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STUDY OF INTERMEDIATE SPECIES INVOLVED IN THE FORMATION OF ACRYLONITRILE*—II

CHARGE AND SPIN-POLARIZATIONS AND THEIR RELATION TO CHEMICAL STRUCTURE AND ACTIVITY

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Abstract—We present several charge and spin density graphs for the different species involved in the formation of acrylonitrile through the reactions $C_2H_2 + HCN$ and $C_2H_3 + CN$. These graphs were plotted using a modified version of the ISODENS program. Some interesting aspects of polarization shown by comparing charge densities in the different fragments and in acrylonitrile itself are discussed. We also analyse total and individual MO spin polarizations in the C_2H_3 and CN radicals.

INTRODUCTION

THE importance of molecular charge distribution in the theory of chemical binding is well known.[1] Recent results[2] on the transferability of energy for bonded fragments have opened the possibility of studying all the properties of large molecules using the results of the individual fragments.[3] On the other hand the study of spin polarization in relation to the classical chemical picture of bonding as an electron spin pairing process has also developed new interest.[4]

In part I,[5] we carried out CNDO/2 calculations on several molecules, ions and radicals involved in the formation of acrylonitrile. We here present the charge and spin density plots obtained from the population analysis of ionic and radical species obtained in I.

Such density contour maps were plotted by the ISODENS program modified to include open-shell systems. The resulting graphs are present in the following sections. In section 4 we discuss these results.

Charge density contours

In part I we analysed the reaction

$$CH{\equiv}CH + HCN \rightarrow C^+H{=}CH_2 + CN^- \qquad (1a)$$

$$CH_2{=}CH^+ + CN^- \rightarrow CH_2{=}CH - C{\equiv}N \qquad (1b)$$

obtaining the energies, dipole moments and density and bond order matrices of the different reagents and intermediates through a CNDO/2 calculation. Here we

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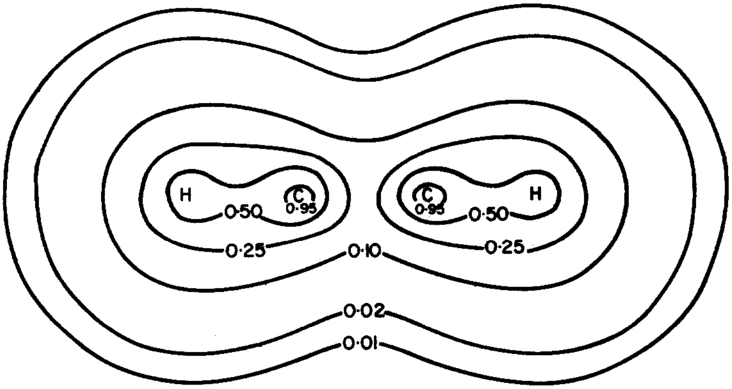

FIG 1. Total valence-electron (v.e.) charge distribution contours for the acetylene molecule. This and following figures correspond to the principal molecular plane except Fig 11.

use the ISODENS/2 program in the version of B.Mély to plot the corresponding density contours.

In Figs. 1 and 2 we show the plots for the neutral molecules C_2H_2 and HCN respectively, and in Figs 3 and 4 the intermediates $C_2H_3^+$ and CN^- are shown, where all molecular structures correspond to those reported in I (in all figures the contours correspond to total valence-electron charge densities and the high concentration of inner-shell charge in the N atom for example does not appear). In Fig 4 the outer contours seem similar to those of the N_2 molecule[6] showing an accumulation of diffusely distributed charge behind C (comparing with Fig 2 we see that the diffuse region behind C is an ideal site for proton attack, thus reforming HCN). This explains the apparently anomalous result obtained in part I where a high dipole moment (– 3·9 d.) is directed towards the most electronegative atom N. This was

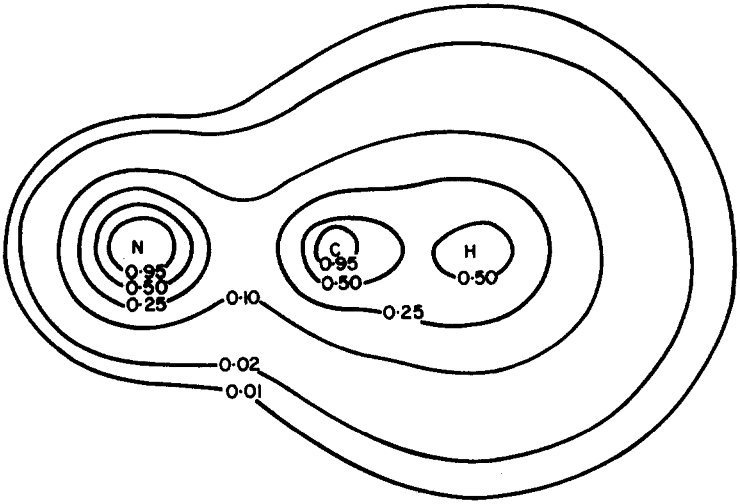

FIG 2. Total v.e. charge contour map for HCN.

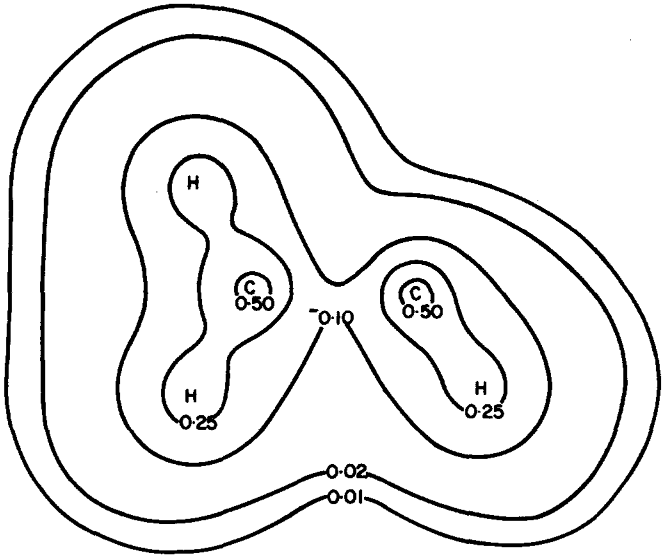

FIG 3. Total v.e. charge contour map for the cation $C_2H_3^+$.

partially explained by the fact that C is slightly more populated than N, but the main contribution comes from the charge contours behind C, a fact that corroborates the chemically intuitive picture of a directed lone pair of electrons.

Moreover we include the charge densities corresponding to the CN· radical and the positive ion CN^+ in Figs 5 and 6. The dipole moments in CN·(0·96 d.) and CN^+ (5·63 d.) are now directed towards C which can be related to the fact that in 5 and 6 the contours are tighter in the outer region of C. This is more true for CN^+, of course, but it is notable that in Fig 5 the unpaired electron can no longer remain directed

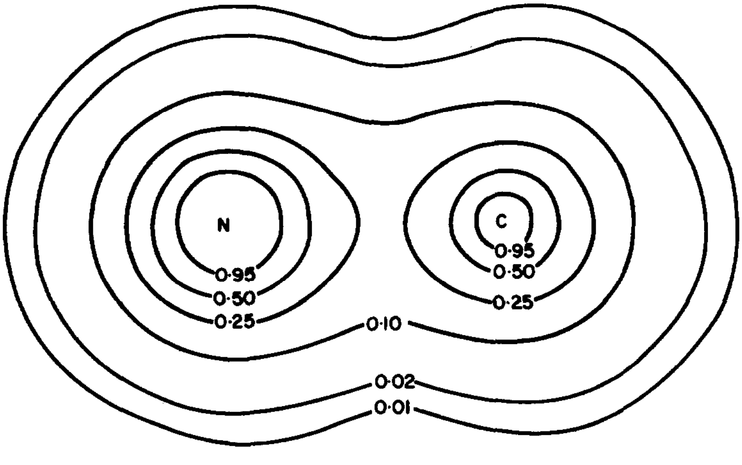

FIG 4. Total v.e. charge contour map for the CN^- anion.

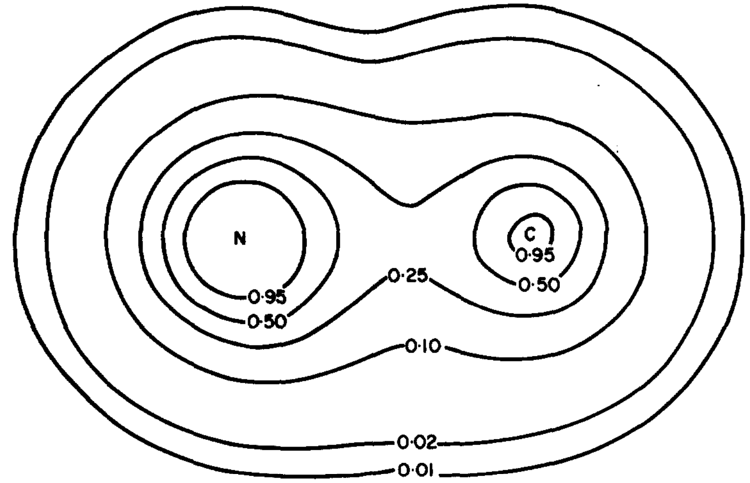

FIG 5. Total v.e. charge contour map for the CN· radical.

outwardly, but seems to reinforce the N—C region, making for a dense N—C bond.

Consider Fig 7 which represents acrylonitrile itself. As was mentioned in part I, the second step in equation (1) is highly exothermic. The relative stability of C_3H_3N with respect to the fragments is apparent from a comparison of Figs. 3 and 4 with Fig 7. The two bonds in the CH_2 part are evidently reinforced in 7 with respect to those in 3, and there is a higher density in the CN region also with respect to that shown in 4.

A point worth noting is: in the CN fragments the π orbital densities are always polarized to the more electronegative atom (N). But in all C—C double bonds the π MO is always counter polarized; that is, the π MO density is always polarized to the

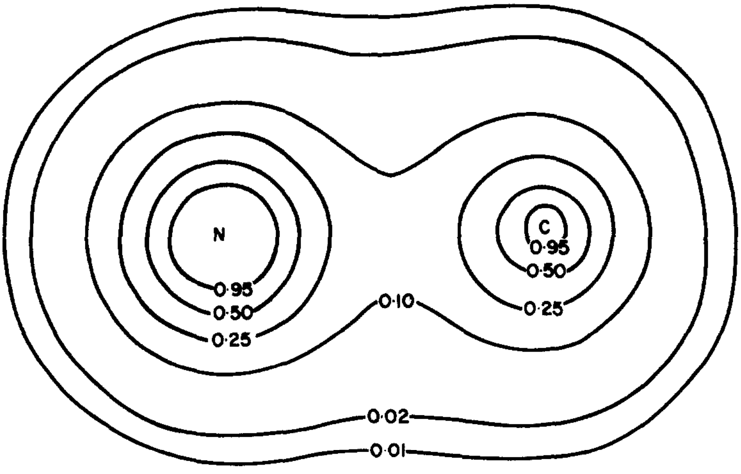

FIG 6. Total v.e. charge contour map for the CN$^+$ cation.

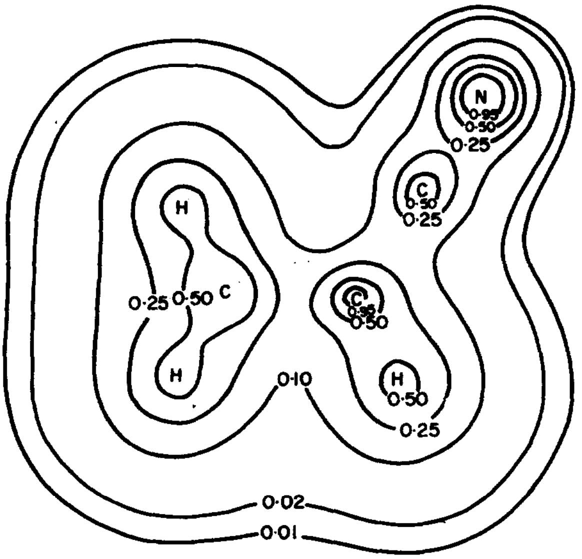

FIG 7. Total v.e. charge contour map for the acrylonitrile molecule.

less populated C atom (*i.e.* that with less total electron charge density). This is shown in Table 1 for Acrylonitrile and for the fragments $C_2H_3^+$, $C_2H_3^-$ and the radical C_2H_3.

TABLE 1. TOTAL ATOM ELECTRON POPULATIONS FOR THE CARBON ATOMS OF THE CATION $C_2H_3^+$, THE RADICAL $C_2H_3\cdot$, THE ANION $C_2H_3^-$ AND ACRYLONITRILE

	Molecule / Atom	$H_2C_1{=}C_2^+{-}H$	$H_2C_1{-}C_2H\cdot$	$H_2C_1{-}C_2^-H$	$H_2C_1{=}C_2H{-}C_3N$
Total Charge Population	C_1	3·999	4·056	4·106	4·011
	C_2	3·640	4·067	4·515	3·994
π-molecular orbital Population	C_1	0·8622	1·0443	1·2436	0·9859
	C_2	1·1377	0·9556	0·7563	0·9990

Spin densities and spin polarization

In I we also discussed the radical reaction:

$$CN\cdot + C_2H_3\cdot \rightarrow C_3H_3N \qquad (2)$$

As both reactants are open-shell systems we modified ISODENS to calculate spin densities. In Figs 8a and 8b the $C_2H_3\cdot$ charge densities corresponding to all α- and all β-spin electrons are shown and in Fig 9 we show the $C_2H_3\cdot$ spin density.

It is noteworthy in Fig 9 that the excess α-spin though largely concentrated in the carbon in the region where 'the 4th H atom' would enter in ethylene, is also present

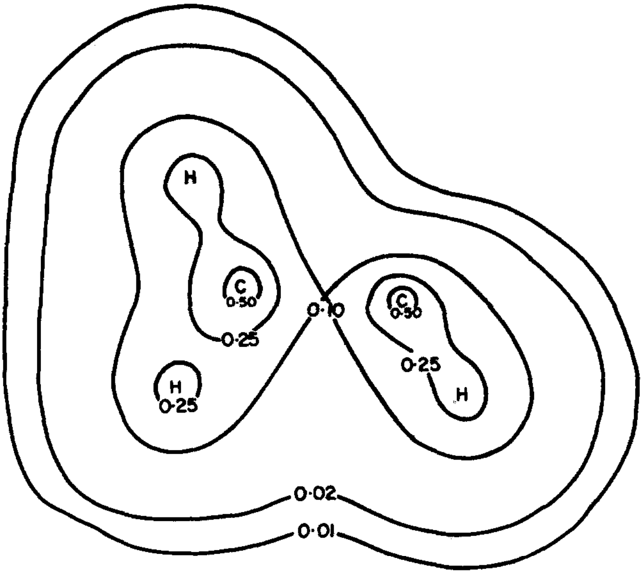

FIG 8a. Total α-spin electron charge distribution for the $C_2H_3\cdot$ radical.

in the other CH bonds, especially in the C_1H_2 region. Notice also the excess β-spin that appears behind the C_1 atom and which is slightly directed to H_2. So the concentration of α-spin in H_2 appears to come not only from the delocalization of the unpaired electron but also from a spin-polarization effect of the C_1H_2 bond. This concentrates β-spin in C_1 and corresponds to an uncoupling mechanism[4] and which accounts for the relative weakness of this bond which is evident in Figs 8.

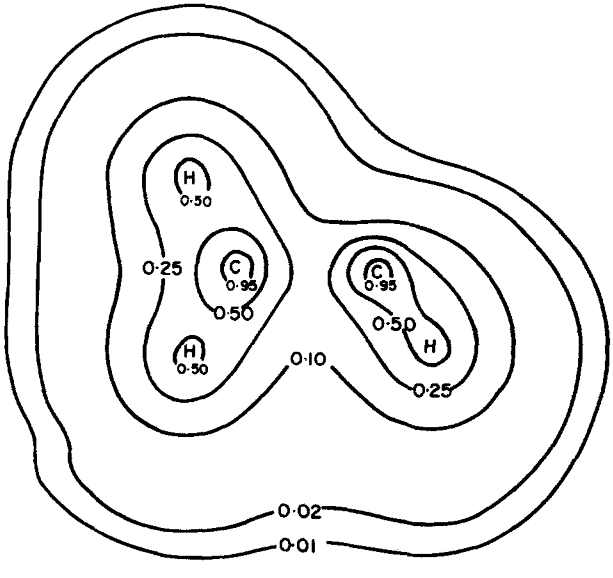

FIG 8b. Total β-spin electron charge distribution for the $C_2H_3\cdot$ radical.

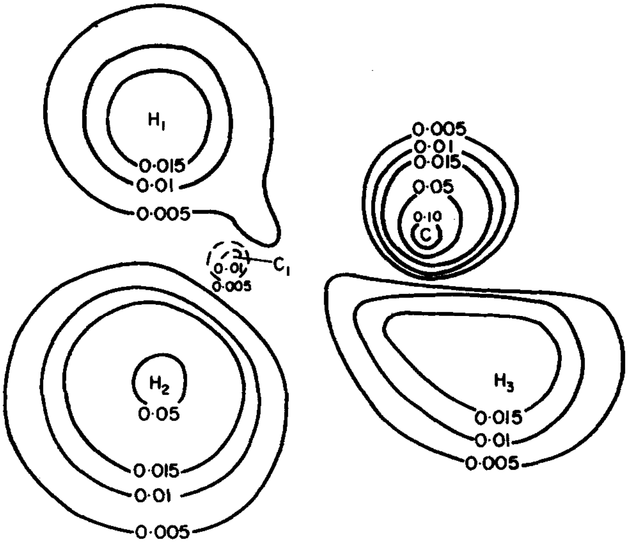

FIG 9. Contour map for the total spin distribution for the $C_2H_3\cdot$ radical with an unpaired α-spin electron. Solid lines denotes excess α-spin, while dashed lines correspond to excess β-spin contours.

Fig 10 shows the spin density for the CN• radical. We see that while the unpaired electron is largely located behind the C atom, it is rather tighter than the contours usually associated with directed lone-pair type electrons. In fact, the diffuseness behind C is balanced by the α-spin contours behind N and so the unpaired electron does not contribute much to the dipole moment (compare the discussion of Fig 4 in section 2). Also to be noted is the appearance of spin polarization in the CN bond.

Fig 11 shows the spin density for the π-MO at a distance of 0·2 Å above the molecular plane. Here we notice a sort of 'spin counterpolarization' in the sense discussed in section 2 for the charge density. It is now the first C atom that has an excess α-spin density, while the second carbon has, for this particular MO, excess β-spin.

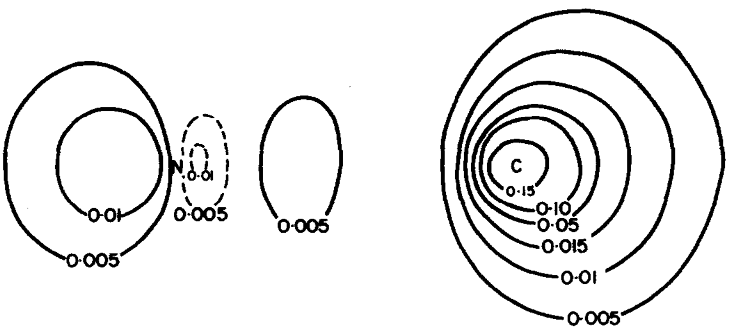

FIG 10. Contour map for the spin distribution for the CN. radical with an unpaired α-spin electron. As in Fig 9 excess α-spin and excess β-spin are denoted by continuous and dashed lines respectively.

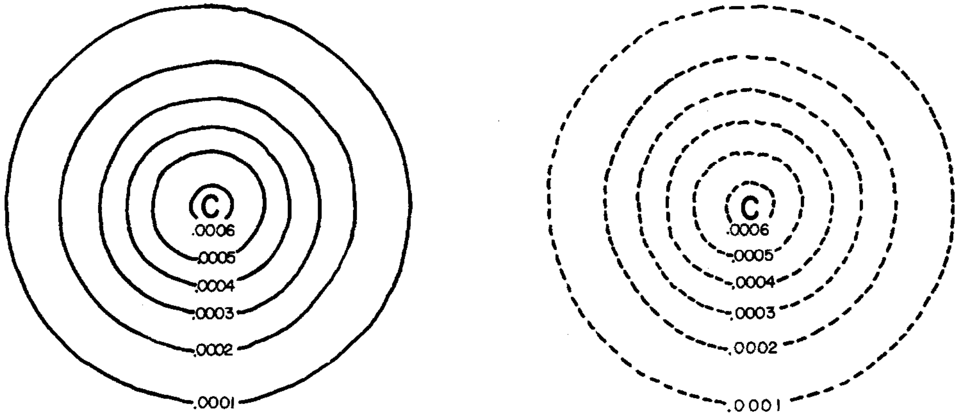

FIG 11. Spin density for the π Mo in the radical $C_2H_3\cdot$. This figure corresponds to a plane parallel to the molecular plane at a distance of 0·2 Å above it. Notice that excess α-spin (solid lines) is located at the 1st carbon while the other one, at which the unpaired electron is located has excess β-spin (dashed lines) for this particular MO.

DISCUSSION

The analysis of the charge contours largely corroborates the conclusions of part I[5] concerning the general trends in the processes of equations (1) and (2). The spin densities of Figs 9 and 10 show interesting polarization effects in the molecular bonds. We have noted an interesting counter-polarization of charge and spin that occurs in all C—C π-bonds studied in this paper and which seems to compensate for the general trend in the total densities.

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REFERENCES

[1] R. F. W. Bader, W. H. Henneker and P. E. Cade. *J. Chem. Phys.* **46**, 3341 (1967)
[2] R. F. W. Bader and P. M. Beddall. *Chem. Phys. Lett.* **8**, 29 (1971)
[3] R. F. W. Bader (private communication)
[4] R. F. W. Bader and R. A. Gangi, *Chem. Phys. Lett.* **6**, 312 (1970)
[5] G. del Conde and O. Novaro *Tetrahedron* **28**, 1789 (1972)
[6] See, for instance, R. F. W. Bader and A. D. Bandrauk. *J. Chem. Phys.* **49**, 1653 (1968)