

Valence Charge Distribution in Some Molecules with Functional Groups*

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Valence charge densities of some rather small molecules with functional groups have been calculated in the charge iterative extended Hückel approach and the results presented in the form of contour diagrams of pertinent sections of the molecules. The diagrams are commented on in the terminology of the organic chemist. The molecules treated are: methanol, nitromethane, formamide, acetone, nitrile and malononitrile.

In some recent papers^{1,2} the author emphasized the value of the valence charge distribution in the description of several all-valence-electron properties of molecules. This distribution can be visualized in the form of topographical maps of pertinent sections of the molecule. These contour diagrams are easily interpreted by inspection even by chemists not directly trained in the reading and interpretation of tables and other representations of quantum mechanical data. The valence charge distribution is to be preferred to hybrids as a tool to illustrate bond properties since no assumptions about hybrids are necessary in LCAO-MO treatments. In addition, one can get an idea about the hybridization from the valence charge distribution.

In this paper valence charge distributions are presented for some molecules with functional groups not treated before in this series. They were chosen sufficiently small to be accessible by more rigorous methods so that a comparison of results will be possible.

METHOD

Since we use the same method as previously for the calculation of eigenvectors and electron densities and the same plotting procedure, only references are given.^{1,3} However, it should be pointed out, that in some of the first

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papers the value 1.0 according to Slater's rules was used for the exponent of the hydrogen $1s$ Slater orbital. In later calculations the "molecular value" 1.2 was introduced.⁵ The charge density is expressed in atomic units or $e (a.u.)^{-3}$. The contours represent the levels 0.01, 0.03, (0.03), 0.30, (0.05), 0.50, (0.20), 1.50 (the steps between the contours are given in parenthesis).

The geometries of the molecules treated were taken from *Tables of Interatomic Distances*,⁴ and are as follows:

Methanol	C-O	1.428 Å	angle COH	109°
	O-H	0.96		
Nitromethane	C-N	1.47	ONO	127°
	N-O	1.21		
Formamide	C-H	1.094	HNH	119.0°
	C-O	1.243		
	N-H	0.995	NCH	103.9°
	C-N	1.343		
Acetonitrile	C-C	1.458		
	C-N	1.157		
	C-H	1.112		
Malononitrile	C-C	1.460	HCH	105.6°
	C-N	1.158		
			CCC	113.6°

Unless otherwise stated the interatomic distance of a C-H bond was assumed to be 1.09 Å. Methyl groups were assumed to have tetrahedral symmetry. The rotational conformation was chosen so that the highest symmetry was obtained.

COMMENTS ON THE DIAGRAMS

Methanol. Fig. 1 a displays the valence charge distribution in the symmetry plane of the conformation chosen (through the atoms H-C-O-H). The polarization of the C-O and O-H bonds is seen. Obviously there is some tendency of lone pair formation at the oxygen atom, and as can be expected from the geometry sp^3 hybridization type can be ascribed to the oxygen atom. This can also be observed in Fig. 1 b, which gives the charge distribution in a section through the C-O interatomic vector and perpendicular to the symmetry plane shown in Fig. 1 a. This is also confirmed by Fig. 1 c, which shows the density distribution in a section through the oxygen atom and perpendicular to the C-O interatomic vector. The difference in charge distribution of the hydroxyl oxygen atom as compared with that of carbonyl is striking (compare with the oxygen atom of nitromethane in Fig. 2 a, and of formamide in Fig. 3 a).

Nitromethane. In addition to the polarization of the N-O bonds within the nitro group, we observe a strong displacement of charge towards the nitrogen atom in the C-N bond. As shown in Fig. 2 a, *i.e.* in the plane of the nitro group, this effect is essentially of σ type. The tendency of double lone pair formation at the oxygen atoms is also pronounced. The polarization of the C-N bond is also obvious from the section through the C-N interatomic

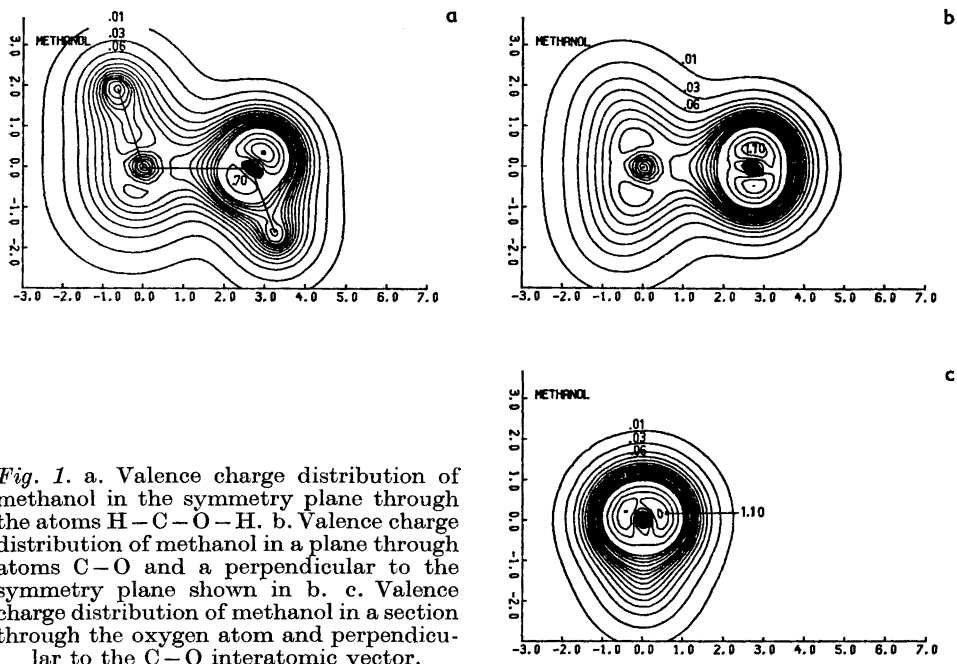


Fig. 1. a. Valence charge distribution of methanol in the symmetry plane through the atoms H-C-O-H. b. Valence charge distribution of methanol in a plane through atoms C-O and a perpendicular to the symmetry plane shown in b. c. Valence charge distribution of methanol in a section through the oxygen atom and perpendicular to the C-O interatomic vector.

vector, perpendicular to the symmetry plane and shown in Fig. 2 b. The high valence charge in the region between the oxygen atoms of the nitro group should also be observed in Fig. 2, a and c. This last figure shows the charge distribution in a section through the oxygen atoms and perpendicular to the plane of the nitro group. Thus, according to this approach to valence charge, it is not distinctly wrong to symbolize the nitro group by a classical valence

line between the oxygen atoms, *i.e.* $-\text{N} \begin{array}{l} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, although a bent line would be

more illustrative.

Fig. 2 d shows the charge density distribution from the valence orbitals containing contributions only from the $1s$ orbitals of the two hydrogen atoms outside the symmetry plane and the four $2p$ orbitals perpendicular to this plane. This means that we have six electrons in three valence orbitals. The section is taken 1.5 a.u. above the symmetry plane in which the σ valence skeleton of the planar part of nitromethane ($\text{H}-\text{C}-\text{N}=\text{O}_2$) is drawn. The figure illustrates the interaction between the methyl group and the conjugated system of the nitro group (hyperconjugation).

Since one of these three valence orbitals is predominated by terms from the two p orbitals of the oxygen atoms and the contribution from the two hydrogen $1s$ orbital coefficients is very small, the four electron density of the two remaining valence orbitals, which represent the main interaction, has been

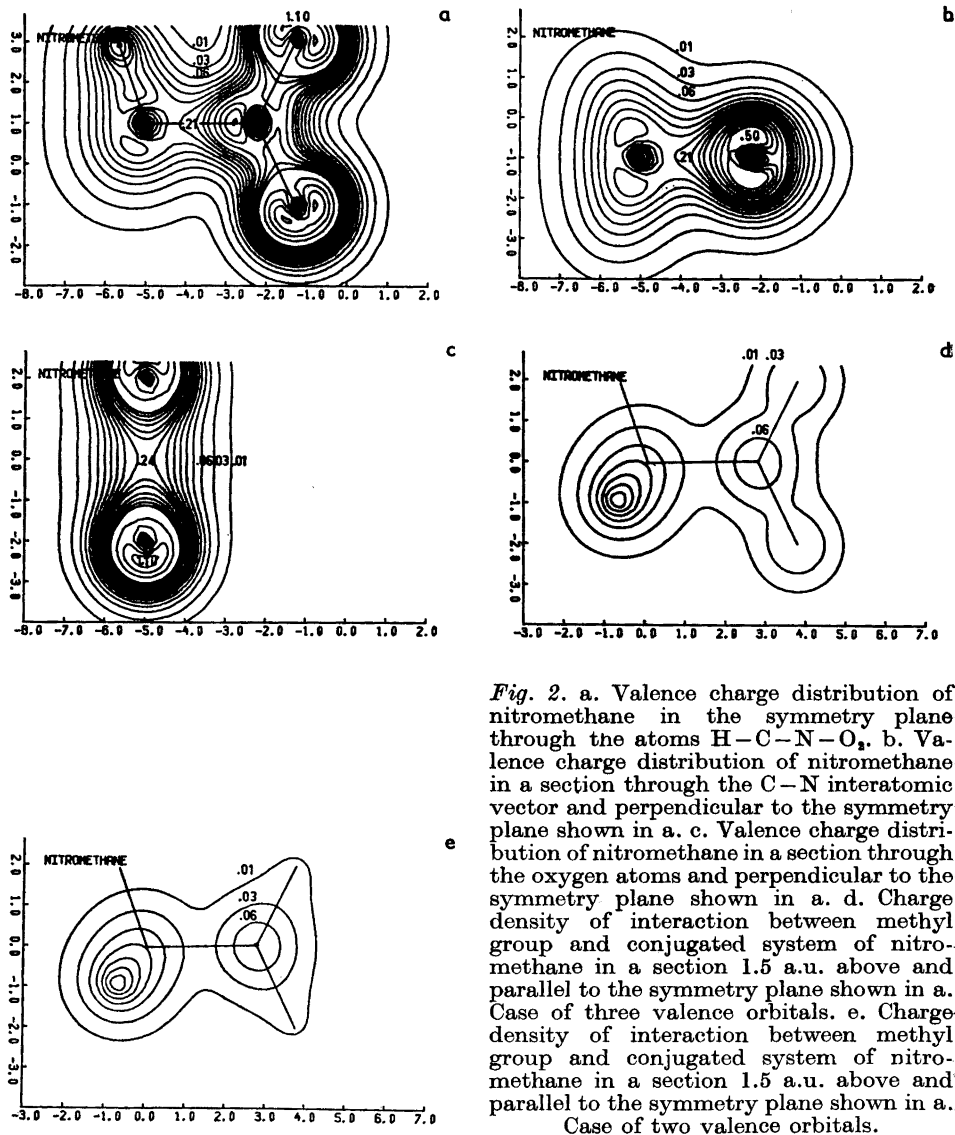


Fig. 2. a. Valence charge distribution of nitromethane in the symmetry plane through the atoms H-C-N-O₂. b. Valence charge distribution of nitromethane in a section through the C-N interatomic vector and perpendicular to the symmetry plane shown in a. c. Valence charge distribution of nitromethane in a section through the oxygen atoms and perpendicular to the symmetry plane shown in a. d. Charge density of interaction between methyl group and conjugated system of nitromethane in a section 1.5 a.u. above and parallel to the symmetry plane shown in a. Case of three valence orbitals. e. Charge density of interaction between methyl group and conjugated system of nitromethane in a section 1.5 a.u. above and parallel to the symmetry plane shown in a. Case of two valence orbitals.

mapped for the same section (Fig. 2 c). The picture is essentially the same as in the preceding figure but the extensive maximum over the oxygen atoms has disappeared.

Formamide. Fig. 3 a shows the σ charge distribution in the molecular plane (the most extensive conjugation is obtained with the amide group coplanar with the aldehyde group). Polarization of the C-N and C-O bonds and the

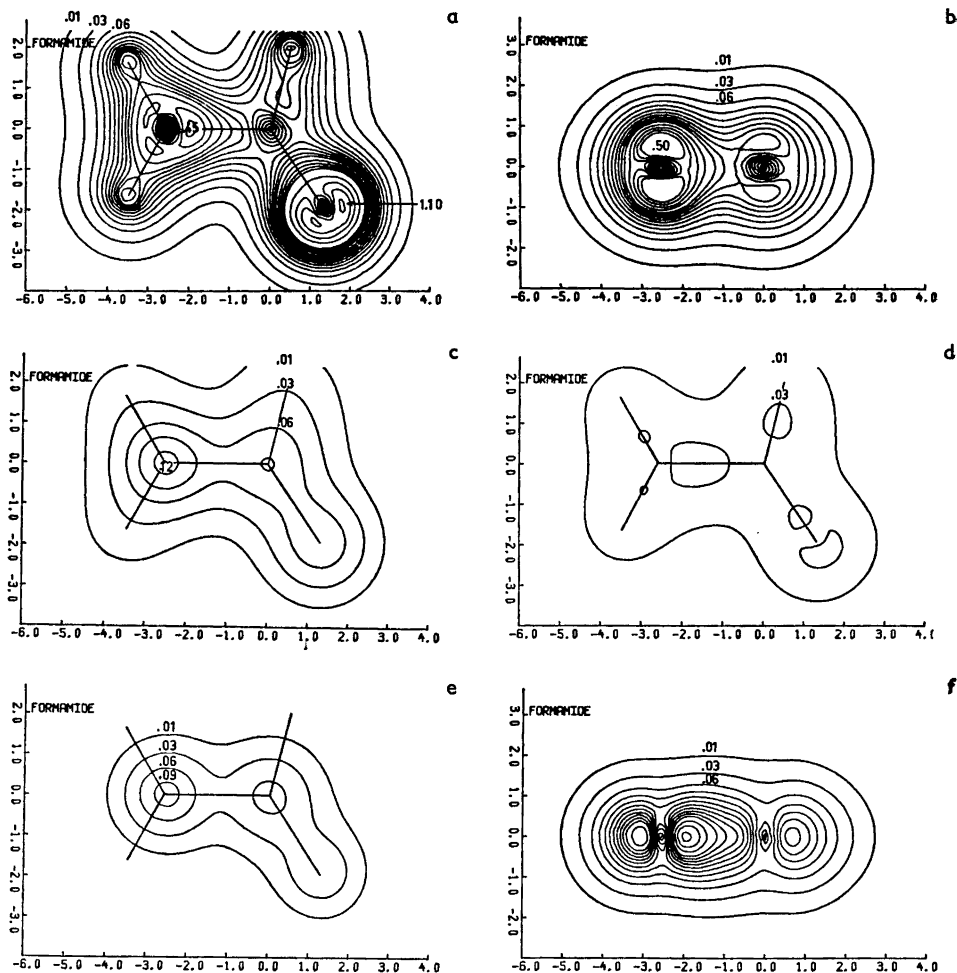


Fig. 3. a. Valence charge distribution of formamide in the symmetry plane through the atoms $H_2-N-COH$. b. Valence charge distribution of formamide in a section through the $N-C$ interatomic axis and perpendicular to the symmetry plane shown in a. c. Valence charge distribution of formamide in a section 1.5 a.u. above and parallel to the symmetry plane shown in a. d. σ -Charge distribution of formamide in a section 1.5 a.u. above and parallel to the symmetry plane shown in a. e. π -Charge distribution of formamide in a section 1.5 a.u. above and parallel to the symmetry plane shown in a. f. σ -Charge distribution of formamide in a section through the $N-C$ interatomic vector and perpendicular to the symmetry plane shown in a.

obvious tendency of double lone pair formation at the carbonyl atom are seen. The bonds are straight or almost so except for the $C-H$ bond which is somewhat influenced by the oxygen atom, too. The valence charge in a section through the $C-N$ interatomic vector and perpendicular to the molecular plane

is shown in Fig. 3 b. The σ and π parts of this valence charge can be studied in Fig. 3, f and g, respectively. The double bond nature of the C–N bond is obvious from Fig. 3 g. Classically this is written as a single bond.

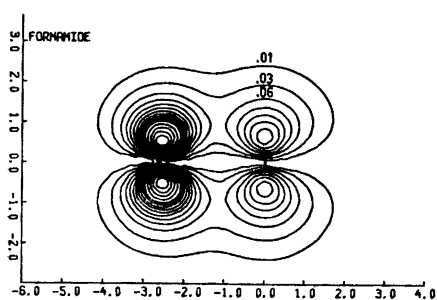


Fig. 3. g. π -Charge distribution of formamide in a section through the N–C interatomic vector and perpendicular to the symmetry plane shown in a.

The distribution of the valence charge in a section 1.5 a.u. above the molecular plane is shown in Fig 3 c, and its σ and π parts in Fig. 3, d and e, respectively. The σ charge maxima over the bonds and of the double lone pair formation are still visible but the π charge seems to predominate in this sections (*cf.* Fig. 3, d and e).

Acetonitrile. The section through the atoms H–C–C–N chosen as symmetry plane of the molecule gives the valence charge distribution shown in Fig. 4 a. In addition to the polarization within the cyano group, this group causes a polarization of the C–C bond. At the nitrogen atom a lone pair is

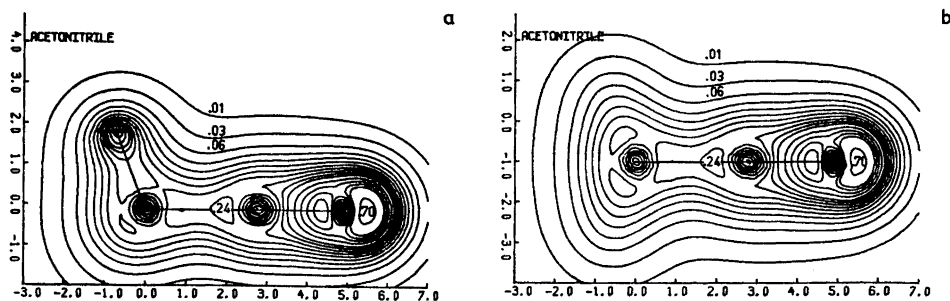


Fig. 4. a. Valence charge distribution of acetonitrile in the symmetry plane through the atoms H–C–C–N. b. Valence charge distribution of acetonitrile in a section through the C–C–N interatomic line and perpendicular to the symmetry plane shown in a.

formed. The contribution from this atom to the charge of the highest occupied valence orbital is 1.52 electrons. A section in the middle of and perpendicular to the C–N interatomic vector shows a circular valence charge distribution (not illustrated here). The interaction between the methyl group and the π bond system of the cyano group does not differ principally from that of nitromethane (see above) but is twofold because of the triple bond nature of

the cyano group. Like the nitro group, the cyano group is "activating" the hydrogen atoms on a neighbouring carbon atom (α position), but this effect is more pronounced in the case of a nitro group.

Malononitrile. This molecule has been included mainly in order to show the increased influence of two cyano groups on the "mobility" of the hydrogen atoms at the carbon atom in α position. The successive replacement of hydrogen atoms in methane by cyano groups leads to an increased positive net charge of the α carbon atom and an increased "acidity" of its hydrogen atom(s). In this

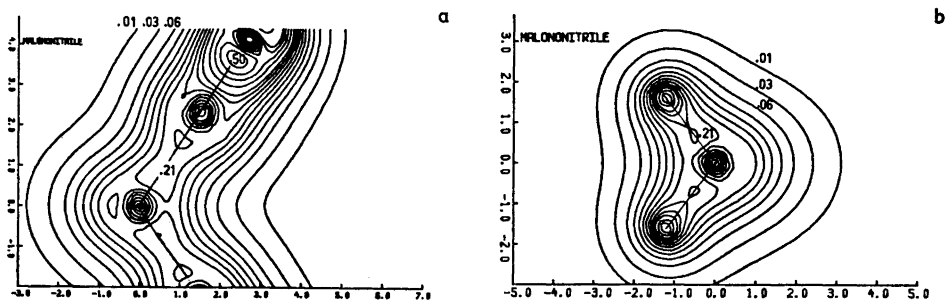


Fig. 5. a. Valence charge distribution of malononitrile in the $C=(CN)_2$ symmetry plane. b. Valence charge distribution of malononitrile in the symmetry plane of the methylene group (perpendicular to the symmetry plane of a).

approach the net charge of the α carbon atom is 0.05 in acetonitrile as compared to 0.09 in malononitrile. In Fig 5 a we see the polarization of the C—C bonds, and in Fig. 5 b its effect on the C—H bonds, the valence charges of which are spread out.

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REFERENCES

1. Mårtensson, O. and Sperber, G. *Acta Chem. Scand.* **24** (1970) 1749.
2. Mårtensson, O. *Acta Chem. Scand.* **24** (1970) 1495, 2673, 3116, 3123, 3417, 3767.
3. Karlsson, G. and Mårtensson, O. *Theor. Chim. Acta* **13** (1969) 195; Karlsson, G. *Int. J. Quantum Chem.* **4** (1970) 127.
4. Sutton, L. E. (Sci. Ed.) *Tables of Interatomic Distances and Configuration in Molecules and Ions*, *Chem. Soc. Spec. Publ.* **11** (1958) and **18** (1965).
5. Mårtensson, O. *Acta Chem. Scand.* **24** (1970) 2673.

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