Nature of the Chemical Bonds in HCN and C$_2$N$_2$

By

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The function $\delta (M)$, which measures the effect of the bond formation on the electron density distribution, has been calculated for HCN and C$_2$N$_2$. The charge build up in the CN bonds is found to be quite the same in both molecules, which indicates that the outer bonds of C$_2$N$_2$ are practically unaffected by conjugation.

Since its introduction by DAUDEL and his collaborators [13, 14], the calculation of the difference density in molecules, now customarily referred to as the function $\delta (M)$, has proved to be a very useful means of getting information on the nature of the chemical bonds. The method has so far been applied to various groups of diatomic and to several simple polyatomic molecules [15—17]. In a recent study by ROSENFELD [12], which contains a detailed analysis of the nature of the function $\delta (M)$, the interest of the method has been emphasized, and a relation has been shown to exist, in $\sigma$ bonds, between the maximum of the function along the internuclear axis and the strength of the bond. A systematic application of the method to polyatomic molecules would obviously be of interest, in view of the comparisons this would make possible. It seems legitimate to hope that from such a study suitable concepts would emerge which would help the understanding of the chemical binding.

The present work, concerned with hydrogen cyanide and cyanogen, has been undertaken with this aim in mind. By considering these two molecules, one of our purposes was to study how the density distribution in the CN bonds is affected by conjugation. The question of the conjugation effects has been much debated those recent years, and therefore we have felt that a study of them by means of the function $\delta (M)$ would be useful.

In the calculations, all-electron SCF wave functions, as determined for HCN by McLEAN [8] and for C$_2$N$_2$ by CLEMENTI and McLEAN [4], have been used. These authors have not varied the orbital exponents. We have calculated the molecular

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density as well as that due to the unperturbed atomic orbitals with the same set of orbital exponents. As usual, the atomic density of carbon has been obtained by considering the $(1s)^2 (2s)^2 (2p)^2$ configuration, with the density averaged over all directions in order to obtain a spherical distribution:

$$q_c = 2 \ 1s^2 + 2\ 2s^2 + 2\ 2p^2.$$  

Here, $2p^2$ stands for the averaged $2p$ density, which is defined as follows:

$$\overline{2p^2} = \frac{\int 2p^2 \sin \theta \, d\theta \, d\varphi}{\int \sin \theta \, d\theta \, d\varphi}$$

Contour maps of the function $\delta (M)$ are given in Fig. 1 and 2 for HCN and C$_2$N$_2$, respectively. The values indicated in the figures are expressed in atomic units (i.e. $e/a_0^3$) which are used throughout this paper.

Note that in the CN bond the charge pile up takes place predominantly at some distance from the internuclear axis. This effect has already been observed in various molecules with multiple bonds [15, 16, 17]. It has been attributed to the fairly large amount of electrons taking part in the formation of those bonds [2, 5].

A striking feature which emerges from the curves is that the distribution of the function in the neighborhood of nitrogen is quite similar in both cases. Namely, the equidensity curves in the region of the lone pair, around the nitrogen nucleus and in the positive zone of the CN bond are almost identical in the two molecules. The integration of the function provides a quantitative confirmation of this point.

The results of the integration, given in the table*, clearly indicate that the CN

* A small discrepancy appears in the results concerned with C$_2$N$_2$. Namely, the total charge built up differs by 2% from that removed. This is very probably due to the inaccuracy affecting the various integrations.