

plane is inclined to that of the benzene ring at an angle of some 10° about the N_2-C_5 bond. The packing of the molecules is reasonable and is consistent with inter-molecular binding by Van der Waals forces, the molecules themselves being arranged substantially in layers of the order of 3.3 \AA apart and parallel to the $(10\bar{1})$ planes. The shortest intermolecular contact within a layer is an $O \cdots C$ distance of length $3.33 \pm 0.04 \text{ \AA}$ and the shortest contact between layers is again an $O \cdots C$ distance of length $3.32 \pm 0.04 \text{ \AA}$; the length of the intermolecular $S \cdots CH_3$ contact is $3.87 \pm 0.02 \text{ \AA}$.

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Effects of Bonding on Electron Diffraction Values of Bond Distances Involving Hydrogen Atoms in Solids

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The effects of bonding on the maximum of the potential of the hydrogen atom are calculated from an approximate model for various data cut-offs and thermal motions as a function of the shift of the electron cloud. It is concluded that the shift of the maximum of potential is much smaller than the shift of the electron cloud and is in the opposite direction. Hence electron diffraction determinations of bond distances involving hydrogen atoms should yield values which are slightly longer than internuclear distances. For typical conditions of data cut-off and thermal motion this lengthening is predicted to be about 0.03 \AA , in good agreement with some recent data obtained by Vainshtein. These results do not negate the argument that the apparent contraction of heavy atom-hydrogen atom bond distances found in X-ray studies is the result of migration of the K electron of the hydrogen atom toward the heavy atom.

Introduction

There are now many well-established cases where X-ray studies have led to anomalously short values of bond distances involving hydrogen atoms. To cite just two examples Marsh (1958) found the C-H distance in glycine to be $0.91 \pm 0.06 \text{ \AA}$ ($\sim 0.18 \text{ \AA}$ short); McDonald (1960) found the N-H distances in NH_4HF_2 to be $0.88 \pm 0.03 \text{ \AA}$ ($\sim 0.15 \text{ \AA}$ short). A qualitative explanation for such apparent shortening is that the K electron of the hydrogen atom as a result of bonding migrates toward the heavy atom. The separation of the maximum electron density of the hydrogen atom from that of the heavy atom, this separation being the one determined in X-ray studies, is then less than the internuclear separation. In atoms heavier than hydrogen the K electrons are not involved in bonding and their contribution to the electron density at the

origin is sufficiently great to keep the maximum electron density coincident with the nucleus. Tomiie (1958) (who gives other examples of short distances) has looked into this problem of short hydrogen distances in detail and concludes that the observed shortenings are reasonable on the basis of a valence bond calculation of bonding effects.

On the other hand bond distances involving hydrogen atoms can be determined by electron diffraction techniques to smaller limits of error than is generally possible with X-ray methods. Such distances, which are in fact the distances between maxima of the potentials of the atoms, are usually within a few hundredths of an Ångström of the internuclear distances. It seems clear then that it is necessary to show that charge migration has only a small effect on the position of the maximum of the hydrogen atom poten-

tial before one can accept charge migration as the explanation of the short X-ray bond values. Recently Shimaoka (1960) found that indeed for a hypothetical 'neutral' hydrogen crystal migration of charge had little effect on the position of the maximum of the hydrogen atom potential. On the other hand, Shimaoka's approach was rather indirect owing to difficulties of convergence of the separate nuclear and electronic contributions to the projected potential. Shimaoka's finding, if general, is an important one not only in electron diffraction but also in X-ray diffraction. It seemed prudent, therefore, to estimate the effects of charge migration on the hydrogen atom potential in the three-dimensional case where a direct calculation can be made.

Theory and method of calculation

The potential of the isolated spherically symmetric hydrogen atom may be written

$$\varphi(r) = (\hbar^2/\pi me) \int_0^{s_0} f_e^H(s) \times \exp[-Bs^2/16\pi^2] ((\sin sr)/sr) s^2 ds. \quad (1)$$

Equation (1) is completely analogous to the usual expression connecting electron density with the X-ray scattering factor. In equation (1) s_0 is the limiting value of

$$s = 4\pi (\sin \theta)/\lambda, \quad (2)$$

where λ is the wavelength of the electron beam and θ is the Bragg angle, one-half the scattering angle. The atomic scattering amplitude f_e^H of hydrogen for electrons may be written as

$$f_e^H = (2me^2/\hbar^2)(1 - f_x^H)/s^2, \quad (3)$$

where f_x^H is the X-ray scattering factor of hydrogen. Substitution of (3) into (1) yields

$$\begin{aligned} \varphi(r) &= (2e/\pi) \left[\int_0^{s_0} \exp[-Bs^2/16\pi^2] (\sin sr/sr) ds \right. \\ &\quad \left. - \int_0^{s_0} f_x^H(s) \exp[-Bs^2/16\pi^2] ((\sin sr)/sr) ds \right] \\ &= \varphi_n(r) - \varphi_e(r). \end{aligned} \quad (4)$$

In the preceding equations B is the usual temperature factor, equal to $8\pi^2\langle u^2 \rangle$, where $\langle u^2 \rangle$ is the mean-square amplitude of vibration. When we write the same B in both integrals of (4) we assume that the nucleus and the electron cloud have the same mean-square amplitudes of vibration. This assumption, which is invariably made in electron diffraction work, seems justified as a first approximation. The first integral of equation (4) is the contribution φ_n of the nucleus to the potential, and the second integral is the contribution φ_e of the electron cloud. As Shimaoka noted, in the two-dimensional projection of potential the separate contributions are individually divergent.

This divergence is what forced Shimaoka to base his calculation on a hypothetical hydrogen crystal. However, both integrals in equation (4) are well behaved.

Let us suppose that the center of the electron cloud is shifted a distance Δ away from the hydrogen nucleus toward the heavy atom in a heavy atom-hydrogen atom bond. (We take this direction as negative.) If we assume that this shifted electron density remains spherically symmetric we may represent the hydrogen atom potential as

$$\varphi(r, \Delta) = \varphi_n(r) - \varphi_e(r - \Delta). \quad (5)$$

This assumption of spherical symmetry of the electron cloud is made mainly for convenience. We are after an estimate, not a precise calculation, of the effects on the maximum of the hydrogen atom potential of charge migration. The labor involved in evolving a physically reasonable model of the electron distribution of the bonded hydrogen atom is not warranted. Moreover, as McDonald (1956, 1960) has emphasized there is no experimental X-ray evidence for a change in the electron distribution of the hydrogen atom on bonding: All that appears to occur is a movement of the distribution toward the heavy atom. Finally, as Shimaoka (1960) has argued, any distortion of the potential which might result from deviations from spherical symmetry of the electron cloud would be expected to have little effect on the position of the maximum of the potential.

In the determination of bond lengths it is the maximum of the potential which is of concern. Accordingly we shall solve the equation

$$d\varphi(r, \Delta)/dr = 0 = \varphi'(r, \Delta) = \varphi'_n(r) - \varphi'_e(r - \Delta), \quad (6)$$

where, for example, $\varphi'_n(r)$ has the form

$$\begin{aligned} \varphi'_n(r) &= (2e/\pi r) \int_0^{s_0} \exp[-Bs^2/16\pi^2] \\ &\quad \times \{\cos sr - ((\sin sr)/sr)\} ds. \end{aligned} \quad (7)$$

Even though f_x^H may be expressed in closed form, the various integrals of (4) and (7) cannot be expressed in closed form, except under certain limiting conditions. However, equation (6) may readily be solved numerically. The required integrations were performed on a Datatron 205 using methods described previously (Ibers, 1961).

Results and discussion

In Fig. 1 we plot the position of the maximum of the potential versus the shift of the electron cloud both relative to the nucleus for various cut-offs and temperature factors. The striking features of Fig. 1 are: (1) the shifts of maximum of potential are much smaller than those of the electron cloud center, in agreement with Shimaoka's calculation; and (2) the potential maximum shifts in a direction *opposite* to that of the electron cloud.

Several features of the shift of the potential maximum with shift of the electron cloud which are not shown or are not obvious in Fig. 1 may be understood

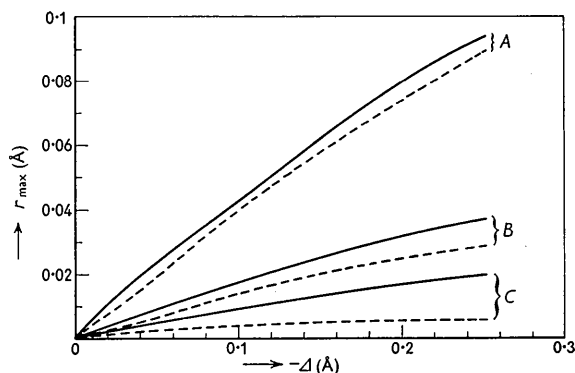


Fig. 1. Shift in maximum of potential r_{\max} , versus the shift in the electron cloud Δ . Solid lines are for $B=3 \text{ \AA}^2$, dashed lines for $B=1 \text{ \AA}^2$. Curves A, B, and C correspond to data cut-offs $(\sin \theta)/\lambda=0.43, 0.65, \text{ and } 1.40 \text{ \AA}^{-1}$.

from equations (4) or (7). For example, $\varphi_e(r-\Delta)$ will approach zero as $|\Delta|$ gets very large (i.e., as H becomes H^+) and so r_{\max} will approach zero at sufficiently large $|\Delta|$. Moreover, the temperature factor acts as a damping factor and so it is clear from equation (4) that $\varphi_n(r)$ and $\varphi_e(r)$ will reach their limiting values at lower s the higher the B . This is the reason that the separation between curves for $B=3 \text{ \AA}^2$ in Fig. 1 is less than the separation between curves for $B=1 \text{ \AA}^2$. In fact, Curve C for $B=3 \text{ \AA}^2$ represents not only the case for $(\sin \theta)/\lambda=1.40 \text{ \AA}^{-1}$ but also the limiting case $(\sin \theta)/\lambda=\infty$. Finally it is interesting to note that $\varphi_n(r)$ is infinite at $r=0$ if $B=0$ and $s_0=\infty$. Under these conditions (which are never met in practice) a shift of the electron cloud would not affect the maximum of the potential.

Accurate electron diffraction data on hydrogen bonds are scarce. Vainshtein (1958) has called attention to the fact that some heavy atom-hydrogen atom

distances (in particular, C-H distances) tend to be longer than the spectroscopic values. In particular, in what is perhaps the most accurate electron diffraction determination of its kind, Vainshtein, Lobachev & Stasova (1958) have determined that the C-H distance in normal paraffins is $1.125 \pm 0.015 \text{ \AA}$. The conditions of data cut-off and temperature factor in this determination were typical: The cut-off was about 0.6 \AA^{-1} and, as nearly as we can judge from the peak height of the hydrogen atom, the temperature factor for hydrogen is 3 to 4 \AA^2 . If we take a shift of the electron cloud of 0.18 \AA (in accordance with typical X-ray data on C-H distances) we predict from Fig. 1 that the maximum of the potential should be shifted by about 0.03 \AA . This is very near to the amount by which the electron diffraction value exceeds the internuclear paraffin C-H distance of 1.09 \AA , as determined spectroscopically.

It is possible, then, that electron diffraction values of bond distances involving hydrogen atoms will be slightly longer than internuclear distances, owing to the effects of charge migration on the maximum of the potential. However, in general such lengthening will be small and will be within the limits of error currently associated with such determinations. Hence, the fact that electron diffraction distances are normal or approximately normal in no way negates the argument that the short heavy atom-hydrogen atom bond distances found in X-ray studies are the result of charge migration.

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