Theoret. chim. Acta (Berl.) 2, 177—180 (1964)

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# Nature of the Chemical Bonds in HCN and $C_2N_2$

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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 $C_2N_2$. 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 $C_2N_2$ are practically unaffected by conjugation.

La fonction $\delta$ (M), qui mesure l'effet de la formation des liaisons sur la distribution de la densité électronique, a été calculée pour HCN et $C_2N_2$. D'après les calculs, l'accumulation de charge dans les liaisons CN est pratiquement la même dans les deux molécules. ce qui indique que les liaisons extérieures de $C_2N_2$ ne sont en fait pas affectées par la conjugaison.

Die Funktion $\delta$ (M), ein Maß für die Änderung der Elektronendichteverteilung durch Bildung von Bindungen, wurde für HCN und $C_2N_2$ berechnet. Danach ist die Ladungsanhäufung in den CN-Bindungen für beide Moleküle praktisch gleich, was darauf hinweist, daß die äußeren Bindungen im $C_2N_2$ durch die Konjugation kaum verändert werden.

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 $C_2N_2$ 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:

$$\varrho_C = 2\,1s^2 + 2\,2s^2 + 2\,\overline{2p^2}.$$

Here, $\overline{2p^2}$ 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 $C_2N_2$, respectively. The values indicated in the figures are expressed in atomic units (i. e. $e/a_0^3$) which are used throughout this paper.

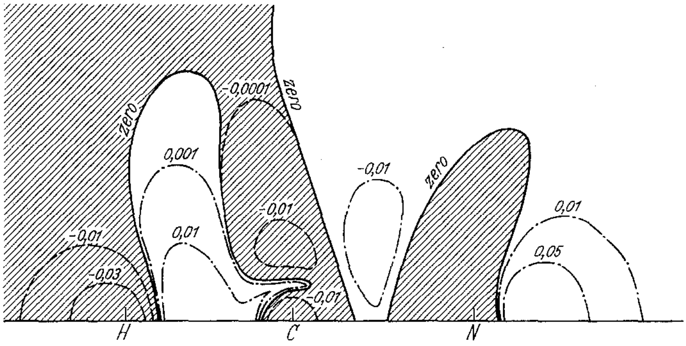

Fig. 1. Contour map of the function $\delta$ (M) in HCN

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*].

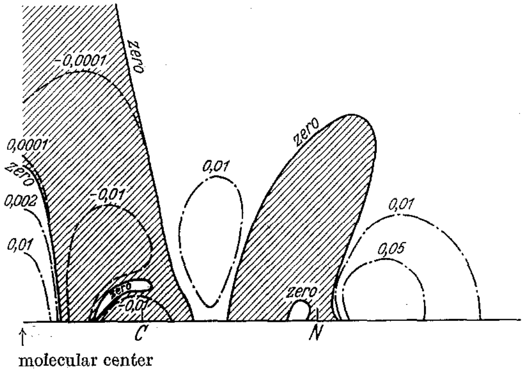

Fig. 2. Contour map of the function $\delta$ (M) in $C_2N_2$. Only a quarter of space is represented

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

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* A small discrepancy appears in the results concerned with $C_2N_2$. Namely, the total charge built up differs by 2% from that removed. This is very probably due to the inaccuracy affecting the various integrations.

bonds are almost identically the same in the two compounds (except for a small difference in the charge removed from nitrogen, which we will not be concerned with here). It is particularly remarkable that the charge accumulation characterizing the CN bond is constant, whereas it would be expected that in $C_2N_2$ conjugation between the two triple bonds would reduce somewhat the charge build up in the two outer bonds. However, the discrepancy is not so important, for it is now established that outer bonds are very little affected by conjugation, as DUCHESNE showed some time ago [*7*]. MULLIKEN [*9, 10*] has moreover emphasized that bond length changes predicted for these bonds by the latest applications of MO theory are comparable with experimental errors.

Table. *Charge drifts in the various parts of the molecules of hydrogen cyanide and cyanogen*

| | HCN | $C_2N_2$ |
|---|---|---|
| charge built up in the nitrogen lone pair ...... | 0.230 | 0.233 |
| charge removed from nitrogen ............... | 0.237 | 0.274 |
| charge built up in a CN bond ............... | 0.169 | 0.169 |
| charge removed from carbon.................. | 0.085 | 0.132 |
| charge built up in the CC bond .............. | | 0.023 |
| charge built up in the CH bond ............. | 0.055 | |
| charge removed from hydrogen .............. | 0.131 | |

If one uses the change in overlap population as a measure of conjugation, there is found a small decrease when passing from HCN to $C_2N_2$ [*3*]: the $\pi$ overlap population of CN goes from 0.953 to 0.937, whereas the total $(\sigma + \pi)$ population goes from 1.472 to 1.432. The results of the present work, namely that conjugation effects are found to be zero, are in slight disagreement with those of the electron population analysis; they support DEWAR's views [*6*] that conjugation in chain systems is practically non existent.

A comparison of the CH bonds in HCN and $C_2H_2$ may be useful. In acetylene, the charge removed from hydrogen amounts to 0.116 e, and the charge built up in a CH bond to 0.050 e [*17*]. Furthermore, the maximum of the function $\delta$ (M), along the internuclear axis, takes place at the very same point as in HCN, i.e. at 1.2 a. u. from carbon. These features suggest the same bond strength and the same bond polarity in the two molecules.

In conclusion, the study of the function $\delta$ (M) proves to be a valuable means of studying the properties of chemical bonds. In our opinion, compared to Mulliken's electron population analysis, it appears to be an equally valid, alternative procedure. The differences which arise between the two methods might be due to the fact that the function $\delta$ (M) may be integrated without introducing any arbitrariness, whereas Mulliken's method implies integration over not well defined zones. It is also possible that in the frame of a more accurate MO theory the disagreement between the two methods would eventually disappear.

We are thankful to Miss Cl. LITT for programming the calculation of the function and to Mrs. M. HENSEVAL for drawing the density contours.

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*(Received February 17, 1964)*