

## The Electron-Density Distribution in 1,3,5-Triacetylbenzene

BY B. H. O'CONNOR\* AND E. N. MASLEN

Department of Physics, University of Western Australia, Nedlands, Western Australia

(Received 2 April 1973; accepted 18 September 1973)

The electron-density distribution in crystalline 1,3,5-triacetylbenzene,  $C_6H_3(O.CO.CH_3)_3$ , has been analysed using combined X-ray and neutron diffraction data. Population coefficients for the valence electron density distribution were determined with Hartree-Fock and Slater-type orbitals, the latter giving the more acceptable results. Charge movements evident from the STO refinement are in accordance with the bonding arrangement. The carbonyl bonds are strongly polar and there is a regular alternation of charges throughout the molecule. The gross atomic populations are in agreement with semi-empirical theoretical calculations. The distributions surrounding the trigonally bonded sites appear to be concentrated more heavily in the bond plane than in the corresponding atomic systems, resulting in a local quadrupole around the carbon nuclei.

### Introduction

Diffraction data are usually analysed in terms of parameters which describe a set of positions and mean square vibration amplitudes for the atomic centres in the diffracting material. In the case of X-ray diffraction, for which the structure factor is given by the Fourier transform of the time-average electron density, the parameter set may be extended to include terms describing the 'at-rest' density, *i.e.* the electron distribution for the hypothetical situation of static nuclei. This provides information on the redistribution of electron density due to chemical bonding and intermolecular forces.

A technique for such analyses has been proposed by Stewart (1969*b*, 1970*b*) in which the electron density is expressed in the form

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}),$$

where the  $\chi$  are a set of basis functions, and the  $P_{\mu\nu}$  are population coefficients which may be determined by least-squares analysis of the diffraction data in the usual manner.

The present paper, which describes the application of these techniques to a symmetrically substituted benzene derivative, is the first of a series of investigations on similar compounds. These compounds frequently have two or more regions within the asymmetric unit of the crystal structure which are chemically equivalent, except for the effect of intermolecular forces. This redundancy provides a check on the validity of any conclusions which may be drawn, and averaging over chemically equivalent regions gives greater accuracy than would otherwise have been obtained.

The structure of 1,3,5-triacetylbenzene was estab-

lished previously by conventional X-ray (O'Connor, 1973) and neutron diffraction (O'Connor & Moore, 1973) methods.

### Basis functions

Scattering amplitudes are determined by the Fourier transform of the electron density, and population coefficients for charge densities are defined in terms of density basis functions. Nevertheless comparison with theory is facilitated if the density functions are constructed from atomic amplitude functions, *i.e.* atomic orbitals. This is compatible with the Linear Combination of Atomic Orbitals approach to the evaluation of molecular wave functions.

Two types of atomic functions are in common use for this purpose – atomic self consistent field (SCF) and Slater-type orbitals (STO). The SCF functions, which are optimized to give self-consistent field solutions to Schrodinger's equation in the atomic case, have been tabulated by Clementi (1965). Their principle disadvantage is that, as numerical functions, they cannot be manipulated readily by analytical methods. The STO functions have simple analytic forms, but are less convenient for accurate calculations on atomic systems. Single term STO functions are not orthogonal in general, but may be orthogonalized by the Schmidt procedure. The density functions corresponding to orthogonal orbitals are not necessarily orthogonal. Sets of density functions with the orthogonality property may be derived, but these are not readily interpreted in terms of atomic wave functions. Observed and calculated electron densities are compared more readily by projecting both onto the same simple set of density basis functions. This set need not necessarily be orthogonal, but must span the space efficiently, which implies near-orthogonality.

In molecules where the electron density is strongly perturbed by chemical bonding, atomic SCF orbitals do not retain their self-consistent field character, and

\* Present address: Department of Physics, Western Australian Institute of Technology, Bentley, Western Australia.

in view of their simplicity the STO's may be preferred for the construction of the density basis functions. Operationally the STO's have an additional attraction for work of the present type. The  $2s$  function vanishes at a radial atomic coordinate of zero, whereas the corresponding SCF function has a cusp at the origin. In a diffraction analysis the corresponding regions of space are the atomic centres which are strongly biased by residual scale and temperature factor errors (Maslen, 1968; Stewart, 1968). Population coefficients based on STO's should be affected less strongly by such errors than those based on SCF functions.

In calculating scattering cross sections, the Fourier transforms of products of orbitals must be evaluated. The transforms may be evaluated efficiently by representing the orbital as a series of Gaussian terms, with a length adjusted according to the accuracy required. Gaussian approximations to the atomic SCF and STO orbitals suitable for diffraction calculations have been evaluated by Stewart (1969*a*, 1970*a*). Their use in the calculation of molecular wave functions is discussed by Hehre, Stewart & Pople (1969), and the transformation properties are described by Stewart (1969*b*).

#### Electron-density model

In principle the set of products  $\chi_\mu\chi_\nu$  should be complete, but this involves more population coefficients than can be determined reliably from the analysis of diffraction data. In practice we attempt to select the minimum set that gives a representation of the electron density comparable in accuracy with that of the experimental data.

Theoretical calculations on molecular systems (*e.g.* Clementi, 1967) have shown that the  $1s^2$  core for the first row atoms is almost invariant to chemical bonding. We may regard the density distribution for a molecular system formed from such atoms as comprising a set of atomic cores plus a valence distribution. At the minimum basis set level we might hope to define the valence distribution in terms of a  $2s$  and three orthogonal  $2p$  functions for atoms such as carbon and oxygen and a  $1s$  function for hydrogen. In a charge-density analysis, however, some of the orbital products generated from a minimal basis set of atomic orbitals project into one another with high efficiency. The corresponding population parameters are highly correlated, so that some of these parameters are redundant.

A drastic reduction in the number of coefficients is achieved if we neglect all the products where  $\chi_\mu$  and  $\chi_\nu$  belong to different atomic centres. This approximation is valid in so far as the two centre terms project into the one centre terms which are included in the refinement. The validity of the approximation has been clearly established by Newton (1969). In a charge-density analysis the subdivision into  $\chi_s^2$  and linear combinations of  $\chi_{px}^2$ ,  $\chi_{pz}^2$  and  $\chi_{py}^2$  products is arbitrary. Only the gross population and the difference between the  $\chi_p^2$  populations is meaningful.

In general the contribution of a single first-row atom to the valence distribution may be written

$$\begin{aligned} \rho(\mathbf{r}) = & P_{s2}\chi_s^2 + P_{sp_x}\chi_s\chi_{p_x} + P_{sp_y}\chi_s\chi_{p_y} + P_{sp_z}\chi_s\chi_{p_z} \\ & + P_{p_x^2}\chi_{p_x}^2 + P_{p_x p_y}\chi_{p_x}\chi_{p_y} + P_{p_x p_z}\chi_{p_x}\chi_{p_z} \\ & + P_{p_y^2}\chi_{p_y}^2 + P_{p_y p_z}\chi_{p_y}\chi_{p_z} \\ & + P_{p_z^2}\chi_{p_z}^2. \end{aligned}$$

Note, however, that a combination of  $\chi_{p_x}^2$ ,  $\chi_{p_y}^2$  and  $\chi_{p_z}^2$  in equal amounts gives a density function similar in form to  $\chi_s^2$ . If the radial parts of the functions are the same the two are indistinguishable.

For distributions containing elements of symmetry the terms may be further reduced. Thus for a system with a mirror plane perpendicular to  $z$ ,  $P_{sp_z}$ ,  $P_{p_x p_z}$  and  $P_{p_y p_z}$  vanish since the corresponding density functions are antisymmetric in  $z$ . Further reductions follow for higher symmetries.

Simplifications of this type will be roughly valid for distributions with approximate symmetry, and relations between populations may be deduced by chemical inference if a well defined hybridization can be assumed.

Thus a single  $sp^2$  hybrid orbital is represented by the linear combination  $1/\sqrt{3}(\chi_s + \sqrt{2}\chi_p)$ , where  $p$  is an appropriately directed  $p$  orbital. The populations for the corresponding products  $\chi_s^2$ ,  $\chi_s\chi_p$  and  $\chi_p^2$  will be in the ratios  $\frac{1}{3}:2\sqrt{2}/3:\frac{2}{3}$ . These ratios are preserved for linear combinations of trigonally disposed hybridized orbitals. Note that in the case where three such orbitals have equal populations the  $sp$  contributions sum to zero and the total density has cylindrical symmetry.

Since in the subdivision of charge density the difference between a  $\chi_s^2$  function and a linear combination of  $\chi_p^2$  functions is arbitrary, the assumption regarding

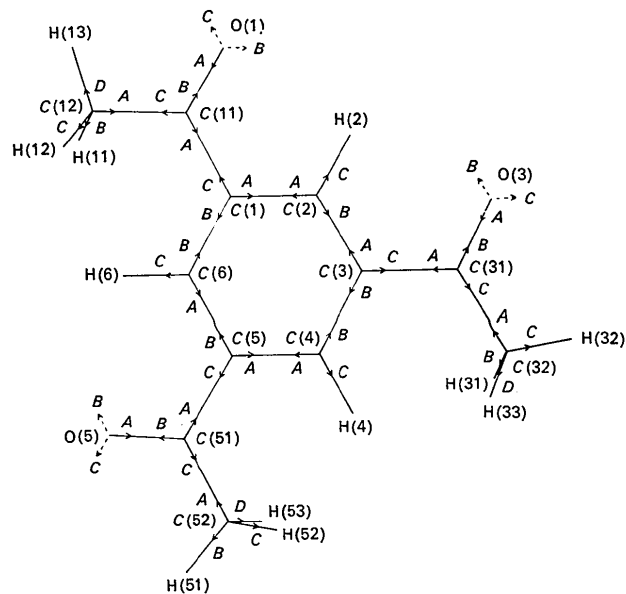


Fig. 1. Numbering of the atoms and orbitals used to represent the electron density in 1,3,5-triacetylbenzene.

hybridization is equivalent to asserting that the local dipole and quadrupole moments surrounding the nuclei are related. An examination of residual electron densities in difference syntheses supports this assumption.

It is helpful to consider this problem in terms of an over-complete set of  $p$  functions. For trigonally bonded carbon we may choose three  $p$  functions parallel to the  $\sigma$  bonds and one normal to the  $\sigma$  bond plane, making four in all, or one more than is required to define the distribution uniquely. However, the interpretation of the population coefficients is simplified and approximations involved in relating the coefficients follow in a more obvious manner.

### Density analysis

The numbering of the atoms in the 1,3,5-triacetylbenzene structure is given in Fig. 1. In the analysis of the electron density each of the carbon and oxygen atoms was assigned a  $1s^2$  core and the valence electron density was built up by associating groups of orbitals with atoms as follows: each of C(1), C(2), C(3), C(4), C(5),

C(6), C(11), C(31), C(51), O(1), O(3) and O(5) was assigned three  $sp^2$  combinations and a  $p$  orbital normal to the  $sp^2$  plane; for carbon atoms C(12), C(32) and C(52) there were four  $sp^3$  combinations; and for each of the hydrogens a  $1s$  orbital. The hybrid orbitals for the carbon atoms were directed along the C-C or C-O bonds, while those for the oxygens were directed along O-C bonds and trigonally related directions. These are represented diagrammatically in Fig. 1. The density function was constructed with hybridized orbital products, constructed for these orbitals as described in the previous section. For the hydrogen atoms a single one-centre  $1s^2$  function only was involved. Each product in the valence distribution was assigned a single population parameter, which was varied in the refinement.

Five refinements were performed, combining three sets of basis functions with two sets of variable parameters. Throughout the refinements the scattering factors were evaluated using three-term Gaussian approximations to the corresponding SCF or STO functions.

The carbon and oxygen core contributions were evaluated with SCF functions and a fixed population

Table 1. *The STO(FPT)-refinement populations for STO basis functions, with the positional and thermal parameters fixed at the values from the ND-refinement*

Symbols  $Z$  and  $Z'$  designate the unscaled and scaled gross atomic population.

	$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$\langle 2sp^2 \rangle$	$2p_z^2$	$Z$	$Z'$
C(1)	1.19 (6)	1.02 (6)	0.96 (6)	1.06 (4)	0.63 (9)	5.80 (7)	6.10
C(3)	1.15 (6)	1.06 (6)	1.18 (4)	1.13 (4)	0.26 (9)	5.65 (8)	5.94
C(5)	1.01 (6)	1.13 (6)	0.96 (6)	1.03 (4)	0.68 (8)	5.78 (7)	6.08
Mean	1.12 (4)	1.07 (4)	1.03 (4)	1.07 (2)	0.52 (5)	5.74 (4)	6.04
C(2)	0.95 (6)	1.00 (6)	0.96 (6)	0.97 (4)	0.61 (9)	5.52 (7)	5.80
C(4)	1.11 (6)	0.97 (6)	0.91 (6)	1.00 (4)	0.53 (8)	5.52 (7)	5.80
C(6)	1.04 (6)	1.21 (6)	1.13 (4)	1.13 (4)	0.40 (8)	5.78 (7)	6.08
Mean	1.03 (4)	1.06 (4)	1.00 (4)	1.03 (2)	0.51 (5)	5.60 (4)	5.90
C(11)	0.96 (6)	0.86 (7)	1.05 (7)	0.96 (4)	0.36 (10)	5.23 (7)	5.49
C(31)	1.18 (6)	1.04 (6)	1.08 (6)	1.10 (4)	0.35 (9)	5.65 (7)	5.94
C(51)	0.92 (6)	1.18 (6)	1.01 (6)	1.04 (4)	0.45 (9)	5.56 (7)	5.85
Mean	1.02 (4)	1.03 (4)	1.05 (4)	1.03 (3)	0.38 (5)	5.48 (4)	5.76
	$2sp^3(A)$	$2sp^3(B)$	$2sp^3(C)$	$2sp^3(D)$	$\langle 2sp^3 \rangle$	$Z$	$Z'$
C(12)	1.18 (7)	0.63 (7)	0.85 (7)	0.92 (7)	0.90 (2)	5.58 (8)	5.87
C(32)	0.98 (6)	0.72 (7)	1.00 (6)	1.11 (7)	0.95 (2)	5.81 (8)	6.12
C(52)	1.06 (6)	0.99 (6)	0.99 (6)	0.58 (7)	0.90 (2)	5.62 (7)	5.91
Mean	1.07 (4)	0.78 (4)	0.95 (4)	0.87 (4)	0.92 (2)	5.67 (5)	5.96
	$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$\langle 2sp^2(BC) \rangle$	$2p^2z$	$Z$	$Z'$
O(1)	1.57 (8)	1.71 (8)	1.56 (8)	1.63 (7)	1.05 (14)	7.89 (7)	8.36
O(3)	1.32 (6)	1.58 (6)	1.40 (7)	1.49 (5)	1.52 (10)	7.82 (5)	8.29
O(5)	1.54 (6)	1.50 (7)	1.56 (6)	1.53 (5)	1.29 (11)	7.89 (6)	8.36
Mean	1.48 (4)	1.60 (4)	1.51 (4)	1.55 (3)	1.29 (7)	7.87 (4)	8.34
	$1s^2$		$1s^2$				
H(2)	1.12 (7)	H(11)	0.79 (7)				
H(4)	1.15 (6)	H(12)	0.88 (6)				
H(6)	1.02 (6)	H(13)	0.77 (7)				
Mean	1.10 (4)	H(31)	1.08 (8)				
		H(32)	0.92 (7)				
		H(33)	1.30 (8)				
		H(51)	0.85 (7)				
		H(52)	1.02 (7)				
		H(53)	1.09 (7)				
		Mean	0.97 (3)				

of 2.00. Dispersion terms were not included because parallel refinements on related structures indicated that the dispersion corrections were unreliable. Moreover the population coefficients are remarkably insensitive to the dispersion terms.

All two-centre contributions and products between different groups of orbitals were excluded from the calculations.

Throughout the refinements  $\sum \omega(F_o^2 - F^2)^2$  was minimized using the weighting factors from O'Connor (1973). As the least-squares matrix for the larger parameter sets exceeded the capacity of the computing system available, the block-diagonal approximation was used, taking a  $1 \times 1$  block for the scale factor and

one block for each atom. Apart from special calculations discussed later the five refinements were performed as follows:

(1) STO(FPT). The valence electron scattering factors were evaluated using STO's with the standard molecular exponents of Hehre, Stewart & Pople (1969), except for hydrogen for which the value used was that for molecular hydrogen (Stewart, Davidson & Simpson, 1965). The positional and thermal parameters were held fixed at the values from the neutron diffraction refinement (O'Connor & Moore, 1973). The scale factor and the population coefficients were refined.

(2) STO(FP). The scattering factors were identical to those of the preceding refinement, but with the par-

Table 2. Summary of mean populations for the chemically equivalent atoms in each of the five refinements

The two numbers given in parentheses for each population are (i) the standard deviation, (ii) the maximum deviation from the mean for the atoms averaged, the numbers being scaled by a factor of  $10^2$ .

Reference*	$2s_{(cusp)}^2$	$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$\langle 2sp^2 \rangle$	$2p_z^2$	Z	Z'	
C(1,3,5)	1		1.12 (4,11)	1.07 (4,6)	1.03 (4,15)	1.07 (2,6)	0.52 (5,26)	5.74 (4,9)	6.04
	2		1.01 (4,11)	0.95 (4,16)	0.93 (4,10)	0.96 (3,4)	0.80 (8,14)	5.69 (4,5)	6.03
	3		1.23 (4,14)	1.19 (4,5)	1.12 (4,16)	1.18 (3,6)	0.53 (6,32)	6.07 (5,13)	6.05
	4		1.12 (4,20)	1.04 (4,14)	0.99 (5,9)	1.05 (3,3)	0.81 (8,15)	5.96 (5,5)	6.10
	5	-0.29 (4.0)	1.22 (4,16)	1.16 (4,9)	1.12 (4,17)	1.17 (3,8)	0.66 (5,32)	5.87 (5,6)	6.18
C(2,4,6)	1		1.03 (4,8)	1.06 (4,15)	1.00 (4,13)	1.03 (2,10)	0.51 (5,11)	5.60 (4,18)	5.90
	2		0.94 (4,13)	1.00 (4,12)	0.98 (4,10)	0.97 (3,6)	0.72 (8,2)	5.64 (4,17)	5.98
	3		1.14 (4,7)	1.18 (4,14)	1.16 (4,12)	1.16 (3,7)	0.56 (6,9)	6.04 (5,12)	6.04
	4		1.00 (4,17)	1.09 (5,18)	1.08 (4,10)	1.06 (3,4)	0.79 (8,6)	5.96 (5,13)	6.10
	5	-0.27 (4.6)	1.11 (4,13)	1.15 (4,10)	1.12 (4,6)	1.13 (3,3)	0.63 (5,7)	5.74 (5,8)	6.04
C(11,31,51)	1		1.02 (4,16)	1.03 (4,17)	1.05 (4,4)	1.03 (3,7)	0.38 (5,7)	5.48 (4,25)	5.76
	2		0.93 (4,7)	0.87 (4,24)	0.94 (5,3)	0.91 (4,9)	0.67 (9,14)	5.41 (4,26)	5.73
	3		1.13 (4,17)	1.24 (4,15)	1.16 (4,5)	1.18 (3,6)	0.43 (6,3)	5.96 (5,21)	5.95
	4		0.96 (5,12)	0.90 (5,25)	0.98 (5,7)	0.95 (3,13)	0.81 (8,10)	5.65 (5,33)	5.77
	5	-0.18 (4.9)	1.06 (4,20)	1.02 (4,23)	1.06 (4,10)	1.05 (3,13)	0.50 (6,6)	5.46 (5,33)	5.75
C(12,32,52)			$2sp^3(A)$	$2sp^3(B)$	$2sp^3(C)$	$2sp^3(D)$	$\langle 2sp^3 \rangle$	Z	Z'
	1		1.07 (4,11)	0.78 (4,21)	0.95 (4,10)	0.87 (4,29)	0.92 (2,3)	5.67 (5,15)	5.96
	2		1.08 (4,12)	0.84 (4,23)	0.92 (4,15)	0.91 (4,25)	0.94 (2,4)	5.75 (4,17)	6.11
	3		1.15 (4,16)	0.96 (5,19)	1.02 (5,13)	1.00 (5,26)	1.03 (2,5)	6.13 (5,17)	6.13
	4		1.16 (4,19)	0.96 (5,26)	0.98 (5,22)	0.98 (5,26)	1.02 (2,5)	6.08 (5,20)	6.22
5	-0.20 (5.7)	1.11 (4,18)	0.92 (4,13)	1.00 (4,11)	0.92 (4,31)	0.99 (3,6)	5.75 (5,17)	6.04	
O(1,3,5)			$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$\langle 2sp^2(B, C) \rangle$	$2p_z^2$	Z	Z'
	1		1.48 (4,16)	1.60 (4,11)	1.51 (4,11)	1.55 (3,8)	1.29 (7,24)	7.87 (4,5)	8.34
	2		1.62 (9,48)	1.66 (9,36)	1.58 (9,41)	1.62 (9,37)	0.87 (23,113)	7.73 (4,13)	8.28
	3		1.51 (4,13)	1.72 (4,15)	1.58 (4,14)	1.65 (3,11)	1.23 (7,26)	8.04 (4,7)	8.03
	4		1.53 (8,39)	1.59 (8,27)	1.45 (8,33)	1.52 (8,29)	1.28 (20,90)	7.85 (4,12)	8.04
5	0.33 (7.7)	1.45 (4,19)	1.53 (4,17)	1.42 (4,15)	1.47 (3,13)	0.90 (10,42)	7.63 (5,7)	8.08	
H(2,4,6)		$1s^2$							
	1		1.10 (4.8)						
	2		1.08 (6.4)						
	3		0.96 (4.8)						
	4		0.95 (6.1)						
5		1.03 (4.9)							
H(acetyl)	1		0.97 (3.33)						
	2		0.93 (4.22)						
	3		0.94 (3.34)						
	4		0.94 (4.22)						
	5		0.96 (3.34)						

\* 1: STO(FPT).  
 2: STO(FP).  
 3: SCF(FPT).  
 4: SCF(FP).  
 5: STOC(FPT).

ameter set extended to include the thermal parameters.

(3) SCF(FPT). This was identical to the STO(FPT) refinement except that STO orbitals for the valence electron scattering of carbon and oxygen were replaced by SCF functions.

(4) SCF(FP). This was identical to the STO(FP) refinement except for the replacement of the STO orbitals with SCF functions.

(5) STOC(FPT). This refinement was conducted after refinements 1 to 4, in order to examine the effect of placing a cusp at the origin of the valence electron scattering for the carbon and oxygen atoms. The parameters were as for the STO(FPT) refinement except for those coefficients associated with the scattering factor set, expanded by the inclusion of an additional term of Slater 1s form, with a standard molecular *L*-shell exponent, for each carbon and oxygen atom.

The complete set of population coefficients for the STO(FPT) refinement are given in Table 1. The coefficients for refinements 2–5 have not been included in full detail, but can be obtained directly from the authors. A summary of the mean populations for the chemically equivalent atoms in each of the five refinements is given in Table 2. The final refinement indices are compared in Table 3. Similar indices for a conventional spherical-atom refinement, with atomic scattering factors evaluated with SCF functions for carbon and oxygen (*International Tables for X-ray Crystallography*, 1968), are given for comparison.

Table 3. *Final agreement indices for different refinement models*

$$R(F_o) = \frac{\sum |F_o - F_c|}{\sum F_o} \quad R(F_o^2) = \frac{\sum |F_o^2 - F_c^2|}{\sum F_o^2}$$

$$\omega \Delta^2 = \omega [F_o^2 - F_c^2]^2 \quad R_{\omega}(F_o^2) = \frac{\sum \omega |F_o^2 - F_c^2|}{\sum \omega F_o^4}^{1/2}$$

$$G = [\sum \omega \Delta^2 / (m - n)]^{1/2}$$

Model	$R(F_o)$	$R(F_o^2)$	$R_{\omega}(F_o^2)$	$\omega \Delta^2$	G
STO(FPT)	0.109	0.154	0.316	4507	1.514
STO(FP)	0.094	0.131	0.285	3249	1.342
STOC(FPT)	0.103	0.142	0.312	4029	1.434
SCF(FPT)	0.105	0.146	0.315	4309	1.477
SCF(FP)	0.094	0.135	0.280	3209	1.330
FASCF*(FP)	0.096	0.128	0.290	3463	1.357

\* Free-atom SCF form factors with exchange (*International Tables for X-ray Crystallography*, 1968).

### Discussion

A feature of these refinements is the increase in correlation between the population parameters with large thermal motion, which is further enhanced when the thermal parameters are included in the refinement. The correlation coefficients for the STO(FPT) and STO(FP) refinements for atoms C(1) and O(1), which have small and large motions respectively, are given in Table 4(a) and (b). The increase in correlation with thermal smearing is clearly evident. The effects are also reflected in the standard deviations of the population coefficients, and provide a strong case for collecting experimental data at low temperature.

An encouraging aspect of the results is the general agreement between chemically equivalent populations at a level of accuracy commensurate with the standard deviations. This suggests that the calculated standard deviations are a reasonable guide to accuracy. It also indicates that perturbations due to intermolecular interactions are not serious in this structure at the present level of accuracy.

In view of this agreement it is legitimate to average chemically equivalent populations, reducing statistical fluctuations and enhancing precision. This averaging has been carried out in Table 2.

The refinements based on SCF functions for the valence scattering are marginally better than those based on STO's from the point of view of agreement with the scattering experiment. This is not surprising, in view of the simplicity of the latter compared with the heavily optimized character of the former. For the determination of population coefficients, however, the SCF refinements are much less satisfactory. For the atoms where the SCF and Slater functions differ in form, the standard deviations in the population coefficients are greater for the SCF refinements, and this is confirmed by generally poorer agreement among chemically equivalent populations in the SCF refinement.

A further indicator which favours populations from the STO's is the lower sensitivity of the gross atomic populations to changes in the temperature factor. The principal effect of thermal parameter refinement is a redistribution of density among the various orbitals, which is expected in view of the strong correlation involved. The gross valence populations (column 9 in Table 2) are little affected by this correlation. There are no significant changes in the totals for the STO(FPT) and STO(FP) refinements. The average discrepancy is three times larger for the atoms C(1), C(2), C(3), C(4), C(5), C(6), C(11), C(31) and C(51) for the SCF(FPT) and SCF(FP) refinements. These atoms have low temperature factors and therefore dominate the structure factor at high Bragg angles.

The effect is less marked for atoms O(1), O(3) and O(5), and is reversed for C(12), C(32) and C(52), which is not surprising since the low contribution of these atoms to the high-angle data reduces the importance of the difference between the SCF and STO orbitals.

In general the population for the SCF orbitals are closer to the unbound state than those obtained with STO orbitals, in agreement with observations on a number of similar structures by Stewart (1970b). This may be related to the fact that the weighting schemes used in structure analysis tend to favour the high-angle data. The principal contribution to this data comes from the region near the atomic nucleus, which is relatively invariant to bonding. In view of the cusp structure of the SCF orbitals at the nucleus a bias towards the atomic populations is not unreasonable.

Refinement 5 was conducted in order to test this hypothesis, the cusp at the origin of the 2s function

being simulated by the inclusion of the additional Slater term. The populations are strikingly closer to the SCF values for the atoms C(1), C(2), C(3), C(4), C(5) and C(6) which have low thermal motion. This effect is still observed, but is less marked, for the other atoms.

**Charge-density distribution**

The charge-density distribution may be considered very conveniently at the gross atomic population level. In using these populations to estimate nett atomic charges, however, it is necessary to take into account the fact that the sum of the populations is not equal to the number of valence electrons, *i.e.* the molecule is not electrically neutral.

The effect, which has been noted by Stewart (1970*b*), is hardly surprising in view of the limited set of density functions and the approximations implicit in the use of STO orbitals. These approximations are not too drastic for hydrogen, where the valence density decreases monotonically from the centre, and where the argument for the exponential function has been optimized for molecular hydrogen. However for carbon and oxygen the errors involved may be substantial.

Coppens, Csonka & Willoughby (1970) avoid this problem by including electrical neutrality as a constraint in the least-squares refinement. We prefer the alternative approach of unconstrained refinement, regarding equality of the sum of the population coefficients and the number of electrons as a necessary requirement for a good electron density model.

In all cases except the SCF(FPT) refinement a small nett loss of electrons was observed. Stewart (1970*b*) reports a similar experience. In estimating nett atomic

charges the population coefficients for the carbon and oxygen atoms have been rescaled to give a neutral molecule. The rescaled populations are included in column 10 of Table 2.

The results for the STO's are in gratifying agreement with expectation for electronegativities. The oxygen atoms have nett negative charges of -0.34 and -0.28 in refinements 1 and 2 respectively. The SCF and the Slater cusp refinements are less reasonable. This is also consistent with the results of Stewart (1970*b*).

Nett atomic charges for refinements 1 and 2, averaged over chemically equivalent atoms, are given in Fig. 2. The most striking feature is the polar character of the C=O bond. There is a tendency for the alterna-

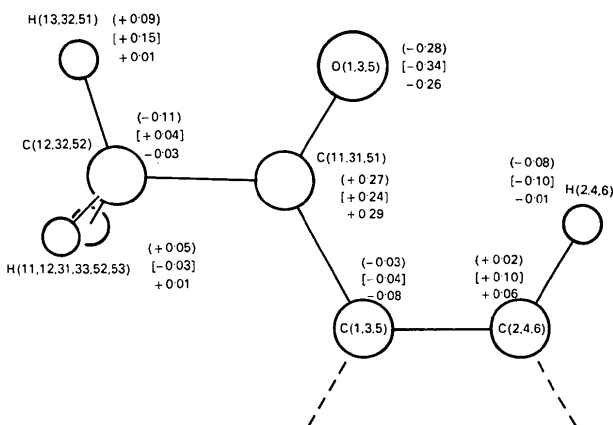


Fig. 2. Nett atomic charges in 1,3,5-triacetylbenzene, averaged over chemically equivalent atoms. The experimental values (FP in round brackets, FPT in square brackets) and the corresponding INDO values (without brackets) are given for each atom.

Table 4. Correlation coefficients

(a) Correlation coefficients ( $\times 10^2$ ) for atom C(1) at the conclusion of the STO(FP) refinement. The corresponding coefficients for the STO(FPT) refinement are enclosed in parentheses.

$2sp^2(A)$	100										
$2sp^2(B)$	38 (6)	100									
$2sp^2(C)$	38 (14)	42 (8)	100								
$2p_z^2$	-64 (-40)	-74 (-53)	-71 (-48)	100							
$b_{11}$	-29	-15	-10	29	100						
$b_{12}$	-6	9	-20	7	6	100					
$b_{22}$	-22	-44	-49	59	-7	7	100				
$b_{13}$	53	52	48	-68	-7	-3	-42	100			
$b_{23}$	-13	-22	-13	22	7	14	13	-12	100		
$b_{33}$	54	59	60	-74	-32	-6	-56	62	-16	100	
	$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$2p_z^2$	$b_{11}$	$b_{12}$	$b_{22}$	$b_{13}$	$b_{23}$	$b_{33}$	

(b) Correlation coefficients ( $\times 10^2$ ) for atom O(1) at the conclusion of the STO(FP) refinement. The corresponding coefficients for the STO(FPT) refinement are enclosed in parentheses.

$2sp^2(A)$	100										
$2sp^2(B)$	88 (27)	100									
$2sp^2(C)$	89 (23)	88 (26)	100								
$2p_z^2$	-95 (-62)	-95 (-67)	-95 (-64)	100							
$b_{11}$	-10	-3	-6	10	100						
$b_{12}$	-6	-11	2	5	0	100					
$b_{22}$	-80	-85	-84	89	-1	4	100				
$b_{13}$	91	90	90	-94	9	-7	-84	100			
$b_{23}$	1	2	-3	-1	2	36	-7	0	100		
$b_{33}$	87	87	87	-89	-6	-7	-82	92	-5	100	
	$2sp^2(A)$	$2sp^2(B)$	$2sp^2(C)$	$2p_z^2$	$b_{11}$	$b_{12}$	$b_{22}$	$b_{13}$	$b_{23}$	$b_{33}$	

tion of positive and negative charges throughout the structure. This effect occurs in cyanuric acid and in uracil, notwithstanding the lower molecular symmetry (Stewart, 1970*b*). Charge alternation, which characterizes ionic structures, seems to occur in molecular systems as well.

The experimental results in Fig. 2 may be compared with those of a semi-empirical theoretical calculation using the INDO method (Pople & Beveridge, 1970), kindly carried out by Mr J. N. Varghese in this Department. In these calculations the molecular geometry given by the neutron diffraction analysis (O'Connor & Moore, 1973) was utilized. The nett atomic charges derived from the gross Mulliken populations, averaged over chemically equivalent atoms, are included in Fig. 2 for comparison with the FP and FPT values. Agreement between the three sets of charges is excellent within the accuracy of the experiment. There is little to choose between the FP and FPT sets on the basis of agreement with the INDO results. However, for hydrogen atoms the FPT populations should be preferred to the FP values on account of the relatively greater sensitivity of the latter to thermal parameter bias. The effect of thermal parameter bias on gross charge values is much more serious for hydrogen than for non-hydrogen populations since the hydrogen atom does not have a core.

The most noticeable feature of the distribution around the nuclei is the enhancement of the in-plane populations at the expense of those normal to the plane. This effect has been noted by Coppens, Pautler & Griffin (1971). This corresponds to a negative population for the  $q_z^2$  quadrupole at the carbon nuclei. In principle this result could be verified by a nuclear quadrupole resonance experiment using isotopically enriched carbon, but suitable data are not yet available. In general trigonal symmetry in the  $sp^2$  systems and tetrahedral symmetry for the  $sp^3$  are quite well preserved. However the population in the direction of the C-C  $\sigma$  bond at the methyl carbon is significantly higher than the mean for the C-H bonds. There is also a suggestion that the population of the  $\sigma$  orbital directed along the O-C bond is lower than those for the lone pairs. A similar effect is observed at a higher level of

significance in potassium oxalate monohydrate (Delaney, 1972).

Comparison of the nett charges on the in-plane and out-of-plane hydrogen atoms suggests that populations of the in-plane hydrogens are biased by a non-bonded interaction between each in-plane hydrogen and its neighbouring oxygen. The mean nett charge for the in-plane hydrogens is +0.15 for the FPT refinement, whereas the corresponding value for the out-of-plane hydrogens is -0.03. These values might explain why each acetyl group has an in-plane hydrogen, although it should be noted that such effects are not evident in the INDO results.

The authors wish to acknowledge the financial support of the Australian Research Grants Committee. One of us (B.H.O'C.) was in receipt of a Queen Elizabeth Fellowship during the course of the work.

#### References

- CLEMENTI, E. (1965). *IBM J. Res. Develop. Suppl.* **9**, 2-19.  
 CLEMENTI, E. (1967). *J. Chem. Phys.* **46**, 4731-4736.  
 COPPENS, P., CSONKA, L. N. & WILLOUGHBY, T. V. (1970). *Science*, **167**, 1126-1128.  
 COPPENS, P., PAUTLER, D. & GRIFFIN, J. R. (1971). *J. Amer. Chem. Soc.* **93**, 1051-1058.  
 DELANEY, W. T. (1972). Ph.D. Thesis. Univ. of Western Australia.  
 HEHRE, W. J., STEWART, R. F. & POPLE, J. A. (1969). *J. Chem. Phys.* **51**, 2657-2664.  
*International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 202-203. Birmingham: Kynoch Press.  
 MASLEN, E. N. (1968). *Acta Cryst.* **B24**, 1172-1175.  
 NEWTON, M. D. (1969). *J. Chem. Phys.* **51**, 3917-3926.  
 O'CONNOR, B. H. (1973). *Acta Cryst.* **B29**, 1893-1903.  
 O'CONNOR, B. H. & MOORE, F. H. (1973). *Acta Cryst.* **B29**, 1903-1909.  
 POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory*. New York: McGraw Hill.  
 STEWART, R. F. (1968). *Acta Cryst.* **A24**, 497-505.  
 STEWART, R. F. (1969*a*). *J. Chem. Phys.* **50**, 2485-2495.  
 STEWART, R. F. (1969*b*). *J. Chem. Phys.* **51**, 4569-4577.  
 STEWART, R. F. (1970*a*). *J. Chem. Phys.* **52**, 431-438.  
 STEWART, R. F. (1970*b*). *J. Chem. Phys.* **53**, 205-213.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.