Coppens, P. (1975). *Phys. Rev. Lett.* **35**, 98–100.

Duijneveldt, F. B. van (1971). *Gaussian Basis Sets for the Atoms* H–Ne *for Use in Molecular Calculations.* IBM Publ. RJ945 (No. 16437).

Fletcher, R. & Powell, M. J. D. (1963). *Comput. J.* **6**, 163–168.

Hariharan, P. C. & Pople, J. A. (1973). *Theor. Chim. Acta*, **28**, 213–222.

Hehre, W. J., Stewart, R. F. & Pople, J. A. (1969). *J. Chem. Phys.* **51**, 2657–2664.

Kurki-Suonio, K. & Salmo, P. (1971). *Ann. Acad. Sci. Fenn. Ser. A*6, No. 269, 25 pp.

Møller, C. & Plesset, N. S. (1934). *Phys. Rev.* **46**, 618–622.

Mulliken, R. S. (1955). *J. Chem. Phys.* **23**, 1833–1840.

Pople, J. A. & Gordon, M. S. (1967). *J. Am. Chem. Soc.* **89**, 4253–4261.

Pople, J. A. & Nesbet, R. K. (1954). *J. Chem. Phys.* **22**, 571–572.

Seeger, R. & Pople, J. A. (1975). *J. Chem. Phys.* **62**, 4566.

Srebrenik, S. & Bader, R. F. W. (1975). *J. Chem. Phys.* **63**, 3945–3961.

Stewart, R. F. (1969). *J. Chem. Phys.* **50**, 2485–2495.

Stewart, R. F. (1970*a*). *J. Chem. Phys.* **53**, 205–213.

Stewart, R. F. (1970*b*). *J. Chem. Phys.* **52**, 431–438.

Acta Cryst. (1978). A**34**, 648–651

The Projection of Molecular Charge Density into Spherical Atoms. II. An Application to X-ray Diffraction Data

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Standard density basis functions for hydrogen and the first-row atoms have been converted to *K*-shell and *L*-shell scattering factors. With the *K* shell fixed at two electrons, these scattering factors have been used for atomic-charge analysis of X-ray structure factors by the method of least squares. Results for cyanuric acid and uracil are given. The net charges for these cyclic amides are in reasonable agreement. It is recommended that scattering factors here be used for atomic-charge analysis of first-row atoms in routine structure refinements of chemically related molecular crystals.

Introduction

In the previous paper (Yáñez, Stewart & Pople, 1978), a set of atomic-density basis functions for first-row atoms were developed for a population analysis of molecular charge densities. These functions can be transformed into suitable scattering factors so that X-ray structure factors may be analyzed for atomic charges by the *L*-shell projection method (Stewart, 1970; Coppens, Pautler & Griffin, 1971).

We report below application of these form factors to atomic charge analysis of cyanuric acid and uracil. These two molecular crystals are closely related chemically since they are cyclic amides. In the present work the scattering factors have not been scaled, although this variation could be easily incorporated into the least-squares equations. The spirit of the approach is to use standard density basis functions for an atomic population analysis of chemically related molecules.

Refinement model and X-ray scattering factors

The atomic scattering factor is split into *K*-shell and *L*-shell functions for the first-row atoms. For the H atom, only a *K*-shell function is used. The outer shell is assigned a variable population parameter and the *K* shell is frozen with a charge content of two electrons. The structure factor model is

$$F_{\mathbf{h}} = \sum_{\text{sym}} \sum_{p=1}^{N} [kf_{pK}(S) + P_p f_{pL}(S)] \exp(2\pi i \mathbf{h}^t \mathbf{x}_p) \exp(-\tfrac{1}{2}\mathbf{S}^t \mathbf{U}_p \mathbf{S}) \qquad (1)$$

where P_p, $\mathbf{x}_p$ and $\mathbf{U}_p$ are least-squares parameters for atom p and k is the overall scale factor. The charge of atom p is

$$q_p = 2 + P_p/k. \qquad (2)$$

In the least-squares fit of (1) to observed structure factors, the inhomogeneous terms for the solution of P_q are,

$$I_q = \sum_{\mathbf{h}} W_{\mathbf{h}} F_{\mathbf{h}}^{\text{OBS}} f_{qL}(S) \exp(-\tfrac{1}{2}\mathbf{S}^t \mathbf{U}_p \mathbf{S}) \exp(-2\pi i \mathbf{h}^t \mathbf{x}_p) \quad (3)$$

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for $q = 1, 2, \ldots N$. We see that (3) is a projection of charge from the $F_{\mathbf{h}}^{\mathrm{OBS}}$ into the form factor. $f_{qL}(S) \exp(-\frac{1}{2}\mathbf{S}^t\mathbf{U}_q\mathbf{S})$, centered at $\mathbf{x}_q$. (The $W_{\mathbf{h}}$ are statistical weights.) The populations determined from (3) are therefore the charge content for an L-shell function convoluted onto anisotropic nuclear motion. To the extent that the density shell function is rigid with respect to the assumed harmonic motion of the nucleus, one may infer that the atomic charges are characteristic of a static molecular density at the equilibrium nuclear configuration. If the overlap of the vibrationally averaged L-shell functions among the atoms is small, then I_q in (3) primarily determines the population for the qth L-shell function. A small overlap will result in small correlation coefficients for the atomic populations.

In addition to (3), one may also constrain the P_p to satisfy the charge-neutrality condition,

$$\sum_{\mathrm{sym}} \sum_{p=1}^{N} P_p = kF_v(000) \tag{4}$$

where F_v is the total valence-charge density in the unit cell.

Table 1. *Coefficients for analytical scattering factor for molecular optimized* H

The power of 10 is given in parentheses.

j	a_j	b_j
1	1·140900 (−3)	1·737600 (−1)
2	2·075760 (−2)	9·483017 (−1)
3	1·547741 (−1)	3·396069
4	4·776157 (−1)	9·955427
5	3·457117 (−1)	2·650937 (1)

The scattering-factor functions are analytical with the form

$$f(y) = \sum_j a_j \exp(-b_j y^2) \tag{5}$$

where $y = \sin\theta/\lambda(\text{Å}^{-1})$. The coefficients for the H atom are given in Table 1. For the first-row atoms, coefficients for both K and L functions are tabulated in Table 2. The L functions are normalized to one electron, but the K functions are normalized to two electrons. These scattering factors were constructed from Tables 1, 4 and 5 in the previous paper (Yáñez, Stewart & Pople, 1978). The K functions are rather similar to the core scattering factors given by Stewart (1970). On the other hand, the L functions are somewhat different from the L-shell scattering factors previously reported (Stewart, 1970). The H scattering factor in Table 1 is rather more diffuse (more contracted in direct space) than the bonded H atom form factor tabulated by Stewart, Davidson & Simpson (1965).

Results and discussion

(*a*) *Cyanuric acid*

X-ray structure factors (not absolute) for cyanuric acid at low temperature (~100 K) were taken from Verschoor & Keulen (1971). The first study consisted of determination of the population parameters only, where atomic coordinates and anisotropic thermal parameters were taken from the neutron diffraction results of Coppens & Vos (1971). [A scale of 0·728 for the U_{ij} (neutron) was used as discussed by Coppens & Vos (1971).] In this case the population parameters were constrained to satisfy (4). The net charges for the atoms are given in the second column of Table 3. The

Table 2. *Coefficients for analytical scattering factors for density basis functions of first-row atoms*

The power of 10 is given in parentheses.

	Shell	a_1	b_1	a_2	b_2	a_3	b_3
Li	*K*	6·347853 (−2)	1·836200 (−1)	6·835616 (−1)	1·030926	1·252959	4·163501
	L	−1·165096 (−1)	1·061410 (1)	1·116510	7·318018 (1)		
Be	*K*	6·197620 (−2)	9·870135 (−2)	6·828745 (−1)	5·510795 (−1)	1·255149	2·176170
	L	7·621377 (−2)	1·037368	−1·396805 (−1)	2·433623	1·063467	4·148705 (1)
B	*K*	6·132441 (−2)	6·164183 (−2)	6·838936 (−1)	3·430694 (−1)	1·254782	1·338895
	L	2·822430 (−2)	4·336438 (−1)	−7·44450 (−2)	1·812982	1·046221	2·416730 (1)
C	*K*	6·090121 (−2)	4·214602 (−2)	6·853655 (−1)	2·340944 (−1)	1·253733	9·080083 (−1)
	L	1·694613 (−2)	2·796505 (−1)	−4·945220 (−2)	1·461999	1·032506	1·823823 (1)
N	*K*	6·068809 (−2)	3·063524 (−2)	6·856238 (−1)	1·699233 (−1)	1·253688	6·552875 (−1)
	L	4·162408 (−3)	9·137451 (−2)	9·149545 (−1)	1·527570 (1)	8·088309 (−2)	8·730390 (1)
O	*K*	6·062425 (−2)	2·330354 (−2)	6·870775 (−1)	1·291322 (−1)	1·252298	4·964753 (−1)
	L	3·560802 (−3)	6·712168 (−2)	8·575924 (−1)	1·054964 (1)	1·388468 (−1)	4·851259 (1)
F	*K*	6·061261 (−2)	1·832896 (−2)	6·884314 (−1)	1·014886 (−1)	1·250956	3·893362 (−1)
	L	3·014597 (−3)	4·946053 (−2)	8·118403 (−1)	7·458641	1·851451 (−1)	3·088916 (1)

Table 3. *Net atomic charges for cyanuric acid*

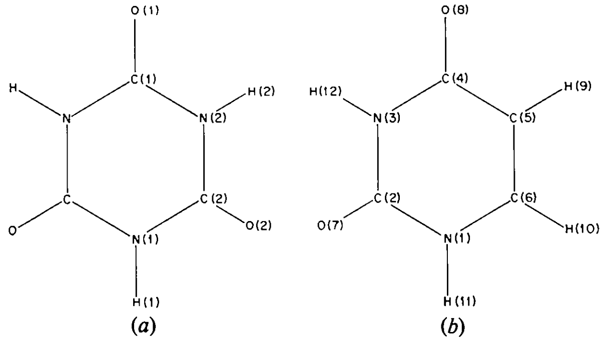
The estimated standard deviation for the last digit is given in parentheses.

	Neutron (constrained)	X-ray (unconstrained)	X-ray (constrained)
O(1)	−0·49 (4)	−0·47 (5)	−0·45 (4)
O(2)	−0·42 (4)	−0·30 (4)	−0·27 (4)
N(1)	−0·53 (7)	−0·56 (8)	−0·56 (6)
N(2)	−0·66 (5)	−0·57 (7)	−0·57 (5)
C(1)	+0·85 (6)	+0·70 (7)	+0·67 (5)
C(2)	+0·71 (4)	+0·67 (5)	+0·65 (4)
H(1)	+0·26 (4)	+0·22 (5)	+0·22 (5)
H(2)	+0·33 (4)	+0·26 (4)	+0·25 (4)
R (%)*	4·5	3·5	3·5
R_w (%)†	4·5	3·2	3·2
Observations	933	933	933
Variables	8	57	56

* $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$.

† $R_w=(\Sigma\,w|F_o-F_c|^2/\Sigma\,w|F_o|^2)^{1/2}$.

atomic numbering, given in column 1, is displayed in Fig. 1 for the cyanuric acid molecule. The atoms O(1), C(1), N(1) and H(1) lie on a twofold axis in the crystal. A second study was a full-matrix least-squares refinement of atomic positions, mean-square amplitudes of vibration and charges without the relative-neutrality constraint, (4). For this result, the valence charges summed to 98·5% of total valence charge. The charge parameters were subsequently scaled by 1·015. The corresponding net charges are listed under column 3 in Table 3. A similar refinement, subject to (4), was carried out, the results of which are tabulated under column 4 in Table 3. As expected, the net charges in columns 3 and 4 are in virtual agreement. On the other hand, O(2) and C(1) have rather different net charges when based upon neutron coordinates compared with corresponding X-ray values. The X-ray coordinates found in the present refinement with the scattering factors in Tables 1 and 2 are all within one standard deviation of the values reported by Verschoor & Keulen (1971). The small differences in the neutron and X-ray structures have been discussed by Coppens & Vos (1971) and need not be included here.



(*a*) (*b*)

Fig. 1. Numbering of the atoms for (*a*) cyanuric acid and (*b*) uracil.

For the X-ray refinements, anisotropic thermal parameters were assigned to C, N and O atoms, but only isotropic vibrational parameters were assigned to the H atoms. For the heavy atoms, the U_{ij} values were comparable to those reported by Verschoor & Keulen (1971). This reflects the similarity of the K-shell scattering factors in Table 2 with SCF atomic-core scattering factors. On the other hand the $\langle U_{\rm H}^2\rangle$ values for the H atoms in this study are ~0·005 Å^2 lower than the values reported by Verschoor & Keulen (1971). This result crudely corresponds to a scaling of Gaussian exponents in the H atom density function by 1·03. Although refinement of $\langle U_{\rm H}^2\rangle$ can mimic the scaling of the H atom scattering factor, it does not give rise to the same least-squares relations for a parameter that multiplies the b_j in Table 1. In any event the correlation parameter between $P_{\rm H}$ and $\langle U_{\rm H}^2\rangle$ is typically 0·8. This means that $P_{\rm H}$ is characteristic of a thermally smeared H atom density function and that $\langle U_{\rm H}^2\rangle$ does not give a simple estimate of the mean square amplitude of vibration for the proton.

(*b*) *Uracil*

Structure factors (not absolute) for uracil, based on room-temperature X-ray diffraction data, were taken from Stewart & Jensen (1967). Full-matrix least-squares refinements with atomic coordinates, thermal parameters, and populations were carried out as for cyanuric acid. The atomic net charges are given in Table 4 under columns 2 and 3. The atomic numbering is shown in Fig. 1. For the unconstrained refinement, 98·4% of the valence charge was accounted for. Both positions and anisotropic thermal parameters agree with the values reported by Stewart & Jensen (1967). The H atom coordinates differed by less than twice the

Table 4. *Net atomic charges for uracil*

The estimated standard deviations for the last digit are given in parentheses.

	X-ray (unconstrained)	X-ray (constrained)
O(7)	−0·45 (4)	−0·43 (3)
O(8)	−0·45 (4)	−0·43 (3)
N(1)	−0·61 (5)	−0·60 (5)
N(3)	−0·62 (5)	−0·62 (4)
C(2)	+0·66 (4)	+0·64 (4)
C(4)	+0·52 (4)	+0·51 (3)
C(5)	−0·14 (5)	−0·15 (5)
C(6)	+0·43 (6)	+0·42 (5)
H(9)	+0·11 (5)	+0·11 (5)
H(10)	−0·01 (5)	−0·01 (5)
H(11)	+0·26 (5)	+0·25 (5)
H(12)	+0·31 (5)	+0·32 (5)
R (%)	3·9	3·9
R_w (%)	3·1	3·1
Observations	1163	1163
Variables	101	100

estimated standard deviations. On the other hand, $\langle U_{\rm H}^2 \rangle$ was ~0·004 Å^2 less than $\langle U_{\rm H}^2 \rangle$ found with a standard refinement. The correlation coefficients between $P_{\rm H}$ and $\langle U_{\rm H}^2 \rangle$ were 0·83 for all four H atoms. Thus the interpretation for the H atoms in uracil is the same as for cyanuric acid (see above).

The dipole moment implied by the charges under column 3 of Table 4 is 4·4 ± 1·3D and at an angle of 66 ± 13° from the N(1)–C(4) internuclear vector towards N(3). This result is very similar to the previous estimate (Stewart, 1970).

(*c*) *Comparison of charges for cyanuric acid and uracil*

The net charges from the X-ray refinements of the two molecular crystals (Tables 3 and 4) are to be compared. The amide N atoms and the correspondingly bonded H atoms for the two compounds have the same net charges within the estimated standard deviations. Both O atoms of uracil and O(1) of cyanuric acid are also the same. On the other hand, O(2) for cyanuric acid has a rather lower net negative charge. It seems unlikely that this is a lattice effect. It may reflect deficiencies in our refinement model or some peculiar error in the data. The net charge for C(2) in uracil is in good agreement with both C atoms in cyanuric acid. The difference in C(4) is probably a genuine chemical effect in uracil since it is conjugated with the C(5)–C(6) double bond in contrast to the corresponding amide linkage in cyanuric acid.

Conclusions

The population analysis procedure in this paper can be easily incorporated into standard structure refinement methods. By fixing the valence charge of the *L* shells in Table 2 to neutral atoms one would have scattering factors suitable for most first-row-atom structure analyses. A final refinement that includes population analysis would entail *N* (for *N* atoms) additional parameters or *N*-1 for the constrained case. It is recommended that this type of population analysis be carried out for similar types of chemical compounds. Also it would be desirable to seek correlations of the atomic charges by this method with other methods such as ^{13}C chemical shifts or ESCA studies. Based on the comparison here of data from cyanuric acid (100 K) and uracil (300 K) it appears that low-temperature data, although desirable, are not essential for an atomic valence charge analysis of these types of organic molecular crystals. Both data sets, however, extend beyond the Cu $K\bar{\alpha}$ sphere out to ~0·8 Å^{-1} in $\sin \theta/\lambda$. Lastly, we point out that projections into the present *L*-shell density functions give a somewhat more polar description of the atoms than earlier work (Stewart, 1970; Coppens, Pautler & Griffin, 1971). The net charges listed in Tables 2 and 3 are somewhat closer in agreement to previous *ab initio* calculations (Stewart, 1970). It is also interesting that unconstrained refinements account for more than 98% of the valence charge for the two examples covered here.

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References

Coppens, P., Pautler, D. & Griffin, J. F. (1971). *J. Am. Chem. Soc.* **93**, 1051–1058.

Coppens, P. & Vos, A. (1971). *Acta Cryst.* **B27**, 146–158.

Stewart, R. F. (1970). *J. Chem. Phys.* **53**, 205–213.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Stewart, R. F. & Jensen, L. H. (1967). *Acta Cryst.* **23**, 1102–1105.

Veschoor, G. C. & Keulen, E. (1971). *Acta Cryst.* **B27**, 134–145.

Yáñez, M., Stewart, R. F. & Pople, J. A. (1978). *Acta Cryst.* **A34**, 641–648.