalism which includes both one- and two-center orbital products was given by Jones, Pautler & Coppens (1972). In the present work, the low-temperature X-ray data of Verschoor & Keulen (1971) were used.

Refinement procedures

A description of the refinement method used in this work is given in part I (Hellner, 1977). In the refined models, described below, the form factors for the core electrons ($1s^2$) were taken from *International Tables for X-ray Crystallography* (1974). At the beginning, charge clouds of bonding electrons were placed at the mid-points of the bonds. Additional point charges at the core positions took account of the higher electron numbers of O and N. The smeared point charges have a Gaussian distribution. The two effects, thermal vibration and smearing of the point charge through bonding, are contained together in the usual anisotropic temperature factor and are represented as an ellipsoid.

Because of the limitations of the computing facilities and programs, the refinement was carried out with alternate parameter sets with a full-matrix program.

The quantity minimized was $\sum w(F_o - |F_c|)^2$. A weighting scheme with the weight (w) as a function of the standard deviations of the structure factors, and a unit weighting scheme were tested. Both refinements gave nearly the same results.

The refinement proceeded with five models (LQ1 to LQ5). In the first model, the positional parameters of both the bond and additional charges were kept fixed. The positional parameters and temperature factors of the core electrons ($1s^2$) and the occupation parameters of the charge clouds were allowed to vary.

The H atoms were given isotropic temperature factors. Attempts to apply anisotropic temperature factors led to unrealistic values for the magnitudes and shifts of the parameters. This was also found by Verschoor & Keulen (1971) and by Coppens & Vos (1971). *R* was 2.62% at the end of the first model refinement (LQ1).

In the second model (LQ2), the previously fixed parameters of the charge clouds were included in the refinement and an improved *R* of 2.52% was obtained. In the other models tested (LQ3–LQ5) the population parameters for the bonding charges were constrained.

With respect to the 'bonding character' the constrained populations were two, *i.e.* single bonding between C–N, C–O and N–H was assumed (LQ3). In the concept of a sharp discrimination between single and double bonding, the population parameters for C–N, N–H were given as two, while those of C–O were given as four (LQ5). An intermediate concept such as π bonding in the whole molecule was defined by the same population parameter (three) for all bonding charges (LQ4).

In Fig. 1 the geometry of the cyanuric acid molecule and the notation of the charges are presented. In the crystal the molecule possesses a twofold axis which coincides with the crystallographic twofold axis.

Results of the refinement and comparison with published data

Positional parameters

A comparison of positional parameters from various refinements is given in Table 1. In columns 1–3 the values from the refinements with the usual spherically symmetric form factors are compared [column 1 is from Verschoor & Keulen (1971), column 2 from Coppens & Vos (1971), and column 3 from the present work]. The results from neutron diffraction (Dietrich & Scheringer, 1978) and the $1s^2$ core positions from this work are in columns 4, 5 and 6 respectively. In Fig. 2(a) and (b) the asymmetric part of the molecule is given. Large-type symbols and the larger circles denote atomic positions. Small circles between bonded atoms denote bond charges. Both bond and additional charges on O and N positions are marked by L1 to L11. In

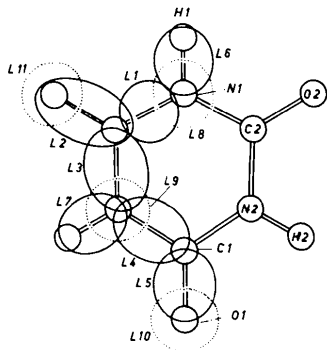


Fig. 1. The molecular frame of cyanuric acid. Small circles represent atomic-core positions. Ellipsoids of bonding electrons and additional charge clouds (dotted) introduced for O and N are labeled L1 to L11.

Table 2. Parameters of the anisotropic vibration ellipsoids ($\times 10^4 \text{ \AA}^2$) for the atoms (cores) in the crystal structure of cyanuric acid

		XR1	XR2	XR3	ND	LQ(1)	LQ(2)	RB
C(2)	U_{11}	85	78 (3)	74 (3)	100 (2)	102 (2)	107 (2)	115
	U_{22}	76	68 (2)	68 (3)	63 (2)	71 (2)	70 (2)	58
	U_{33}	81	75 (3)	71 (3)	74 (2)	83 (2)	89 (2)	80
	U_{12}	-3	-3 (2)	-4 (2)	-2 (2)	-3 (2)	-1 (2)	-2
	U_{23}	5	5 (3)	7 (2)	-2 (1)	2 (1)	3 (1)	0
C(1)	U_{13}	54	50 (2)	46 (3)	65 (2)	66 (3)	65 (3)	75
	U_{11}	109	101 (3)	96 (5)	117 (3)	120 (2)	124 (2)	136
	U_{22}	68	65 (4)	61 (4)	51 (3)	62 (2)	61 (2)	54
	U_{33}	102	95 (4)	91 (5)	98 (3)	105 (2)	112 (2)	110
	U_{13}	74	68 (4)	68 (4)	81 (2)	80 (2)	84 (2)	93
N(2)	U_{11}	146	142 (3)	140 (3)	133 (1)	147 (1)	149 (1)	121
	U_{22}	60	57 (2)	54 (2)	60 (1)	67 (1)	67 (1)	75
	U_{33}	100	94 (3)	92 (3)	95 (1)	100 (1)	102 (1)	92
	U_{12}	-1	-1 (2)	-0 (2)	-2 (1)	-5 (1)	-4 (1)	-3
	U_{23}	8	9 (2)	10 (2)	4 (1)	5 (1)	3 (1)	7
N(1)	U_{13}	96	93 (2)	92 (2)	88 (1)	97 (1)	97 (1)	81
	U_{11}	138	136 (3)	132 (4)	129 (2)	143 (2)	147 (2)	119
	U_{22}	49	40 (3)	37 (4)	55 (2)	49 (3)	52 (3)	54
	U_{33}	86	84 (4)	82 (4)	79 (2)	88 (2)	96 (2)	82
	U_{13}	83	84 (3)	82 (3)	80 (2)	90 (2)	92 (2)	78
O(2)	U_{11}	153	149 (2)	129 (3)	155 (2)	157 (1)	159 (1)	155
	U_{22}	84	80 (2)	63 (3)	73 (2)	77 (1)	84 (1)	106
	U_{33}	101	97 (2)	77 (2)	100 (2)	99 (1)	103 (1)	96
	U_{12}	-7	-7 (2)	-7 (2)	-6 (3)	-4 (1)	-2 (1)	-6
	U_{23}	-11	-11 (2)	-12 (2)	-8 (2)	-9 (1)	-7 (1)	-6
O(1)	U_{13}	99	97 (1)	84 (2)	102 (2)	101 (1)	104 (1)	100
	U_{11}	200	194 (3)	178 (5)	209 (3)	204 (3)	202 (3)	209
	U_{22}	56	53 (3)	30 (3)	55 (3)	46 (2)	52 (2)	54
	U_{33}	174	169 (4)	151 (4)	169 (2)	159 (2)	166 (2)	167
	U_{13}	134	134 (4)	124 (4)	144 (4)	141 (2)	137 (2)	145
H(2)	B		1.2 (2)	-0.3 (3)		1.0 (3)	1.5 (5)	
H(1)	B		1.7 (4)	-0.4 (2)		2.2 (4)	2.7 (8)	

The most striking agreement is between U_{ij} values from neutron diffraction and those of the $1s^2$ core electrons.

Table 3 lists the elements of the U tensors for the 'vibration' ellipsoids of the bond as well as additional charges. The contribution from thermal vibration is of the order of 5–20% (*cf.* Scheringer, 1977). The remainder describes the smearing of the charge clouds of the bonding electrons.

Hamilton test

The model structure described above was fitted to the X-ray data in a two-stage refinement procedure. Refinements with the same intensity data and with spherically symmetric atom form factors gave R values of 3.8% (Verschoor & Keulen, 1971, block-diagonal matrix), 4.18% (Coppens & Vos, 1971, full matrix) and 4.1% (present work, full matrix). In contrast, the model with separate bond electron density distributions converged to 2.62 and 2.52% for the refinements LQ1 and LQ2 respectively. The question arises as to whether this drop in R is significant.

A suitable method for answering this question is provided by the Hamilton (1965) test. The number of

structure factors F_{hkl} is 942 (X-ray data) and the number of variable parameters, including a scale factor, is 118, when the positional parameters of the interatomic charges are kept fixed. The reference quantity is $R_c = 3.8\%$ from Verschoor & Keulen (1971), with 49 variable parameters. The ratio of R for the two refinements is $3.8/2.62 = 1.4504$. The Hamilton quotient for a 0.5% significance level is 1.060. From this point of view the proposed refinement model has a real basis. In addition, the change in R from 2.62 to 2.52% on increasing the number of refined parameters from 118 to 141 is hardly significant (the corresponding Hamilton quotients are still 1.0397 and 1.028).

The models LQ3–LQ5 are restrained with respect to the LQ1 model. As shown in Table 4, these models give higher values of R , *i.e.* $R(\text{LQ1}) = 0.0262$, $R(\text{LQ3}) = 0.0296$, $R(\text{LQ4}) = 0.0323$ and $R(\text{LQ5}) = 0.030$. The appropriate ratios are $R(\text{LQ3})/R(\text{LQ1}) = 1.130$, $R(\text{LQ4})/R(\text{LQ1}) = 1.233$ and $R(\text{LQ5})/R(\text{LQ1}) = 1.145$. The number of parameters refined decreases for all three constrained models from 118 to 61. R , obtained by interpretation for the parameter difference $118 - 61 = 57$ and $942 - 61 = 881$ degrees of freedom, is 1.048 at the 0.005 level. The increase of R for the constrained models LQ3, LQ4 and LQ5 is

Table 3. Parameters U_{ij} ($\times 10^3 \text{ \AA}^2$) for the sum of thermal-vibration and charge-distribution ellipsoids, and charge populations for bonding electrons in cyanuric acid

		LQ1		LQ2	
	U_{ij}	Popula- tion	U_{ij}	Popula- tion	
L1 [N(1)-C(2)]	U_{11}	167 (7)	190 (6)	1.20	1.20
	U_{22}	99 (7)	142 (8)		
	U_{33}	128 (6)	155 (8)		
	U_{12}	6 (4)	-2 (4)		
	U_{23}	10 (4)	2 (6)		
L2 [C(2)-O(2)]	U_{13}	112 (6)	131 (5)	2.63	2.63
	U_{11}	192 (4)	201 (5)		
	U_{22}	196 (8)	170 (13)		
	U_{33}	324 (12)	285 (20)		
	U_{12}	-3 (4)	-4 (5)		
	U_{23}	103 (7)	53 (14)		
	U_{13}	122 (6)	144 (7)		
L3 [C(2)-N(2)]	U_{11}	185 (5)	190 (5)	1.75	1.75
	U_{22}	162 (12)	210 (36)		
	U_{33}	156 (5)	166 (4)		
	U_{12}	-15 (5)	-12 (6)		
	U_{23}	-4 (5)	14 (6)		
	U_{13}	119 (4)	119 (4)		
L4 [N(2)-C(1)]	U_{11}	172 (4)	189 (4)	1.74	1.74
	U_{22}	168 (17)	156 (18)		
	U_{33}	179 (12)	183 (15)		
	U_{12}	-7 (4)	-4 (4)		
	U_{23}	34 (13)	18 (15)		
	U_{13}	103 (5)	117 (6)		
L5 [C(1)-O(1)]	U_{11}	200 (9)	218 (8)	0.74	0.74
	U_{22}	149 (35)	168 (51)		
	U_{33}	145 (6)	153 (5)		
	U_{13}	123 (6)	130 (5)		
L6 [N(1)-H(1)]	U_{11}	90 (11)	113 (9)	0.15	0.79
	U_{22}	86 (10)	174 (46)		
	U_{33}	77 (11)	109 (9)		
	U_{13}	58 (8)	69 (7)		
L7 [N(2)-H(2)]	U_{11}	114 (6)	170 (5)	0.55	1.03
	U_{22}	94 (6)	121 (11)		
	U_{33}	93 (5)	149 (17)		
	U_{12}	-6 (4)	-4 (5)		
	U_{23}	2 (4)	-30 (11)		
	U_{13}	76 (5)	84 (6)		
L8 [N(1)]	U_{11}	198 (3)	210 (5)	3.77	3.03
	U_{22}	160 (5)	157 (7)		
	U_{33}	163 (4)	160 (5)		
	U_{13}	128 (3)	136 (4)		
L9 [N(2)]	U_{11}	196 (4)	216 (7)	2.46	2.29
	U_{22}	122 (3)	137 (4)		
	U_{33}	154 (3)	174 (5)		
	U_{12}	1 (2)	2 (3)		
	U_{23}	-3 (2)	3 (3)		
	U_{13}	126 (3)	140 (5)		
L10 [O(1)]	U_{11}	137 (2)	142 (2)	4.82	4.76
	U_{22}	116 (2)	115 (2)		
	U_{33}	144 (1)	152 (2)		
	U_{13}	91 (1)	95 (1)		
L11 [O(2)]	U_{11}	122 (1)	129 (1)	3.94	4.37
	U_{22}	133 (1)	137 (1)		
	U_{33}	118 (1)	126 (1)		
	U_{12}	-1 (1)	-1 (2)		
	U_{23}	-11 (1)	-10 (1)		
	U_{13}	80 (2)	83 (2)		

Table 4. Population parameters L_{ij} for the core and bonding electrons based on different refinements

Atom or charge	LQ1	LQ2	LQ3 $L_{ij} = 2e$	LQ4 $L_{ij} = 3e$	LQ5
					$L_{C=O} = 4e$ $L_{N-C} = 2e$ $L_{N-H} = 2e$
C(2)	2.00	2.00	2.00	2.00	2.00
C(1)	2.00	2.00	2.00	2.00	2.00
N(2)	4.46	4.29	3.62	4.24	3.55
N(1)	5.77	5.03	3.78	3.00	3.29
O(2)	5.94	6.37	6.78	7.14	6.91
O(1)	6.82	6.76	7.20	7.36	7.10
H(2)	1.00	0.42	0.50	0.00	0.00
H(1)	1.00	0.52	0.51	0.00	0.00
C(1)-N(2)	1.88	1.74	2.00	3.00	2.00
C(2)-N(2)	1.54	1.75	2.00	3.00	2.00
C(2)-N(1)	0.77	1.20	2.00	3.00	2.00
C(2)-O(2)	3.30	2.63	2.00	3.00	4.00
C(1)-O(1)	0.74	1.88	2.00	3.00	4.00
N(2)-H(2)	0.55	1.03	2.00	3.00	2.00
N(1)-H(1)	0.15	0.79	2.00	3.00	2.00
Electron sum for the half molecule	29.68	29.93	31.64	37.56	33.66
Number of parameters	117	140	60	60	60
$R(F)\%$	2.62	2.52	2.96	3.23	3.00
$R_w(F)\%$	1.67	1.60	2.20	2.44	2.33

therefore highly significant and excludes these models from further detailed considerations.

Bonding effects

In the model described above it has been shown that it is possible to refine core and bonding electrons separately. In this way it was possible to reach a better agreement between observed and calculated X-ray intensities. The ellipsoids of vibration for the charge clouds of bonding electrons and additional charges at N and O positions (dotted lines) are given schematically in Fig. 1. The U tensors describing these ellipsoids and the occupation parameters are given in Tables 3 and 4.

For C(1) and C(2), no additional charges were found to be necessary. It can be seen from Fig. 1 that the bonding electrons also make contributions at their core positions and therefore influence the total charge there.

Larger discrepancies arise when constraints are applied to the occupation parameters, as is shown in the refinements LQ3 to LQ5 for the O and N atoms (Table 4). For the models LQ1 and LQ2 (without constraints for charges) the charge distributions at the core positions are comparable. The magnitudes of the deviations are higher in LQ1 than in LQ2. In particular, the occupation parameter of N(2) is markedly smaller than that of N(1).

When the positional parameters of the bonding electrons are allowed to vary, the occupation parameters are also found to change. This is seen in the

Table 5. *Population parameters for the atoms and bonding electrons in cyanuric acid*

Columns I-H and IV-H are those from Jones, Pautler & Coppens (1972). Columns LQ1 and LQ2 refer to the present work.

Atom or charge	I-H	IV-H	LQ1	LQ2
C(2)	5.26	4.68	2.00	2.00
C(1)	5.15	4.64	2.00	2.00
N(2)	6.41	5.79	4.46	4.29
N(1)	6.41	5.77	5.77	5.03
O(2)	7.57	7.21	5.94	6.37
O(1)	7.42	6.93	6.82	6.76
H(2)	0.09	0.68	1.00	0.42
H(1)	-0.29	0.79	1.00	0.52
C(1)-N(2)	0.73	0.47	1.88	1.74
C(2)-N(2)	1.02	1.11	1.54	1.75
C(2)-N(1)	1.07	0.90	0.77	1.20
C(2)-O(2)	0.58	0.72	3.30	2.63
C(1)-O(1)	0.95	1.59	0.74	1.88
N(2)-H(2)	0.46	1.11	0.55	1.03
N(1)-H(1)	-0.11	0.94	0.15	0.079
$R(F)\%$	2.6	3.5	2.62	2.52
$R_w(F)\%$	1.8	3.0	1.67	1.60
Number of positional parameters for the <i>K</i> -shell electrons			16	16
Number of temperature parameters for the <i>K</i> -shell electrons			32	32
Number of positional parameters for the charge clouds			0	21
Number of parameters for the smearing ellipsoids of the charge clouds			58	58
Number of occupation parameters for the charge clouds			11	13
Sum of the refined parameters	62	44	117	140

differences of the resultant occupancies in LQ1 and LQ2. In particular, those of C(2)-O(2) and C(1)-O(1) achieve the more reliable values of 1.20, 2.63 and 1.88 e instead of 0.77, 3.30 and 0.74 e.

As a result of the refinement LQ2 the largest occupation parameter for a charge cloud of bonding electrons is that for C(2)-O(2) with a value of 2.63 e while for C(1)-O(1) the corresponding value is 1.88 e. The occupation parameters for the various C-N bonds lie in the range 1.20-1.75 e, and for the N-H bonds in the range 0.79-1.03 e.

Because of the correlation between the scale factor and the occupation parameters, and the discrepancies mentioned above, the magnitudes of these parameters are only relative. Measurements of absolute intensities are necessary to overcome this limitation.

Comparison of occupation parameters

Occupation parameters for cyanuric acid were given by Jones, Pautler & Coppens (1972). Their results were obtained from atomic-orbital calculations using

Hartree-Fock and Slater-type basis functions, and lead to a 'two-center formalism' for the molecular orbitals. The refinements were carried out with 62, 49 and 44 parameters. For the refinement with Hartree-Fock-type functions similar occupation parameters were obtained for equivalent bonded atoms. In addition, the occupation parameters of the one-centered p_z^2 orbitals for C, N, and O were closely similar. In spite of higher values of R (3.1 and 3.5%), the refinements with fewer parameters (49 and 44) gave better occupation parameters for the O bonds. Correlation effects in the refinement prevented a direct comparison with theoretical results.

The results of the two refinements performed by Jones, Pautler & Coppens (1972) and those from the present work are given in Table 5. In general, the occupation parameters show a large variational spread, so that the question arises as to the physical meaning of these results.

The models LQ3 with the fixed population parameter $n = 2$ for the charge clouds, LQ4 with $n = 3$, and LQ5 with $n = 2$ and $n_{c-o} = 4$, show definite differences in the final results which can be obtained from the same set of X-ray data (Table 4), but the total sum of the charges in the electron density map is not of help for proving the validity of occupation parameters; this result is also true for theoretically derived parameters.

In our case there are some arguments against the results of the restrained models LQ3, LQ4 and LQ5. The total number of electrons is either decreased (LQ3, LQ5) as in the models LQ1 and LQ2 or increased up to 37 (LQ4) instead of 33 electrons per asymmetric unit. Although the total number of electrons varies in the same order in the different models, the values of R of the restrained models are markedly higher than those of LQ1 and LQ2. As mentioned in the previous section, the derived Hamilton values demonstrate the rejection of the restrained models LQ3, LQ4 and LQ5. The truth seems to be not too far from model LQ2, a suggestion that could be better substantiated with a data set of absolute intensities.

The models proposed in this paper require a maximum of 17 parameters for the electron occupations, result in good values of R , give positional and vibrational parameters for the $1s^2$ electrons which approach those from neutron diffraction, and allow a good resolution of the difference density of bonding electrons. Further models for the refinement are probably possible. The method described here, in which charge clouds of bonding electrons are represented by Gaussian distributions, can only be a first step to a description of bonding-electron distributions. An important step would be the determination of occupation and positional parameters by different physical methods, so that it would be possible to decide between the various approaches to the interpretation of the

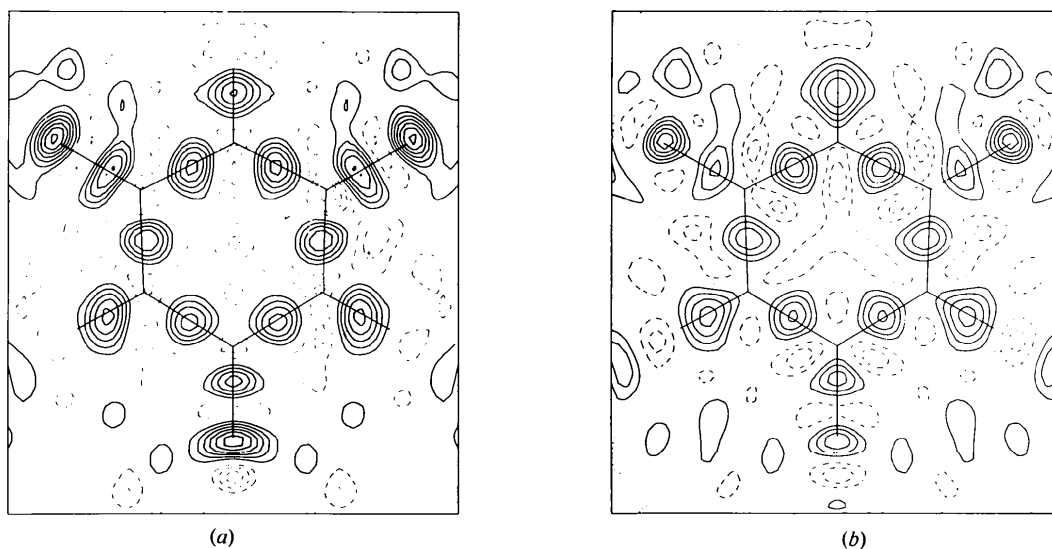


Fig. 3. Comparison of difference syntheses. (a) $F_x - F_v$ synthesis as described in the text. (b) $F_x - F_k$ synthesis as described in the text. All sections are through the molecular plane; contour intervals are $0.10 e \text{ \AA}^{-3}$. Zero contours are dotted, negative contours are shown as broken lines.

electron density. A comparison with the results of Jones, Pautler & Coppens (1972), where occupation parameters were determined for several orbital products by means of X-ray diffraction data, does not appear to be sufficient for this purpose.

Difference synthesis

In Fig. 3 two difference syntheses are shown side by side. Fig. 3(a) gives the $F_x - F_v$ synthesis with the experimental X-ray data of Verschoor & Keulen (1971) and the core parameters given by Dietrich & Scheringer (1978) who carried out a new refinement with the neutron data of Coppens & Vos (1971). Fig. 3(b) is equivalent to Fig. 3(a) except for the fact that the positional and thermal parameters of the $1s^2$ electrons (K -shell parameters) of model LQ2 are used, and hence Fig. 3(b) is denoted as a $F_x - F_k$ synthesis.

The agreement between the two maps is very good for the bonding electrons. Small deviations occur in the lone-pair regions of the O atoms. The form of this charge distribution found in Fig. 3(b) is more concentrated whilst that given with the neutron diffraction parameters seems to broaden the asphericity of the lone pairs around the O atoms.

Conclusion

The simple refinement described above leads to occupation parameters and density distributions for bonding electrons which, if at all physically meaningful, represent a first gross approximation. The results are comparable with those obtained by Jones, Pautler &

Coppens (1972) in their analysis of occupation parameters of orbital products. The latter are always lower, if not negative, for bond populations. The difference syntheses give equally good results for both ways of approach. The simple refinement described in this paper may be continued and expanded in the following way: the lone-pair electrons on the O atoms may be considered separately; the charge clouds of the bonding electrons may be given occupancies of 2 e each; and separate π -electron clouds may be introduced.

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