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The Effect of Asymmetry of the Atomic Charge Distribution on the Positions of Terminal Atoms as Determined with X-rays*

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The centroid of the charge density of terminal atoms generally does not coincide with the nuclear position. Approximate calculations for a terminal oxygen atom in a nitro group show that the direction and the magnitude of the shift is dependent on the hybridization of the oxygen atom. The observed absence of bonding density in terminal bonds is explained in terms of the subtraction in the difference map of a spherical atom rather than an atom in the prepared valence state.

It has been stated by Dawson (1965) that the bond lengths to terminal atoms in a molecule, as determined by X-rays, should be smaller than those obtained by spectroscopic or neutron- and electron-diffraction methods; this is because, as a result of bonding, the centroid of the atomic density is displaced towards its bonded neighbour. This statement has been amply verified for bonds involving hydrogen atoms, of type X–H (X is C, N, O). However, it is the purpose of this note to point out that for most other types of bond (*e.g.* $>C=O$ or $-C\equiv N$) its validity is critically dependent on the hybridization of the terminal atom.

A good example to illustrate our conclusion is in the N–O bonds of a nitro group. O'Connell, Ray & Maslen (1966) made a careful analysis of the difference density in triaminotrinitrobenzene (Cady & Larsen, 1965), and found very little bond-density in the N–O bonds. They explained this situation in terms of a shift of terminal atoms toward the bond peak, as predicted by Dawson (1965).

Let us, therefore, consider a terminal oxygen atom in a nitro group. This oxygen atom has eight electrons, two in the inner shell, one each in σ and π bonding orbitals, and two in each of the two lone-pair orbitals (see Table 2 for hybridization schemes). All but the inner-shell and π-bonding orbitals may be expected to be hybridized in some manner. Now when the atom is 'prepared' in this way (the *valence state* of van Vleck), then – whatever the precise hybridization – it will be the case that one electron in each of the lone-pair orbitals and the π and σ bonding orbitals will give a total charge density which is spherically symmetrical and centred on the oxygen nucleus. The two remaining electrons, one in each lone-pair orbital, may, however, give rise to an appreciable atomic dipole moment; this will be directed away from the N–O bond, *i.e.* in a direction opposite to that of the dipole moment associated with the bonding density. This atomic dipole moment can be calculated as follows (Coulson, 1942, 1948). Let the normalized wave function of a lone-pair hybrid be represented by

$$\Psi = a\varphi(2s) + b\varphi(2p)\,.$$

Then the electron density distribution Ψ^2 contains just one term $2ab\varphi(2s)\varphi(2p)$ which is not centred on the oxygen nucleus. This term gives rise to an atomic dipole. The distance d from the oxygen nucleus to the centroid of the charge-cloud Ψ^2 is given by

$$d = \int 2ab\varphi(2s)\varphi(2p)x d\tau\,,$$

where x is measured from the oxygen nucleus along the axis of the $2p$ orbital. This integral is easily evaluated for Slater-type orbitals by using overlap tables available in the literature (*e.g.* Mulliken, Rieke, Orloff & Orloff, 1949). The displacement of the centroid of the total oxygen charge density is then the vectorial sum of the displacements d due to an electron in each of the two lone-pair orbitals, divided by the total number of electrons (here 8) in the oxygen atom. Some results of the calculations of this displacement for various possible hybridizations of the lone-pair orbitals are given in Table 1.

The effect mentioned by Dawson, *i.e.* the accumulation of charge in the bonding region as a result of overlapping of bonding orbitals on the two atoms of the bond, is quite distinct from the lone-pair effect just described. It may be calculated as follows. In a covalent

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Table 1. *Displacement of centroid of charge density of valence state oxygen atom due to additional electron in lone pair orbitals**

Hybridization of lone-pair orbitals	Displacement of centroid away from bonding orbital	Corresponding atomic dipole moment
sp, $p\pi$	0·041 Å	1·56 D
sp^2, sp^2	0·039	1·48
$sp^{5/3}$, $sp^{5/3}$	0·037	1·41
s, $p\pi$	0	0

* With Slater μ value=2·275. The third row of this table corresponds to bonding orbitals sp^3, p_π.

bond AB the charge density ϱ can be described (Coulson & Rogers, 1961) by

$$\varrho=\Psi_A^2+\Psi_B^2-\frac{S}{1+S}(\Psi_A^2+\Psi_B^2)+\frac{2}{1+S}\Psi_A\Psi_B \quad (1)$$

where $S=\int \Psi_A\Psi_B d\tau$ is the overlap integral of the bonding atomic hybrids Ψ_A and Ψ_B. If we divide the cross-term in (1) equally between atoms A and B, we obtain

$$\varrho=\varrho_A+\varrho_B\,,$$

where

$$\varrho_A=\Psi_A^2-\frac{S}{1+S}\Psi_A^2+\frac{1}{1+S}\Psi_A\Psi_B\,. \quad (2)$$

The first term in (2) represents the charge in the unperturbed hybrid Ψ_A in the absence of any bonding; the last two terms describe the change in density due to bonding. These last two terms may be interpreted as a shift of $S/(1+S)$ electrons from the A nucleus in the direction of the bond.

If Ψ_A and Ψ_B are identical hybrids on the two atoms, then $\int x_A\Psi_A\Psi_B d\tau=\frac{1}{2}RS$, where R is the bond length. Thus the charge represented by $1/(1+S)\Psi_A\Psi_B$ may be treated as if it were located at the mid-point of the bond. The atomic dipole arising from ϱ_A is thus soon calculated. For a typical NO bond, taking $R=1{\cdot}24$ Å, we obtain the results given in Table 2 (columns 3 and 4). It will be seen that the calculated shifts are not very sensitive to changes in the hybridization of the σ-bonding orbital.

Dawson, in his analysis (1965) of the X-ray data for diamond, found that 0·1–0·15 electron per atom per bond was drawn into the bonding region. A similar charge displacement in the N–O σ-bond would correspond to a displacement of the centroid of the oxygen atom charge cloud amounting to 0·008–0·012 Å. This is comparable to the results of our calculations in Table 2.

The various effects that we have considered are summed in the last column of Table 2. It appears that, over an appreciable part of the possible range of hybridization of the oxygen atom, the net shift of charge is away from, and not towards, the nitrogen atom. It should be mentioned that this shift away from the direction of the nitrogen atom would be increased still further if, instead of dividing the overlap density in (1) equally between the atoms, rather more than half was assigned to the smaller (and closer) atom, as in calculations of the homopolar dipole (Coulson & Rogers, 1961).

Thus, without further knowledge of the hybridization of the terminal atom it is not possible to predict the direction of the shift on the centroid of the electron density, which presumably determines the atomic position as determined on conventional X-ray refinement. (An exception to this statement occurs for the hydrogen atom, where there are no lone-pair electrons, and where the much higher energy of the $2p$ atomic orbital relative to the $1s$ orbital severely limits the extent of any hybridization at that end of the bond.) In the case of the difference map of triaminotrinitrobenzene (O'Connell, Rae & Maslen, 1966) the apparent absence of NO bonding density does not by itself indicate a shift of oxygen electrons towards the nitrogen nucleus. This is because, when computing the difference density, these writers adopted the usual convention of subtracting from the measured total electron density the density of a spherical oxygen atom. This may easily cause confusion, because, as stated earlier, the oxygen atom in the 'prepared', *i.e.* valence, state has only one electron in the σ-orbital pointing towards the nitrogen atom. Some purely theoretical calculations for F_2 by B. J. Ransil and J. Sinai (in course of publication: we acknowledge gratefully the receipt of a preprint of this work) show the importance of this distinction if we want to study bonding effects on the atomic charge densities. Another example of this situation is found in the difference map of *cis*-1,2,3-tricyanocyclopropane determined by Hartman & Hirshfeld (1966), where the mid-point of the –C≡N bond was surrounded by an

Table 2. *Displacement of centroid of charge density of oxygen atom in a nitro group**

Hybridization of σ-bonding orbital	Corresponding hybridization of lone-pair orbitals	Displacement of centroid towards nitrogen due to σ-bonding density	Displacement due to π-bond density†	Total shift‡	Corresponding atomic dipole moment
sp	sp,p	0·014 Å	0·007$_5$ Å	−0·020 Å	0·76 D
sp^2	sp^2,sp^2	0·015	0·007$_5$	−0·016	0·61
sp^3	$sp^{5/3},sp^{5/3}$	0·016	0·007$_5$	−0·013	0·49
p	s,p	0·023	0·007$_5$	+0·031	−1·17

* For sp^2 hybridized nitrogen atom, with Slater's $\mu=1{\cdot}95$; and oxygen atom with $\mu=2{\cdot}275$

† For NO bond order 0·67 (Trotter, 1959)

‡ Columns 3 and 4 of this table minus column 2 of Table 1. Negative: away from nitrogen; positive: towards nitrogen.

'unexpected' trough. This trough, however, can be explained in the same way if the nitrogen lone pair orbital has a certain amount of p character.

The argument given above applies also to nitrogen atoms in molecules such as ammonia and hexamethylenetetramine. In fact the experimental data for these two compounds seem to substantiate a shift in the direction of the lone-pair electrons (Coppens & Hirshfeld, 1964). Careful comparative X-ray and neutron-diffraction studies on triazine are presently being undertaken in order to get more information on the direction and the size of this effect.

One other effect must be mentioned briefly. In our example we assumed that the N–O bond was not strongly ionic. It is easy to see that ionic character will impose a further displacement on the atomic charges. In the case of the π-bond, very little difference will be caused by polarity, since the extra charge will be in a $2p_\pi$ atomic orbit whose centre is at the oxygen nucleus. But in the case of the σ-bond, the extra charge is in a hybrid orbital, whose centroid does not coincide with the oxygen nucleus. Moreover, since oxygen is more electronegative than nitrogen, this will bring additional charge to the oxygen atom and reduce the asymmetry of charge. However this situation does not affect the conclusion of this note, though it would have to be taken into account in a detailed numerical study.

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Neue Absorptionsfaktortafeln für den Kreiszylinder

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The well known tables of absorption correction for cylinders (*International Tables for X-ray Crystallography*, Vol. II) have inaccuracies up to 2·5 %. A new table valid for $\mu R \leq 30$ with an accuracy better than 10^{-3} is given, and the principles of its calculation are described.

1. Einleitung

Die Möglichkeit, die Absorptionsfaktoren für elliptisch geformte Körper auf die des Kreiszylinders zurückzuführen (Weber, 1963), haben wir in einem Rechenprogramm verwendet. Als Basis dieses Programmes dient das von Bond (1959) für den Kreiszylinder angegebene Approximationspolynom (1).

Während des Programmtestes zeigte sich, dass das benutzte Polynom (1) bereits für kleine μR Approximationsfehler in der Grössenordnung 1% liefert. Die Fehler haben für $\theta=0°$ und $\theta=90°$ verschiedene Vorzeichen (Fig. 2). So findet man z.B. eine Abweichung von +0,5% für $\mu R=1$ und $\theta=0°$. Die Genauigkeit sinkt auf rund ±2,5% ab für $\mu R=8$ bei $\theta=0°$ (positives Vorzeichen) und bei $\theta=90°$ (negatives Vorzeichen). Die Tabelle 5.3.5B des 2. Bandes der *International Tables for X-ray Crystallography* (1959) ist für $\mu R \leq 8$ mit der Formel (1) berechnet und enthält daher für einige θ-Werte systematische Fehler dieser Grössenordnung. Angaben über die Tafelgenauigkeit fehlten bisher. Da einerseits heute die Messgenauigkeit der Reflexintensitäten die Grössenordnung 1% erreicht, andererseits die Tabelle gelegentlich zur Prüfung von Rechenprogrammen herangezogen wird, die der Absorptionskorrektur dienen (z.B. Coppens, Leiserowitz & Rabinovich, 1965), schien uns eine Neuberechnung der Tafel nützlich und wünschenswert zu sein. Im Ver-