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The Effect of Substitution on the Properties of a Chemical Group

I. An Analysis of the SCF Description of Changes in the CN Group in the Mono-substituted Acrylonitriles

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The effect of a substituent group R(R = F, OH, NH_2, CH_3) on the electron distribution of a set of 16 mono-substituted acrylonitriles has been analyzed. This analysis, which has been made on SCF wavefunctions calculated with the 4-31G basis set, shows that the substitution effects may be fairly well represented by classical electrostatic interactions between the CN group itself and the molecular remainder, with a clear distinction between through bonds and through space effects. The possible practical implications of a classical description of intramolecular interactions are discussed.

Key words: Substitution effects – Through space and through bond intramolecular interactions

1. Introduction

The systematic examination of the effects of the substituents on the chemical properties of a given group constitutes the main line of investigation followed by experimental chemists to gain a deeper understanding of the chemical phenomena. Such analyses find theoretical support in a large variety of approaches to this problem, ranging from qualitative considerations to highly sophisticated methods.

We shall present in this paper a relatively simple method of analysis of the substituent effects relying only on the SCF description of the molecular charge density distribution and resorting to only the strictly necessary paraphernalia of auxiliary concepts and of related quantities. We hope that such a naive approach could be considered as a reasonable compromise between the two opposite characteristics of simplicity and rigorousness which must both be satisfied by an interpretative method.

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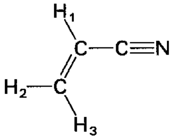
The general outline of this analysis can be summarized in a few words. The SCF description of the charge distribution of a set of related molecules is partitioned into group contributions by means of a well known and straightforward transformation of the molecular orbitals. Some quantities (such as the atomic populations and the local dipole moments) useful in characterizing a specific target group (–C≡N in the present case) are then calculated, and their differences in passing from one molecule of the set to another are correlated with the corresponding changes of the electric field arising from the molecular remainder acting on the target group. The emphasis is thus given to the *classical* effects.

It should be remarked however that even this simple scheme is not devoid of complications, which will be discussed later.

For an application of this scheme of analysis we have selected a set of monosubstituted acrylonitriles. This choice has been dictated by general considerations about the type of effects presumably present in this set more than by a specific interest in the chemical properties of these compounds. In fact the acrylonitriles (I) present some features which are examples of situations of more general occurrence.



(I)

The substitutions can occur at different distances from the target group –CN and there is the possibility of direct comparison between the effects of substituents in *cis* and *trans* position, two facts which will make clearer the importance of effects transmitted through space. Moreover, the presence of a π subsystem coupled to the –CN group will show the importance of the through bond transmission of substitution effects, specific of the π systems.

2. Description of the Molecular Geometries, Computational Details and Method of Analysis

The starting point for the analysis is given by the calculation of the SCF wavefunction for all the molecules of the set.

The calculation has been carried out employing the GAUSSIAN 70 program system [1] with the 4-31G basis set [2]. The set of molecules is composed of acrylonitrile itself and of all the monosubstituted acrylonitriles where an H atom has been replaced by F, NH_2, CH_3, and OH. Since we were interested in examining the effect of substitution on some model compounds we have considered it expedient to adopt a geometry near the experimental one for the acrylonitrile skeleton and standard bond lengths and angles for the substituents [3].[1]

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[1] For the same reason we have not considered it necessary to investigate possible tautomeric transformations, for example the transformation of 3, OH-acrylonitrile into 2-cyanoacetaldehyde.

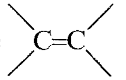
The values of the geometrical parameters are reported in Table 1. Actually the substitution will also produce changes in the geometry; the constraint we have imposed on the geometry can be considered as a separation of effects, to some extent arbitrary, but useful in simplifying the analysis and showing more clearly the reorganization of the charge distribution due to the substitution.

Table 1. Bond lengths[a] and angles[b]

Skeleton[c]		Substituents	
$R_{C=C}$	1.339	R_{C-F}	1.325
R_{C-CN}	1.426	R_{C-OH}	1.360
R_{C-H_1}	1.070	$R_{O-H'} < COH$	0.993, 105°
$R_{C-H_{2,3}}$	1.086	R_{C-NH_2}	1.400
R_{C-N}	1.164	$R_{N-H'} < CNH$	1.010, 120°
$< CCC$	120°	R_{C-CH_3}	1.520
$< HCC$	120°	$R_{C-H'} < CCH$	1.090, 109.47°

[a] Ångstroms.
[b] Degrees.
[c] The values concerning the acrylonitrile skeleton are taken from: Costain, C. C., Stoicheff, B. P.: J. Chem. Phys. **30**, 777 (1959).

The CH_3 group has been kept fixed at a conformation having a C–H bond on the skeleton plane in the syn-periplanar position with respect to the C=C bond. For the OH group we have made separate calculations on planar conformers having the O–H bond syn- and anti-periplanar with respect to the C=C group. On the whole, the set of wavefunctions under examination corresponds to 16 molecular systems having different substituents, placed at different positions or arranged in different conformations. Table 2 gives the names, the total energy and the electric dipole components of these species.

The localization of the canonical SCF orbitals was made according to the Boys procedure [4]. The general shape of the resulting LO's is in accordance with what has been found in many preceding cases: the C=C group is represented by two bananas and the CN group by three bananas and by a lone pair with a well defined *sp* character. We have adopted this type of LO description of the system, rather than the alternative one deriving from a separate localization of the σ and π MO's, because the banana description of the –CN group shows more clearly certain substitution effects, and there are no particular difficulties in using this type of localization to show the transmission of effects through the C=C group. It should be noted that in a parallel study on the analysis of the substitution effects on the  group, which will be the subject of a further paper, it was found slightly more instructive to localize separately σ and π orbitals.

It is well known that the LO's do not constitute a completely satisfactory basis for the description of models of chemical groups, because the presence of non-negligible tails on the other atoms of the molecule makes impossible a *direct* transfer of the corresponding group models from molecule to molecule. The origin and the actual physical importance of these tails have been the subject of numerous papers ([5–9] and references quoted therein). In the context of the present paper it is not

Table 2. Total energy and dipole moment components

Compound		E_{tot} [a]	μ_x [b]	μ_z [b]
I	Acrylonitrile	−169.5133	−0.544	−4.286
II	1, F-	−268.2292	−2.134	−2.783
III	1, OH(sp)-	−244.2456	−1.824	−4.639
IV	1, OH(ap)-	−244.2471	−0.123	−1.617
V	1, NH_2-	−224.4581	0.929	−3.972
VI	1, CH_3-	−208.4952	−0.036	−4.269
VII	2, F-	−268.2357	−0.614	−2.271
VIII	2, OH(sp)-	−244.2549	0.759	−3.671
IX	2, OH(ap)-	−244.2558	−2.946	−3.788
X	2, NH_2-	−224.4713	−1.566	−6.177
XI	2, CH_3-	−208.4949	−0.783	−4.914
XII	3, F-	−268.2344	1.081	−5.173
XIII	3, OH(sp)-	−244.2562	0.847	−3.502
XIV	3, OH(ap)-	−244.2536	−1.206	−6.758
XV	3, NH_2-	−224.4726	−2.299	−4.773
XVI	3, CH_3-	−208.4949	−1.077	−4.328

[a] Hartrees.

[b] Debyes; the *z* axis is colinear to the CN axis and the positive *x* values lie in the halfplane opposite to that containing the C=C bond.

necessary to review this subject, as it is sufficient to see if the occurrence of tails could introduce ambiguities in our analyses of the change in the shape of the group charge distributions and in the mutual interactions between groups. In the next section we shall present the results of numerical tests showing that actually the tails do not introduce serious alterations to the analysis. In passing we may note that for many applications the tails do not constitute a serious problem, since it has already been shown that it is possible to obtain directly from LO models of groups a reasonable picture of the molecular charge distribution [10, 11] as well as the essential pieces for the calculation of the wavefunctions of larger molecules [12, 13]. Transferability in much greater detail can be however achieved by including also the tails as a careful analysis of England *et al.* [14] has shown.

There is a wide choice of quantities related to the –CN group which can be used as a test for examining the influence of the substituent. Some quantities can be experimentally measured (the nuclear quadrupole constant of ^{14}N, the chemical shifts of the C and N atoms, the nuclear spin-spin coupling constants, etc.), but we have preferred to present results concerning a quantity related to a simpler operator, the local component of the dipole moment which, although not directly obtainable from experimental measurements, is particularly suited for showing the effect of the substituents on the electronic distribution of the target group. In fact this quantity has been widely employed as a numerical measure of the spatial features of LO's [15–17]. Another test which has been widely employed by chemists to characterize chemical groups is given by the Mulliken atomic populations. The inconsistencies and the inconveniences of using these atomic populations, which are not observables, for the study of rather fine details of the electronic distribution are so well known that it is not necessary to dwell here on this topic: we shall make a moderate use of the population analysis only to supplement the information arising from the local component of the dipole moment.

Local components of the quadrupole moment provide further complementary information, but we have preferred to omit here the presentation of such data, because they would have made the analysis too cumbersome and introduced the possibility of confusing the main point of interest of this investigation.

In fact, a classical electrostatic interaction between target and remainder, measured with the values assumed by the electric field $\boldsymbol{E}$, generated by the remainder, in the regions where the electron density of the CN group is higher, seems to be sufficient to reproduce fairly well the effects of the substituents. The practical implications presented by this possibility of introducing an electrostatic picture even in the prediction of strong (and inherently non-classical) intergroup interactions will be the subject of the final discussion.

3. Characterization of the –CN Group

The –CN group is represented, in the localized orbital description, by two inner shell orbitals, $1s_C$ and $1s_N$, by a lone pair, l_N and by three banana bonds, β_{CN}, which in linear molecules, like HCN, have their charge-centers located at the vertices of an equilateral triangle which freely rotates in the localization process [15, 18]. In asymmetric compounds, like the acrylonitriles, this local symmetry is perturbed and the rotation of the three β_{CN}'s is no more free[2]: we shall return later to this feature of the LO's. The –CN group is connected to the remainder by means of a single bond, σ_{CC}.

The first question to settle concerns the entity of the charge transfer effects. To this end we are compelled to resort to comparisions among the molecules in our set, because it is not possible to enucleate an isolated CN group as a standard, and consequently we shall make reference to the unsubstituted acrylonitrile (I). The electron shift from the C and N atoms in acrylonitrile (I) towards the molecular remainder, as measured from the gross populations, is of 0.2605 e. A rough idea of the entity of the further charge transfer due to the substitution can be obtained by examining the changes in the total gross atomic charges of the group, $Q_N + Q_C$, reported in the first column of Table 3. It appears that the variations of charge transfer, if one uses $\Delta(Q_N + Q_C)$ to measure this quantity, are not negligible, but confined to limits sufficiently narrow to ensure that the essential features of the bonding effect of –CN to the other moiety of acrylonitrile are still present in the substituted compounds. In fact the electron shift from the C and N atoms in our

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[2] In all the molecules of our set there is a banana bond having its charge center located on the molecular plane: this charge center is placed for all molecules but compound (XIII) at positive x values (i.e. on the molecular half-plane which does not contain the C=C group).

Table 3. Substitution effects on the total and partial gross atomic charges of the CN group

Compound		$\Delta[Q_N+Q_C]_{tot}$[a]	$\Delta[Q_N+Q_C]_{\sigma_{CC}}$[b]	$\Delta[Q_N+Q_C]_{rem}$	$\Delta[Q_N+Q_C]_{\beta_{CN}}$	$\Delta[Q_N+Q_C]_{l_N}$
I	Acrylonitrile[c]	0.0	0.0	0.0	0.0	0.0
II	1, F-	−0.05037	0.01061	−0.05220	−0.00885	0.00007
III	1, OH(sp)-	−0.07528	−0.05513	−0.02087	0.00097	−0.00026
IV	1, OH(ap)-	−0.02141	0.03212	−0.05321	−0.00079	0.00048
V	1, NH_2-	−0.01895	−0.01745	−0.01222	0.00966	0.00107
VI	1, CH_3-	−0.00577	−0.00145	−0.01463	0.00959	0.00071
VII	2, F-	−0.00711	−0.00735	−0.00059	0.00089	−0.00005
VIII	2, OH(sp)-	0.00695	−0.03974	0.04041	0.00594	0.00024
IX	2, OH(ap)-	0.01930	−0.00028	0.01657	0.00294	0.00007
X	2, NH_2-	0.03941	−0.01957	0.05106	0.00758	0.00033
XI	2, CH_3-	0.01485	−0.00028	0.01185	0.00312	0.00015
XII	3, F-	−0.04264	−0.03314	−0.00719	−0.00213	−0.00017
XIII	3, OH(sp)-	0.02909	0.02083	0.01592	−0.00724	−0.00044
XIV	3, OH(ap)-	−0.02546	−0.03210	0.00813	−0.00159	0.00010
XV	3, NH_2-	0.03398	0.00382	0.03151	−0.00130	−0.00005
XVI	3, CH_3-	0.01864	0.01016	0.01171	−0.00249	−0.00074

[a] The charges are given in electrons.

[b] In the original Mulliken's notation [19] $\Delta[Q_N+Q_C]_{\sigma_{CC}} \equiv \Delta[Q(\sigma_{CC}, N)+Q(\sigma_{CC}, C)]$, etc.

[c] The values for acrylonitrile are respectively 0.26050, 0.20252, 0.00013, 0.05597 and 0.00190.

reference compound I, is by far larger than the differential effects displayed in Table 3.[3] In the same table we have reported also a dissection of $\Delta(Q_N+Q_C)_{tot}$, into contributions coming from the σ_{CC} orbital ($\Delta(Q_N+Q_C)_{\sigma_{CC}}$, column 2), from the tails of the molecular remainder ($\Delta(Q_N+Q_C)_{rem}$, column 3), from the three β_{CN} orbitals ($\Delta(Q_N+Q_C)_{\beta_{CN}}$, column 4) and from $l_N(\Delta(Q_N+Q_C)_{l_N}$, column 5).

The contributions coming from the $1s_C$ and $1s_N$ orbitals are by far smaller and have not been reported.

The moderate changes in the total gross atomic charges are due for the main part to the sum of the contributions of the σ_{CC} orbital and of the tails of the other groups present in the molecule. This dissection of the Mulliken population changes shows that the substitution has but little effect on the degree of localization of the six LO's of –CN (see columns 4 and 5 of Table 3).

It may be added that the gross charges suggest a fairly good localization degree of such LO's: in fact in acrylonitrile their contribution to the total charge of atoms C and N amounts to −6.0524 e.

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[3] A parallel analysis performed in terms of separate σ and π orbitals showed that in acrylonitrile (I) there is a shift of 0.039 electrons of π type from C and N to the C=C group. This shift (and the corresponding weight of the resonant structure which may be put forward to interpret such a shift) remains essentially constant along our set of molecules.

The Mulliken gross populations cannot give more than the main features of the dissection we are looking for. The localization degree of the LO's can be better measured by the mean square deviation between the LO and its primary part (renormalized) [20]: this test shows that the localization of the –CN LO's remains constant along our set of molecules and this is slightly better than that found for other groups in other molecules [15, 21, 22].

The charge transfer due to the substitution could be estimated also from the net atomic populations: the smallness of the electron shifts from the –CN LO's turns out even clearer. For the sake of brevity we do not report here the numerical data concerning such tests.

The fact that the –CN LO's do not contribute appreciably to this electron transfer does not imply that they are insensitive to the effects of the group substitution. Particularly important are the polarization effects. A first estimate of such polarizations can be obtained by examining again the subtotal gross populations of the pertinent LO's. In Table 4 we give the value of $\Delta(Q_N - Q_C)_{\beta_{CN}}$ in acrylonitrile. The shift of electrons inside the banana of the –CN group is noticeable and larger than the shift from this group to the molecular remainder (compare with column 4 of Table 3). It is not possible to obtain from the Mulliken populations an analogous estimate on the change in polarization of the l_N orbital.

Table 4. Substitution effects on the difference between the N and C subtotal gross atomic charges of the three β_{CN} bond orbitals ($\Delta(Q_N - Q_C)_{\beta_{CN}}$)

I	Acrylonitrile	0.0						
II	1, F-	−0.103	VII	2, F-	−0.040	XII	3, F-	−0.037
III	1, OH(sp)-	−0.079	VIII	2, OH(sp)-	0.009	XIII	3, OH(sp)-	−0.022
IV	1, OH(ap)-	−0.086	IX	2, OH(ap)-	0.019	XIV	3, OH(ap)-	0.023
V	1, NH_2-	−0.049	X	2, NH_2-	0.077	XV	3, NH_2-	0.080
VI	1, CH_3-	−0.001	XI	2, CH_3-	0.033	XVI	3, CH_3-	0.028

The value of $(Q_N - Q_C)_{\beta_{CN}}$ for acrylonitrile is 0.2497e.

A different test, useful for l_N as well as for the β_{CN}'s is given by the displacement of the orbitalic charge centers. This quantity is of course directly related to the change of the corresponding local dipole moments. We give in Table 5 the changes of the dipole components value of a neutral fragment composed by l_N and two positive charges on N. In Table 6 we give analogous values for the β_{CN}'s: in this case the fragment is composed of the three β_{CN}'s and of 3 unit positive charges on C and 3 on N.

It appears evident that the lone-pairs have a low polarizability and that the polarization effects are essentially confined to the β_{CN} orbitals. The larger propensity of bond orbitals with respect to the lone pairs to change their shape under the influence of changes in the molecular environment has been already shown in studies on the ten electron hydrides [17, 23].

Table 5. Substitution effects on the dipole components of the N lone pair localized orbital (l_N)

Compound		$\Delta\mu_x(l_N)^a$	$\Delta\mu_z(l_N)^a$
I	Acrylonitrile[b]	0.0	0.0
II	1, F-	0.0138	0.0168
III	1, OH(sp)-	0.0218	0.0122
IV	1, OH(ap)-	−0.0437	0.0141
V	1, NH_2-	−0.0182	0.0060
VI	1, CH_3-	−0.0120	−0.0014
VII	2, F-	−0.0047	0.0089
VIII	2, OH(sp)-	−0.0085	0.0034
IX	2, OH(ap)-	−0.0038	−0.0006
X	2, NH_2-	−0.0096	−0.0083
XI	2, CH_3-	−0.0029	−0.0041
XII	3, F-	−0.0242	0.0057
XIII	3, OH(sp)-	0.0627	0.0141
XIV	3, OH(ap)-	−0.0384	−0.0051
XV	3, NH_2-	0.0382	−0.0041
XVI	3, CH_3-	0.0168	0.0017

[a] Debyes.
[b] The values of the dipole components for acrylonitrile are $\mu_x = 0.0149$ and $\mu_z = -3.4575$.

Another test showing the larger sensitivity of the β_{CN}'s with respect to l_N is provided by the changes of the β_{CN} and l_N contributions to the electrostatic molecular potential $V_M(k)$ at a fixed point k of the outer molecular space. We report in Table 7 the differences of the l_N and $3\beta_{CN}$ contributions to V_M (with respect to the acrylonitrile molecule) calculated at the point lying 2.12 Å away from the N

Table 6. Substitution effects on the dipole moment components of the three β_{CN} bond orbitals

Compound		$\Delta\mu_x(3\beta_{CN})^a$	$\Delta\mu_z(3\beta_{CN})^a$
I	Acrylonitrile[b]	0.0	0.0
II	1, F-	0.0388	0.3387
II	1, OH(sp)-	0.0259	0.2605
IV	1, OH(ap)-	−0.0419	0.2254
V	1, NH_2-	−0.0324	0.0995
VI	1, CH_3-	−0.0332	−0.0111
VII	2, F-	0.0010	0.0813
VIII	2, OH(sp)-	0.0117	−0.0629
IX	2, OH(ap)-	0.0086	−0.0915
X	2, NH_2-	0.0164	−0.2584
XI	2, CH_3-	0.0067	−0.0933
XII	3, F-	−0.0415	0.1199
XIII	3, OH(sp)-	0.1522	0.0061
XIV	3, OH(ap)-	−0.0519	−0.0317
XV	3, NH_2-	0.0806	−0.2631
XVI	3, CH_3-	0.0083	−0.0977

[a] Debyes.
[b] The values of the dipole components for acrylonitrile are $\mu_x = 0.1223$ and $\mu_z = -1.1961$.

Table 7. Substitution effects on the l_N and $3\beta_{CN}$ contributions to the electrostatic molecular potential V at 2.12 Å from N on the CN axis

Compound		$\Delta V(l_N)$[a]	$\Delta V(3\beta_{CN})$[a]
I	Acrylonitrile[b]	0.0	0.0
II	1, F-	0.44	2.82
III	1, OH(sp)-	0.32	2.20
IV	1, OH(ap)-	0.36	2.04
V	1, NH_2-	0.16	1.00
VI	1, CH_3-	−0.02	−0.01
VII	2, F-	0.21	0.74
VIII	2, OH(sp)-	0.05	−0.47
IX	2, OH(ap)-	−0.04	−0.72
X	2, NH_2-	−0.24	−2.17
XI	2, CH_3-	−0.11	−0.78
XII	3, F-	0.14	0.99
XIII	3, OH (sp)-	0.32	0.39
XIV	3, OH (ap)-	−0.12	−0.35
XV	3, NH_2-	−0.13	−2.06
XVI	3, CH_3-	0.04	−0.78

[a] V in kcal/mole.

[b] The contributions to V for acrylonitrile due to l_N and to the three β_{CN}'s are respectively −60.9 and 19.47 kcal/mole.

nucleus[4] on the CN axis. Such contributions to ΔV_M, which are given as interaction energies with a unit positive probe charge, refer to the neutral subunits already employed in getting the partial contributions to μ reported in Tables 5 and 6. Because the point selected for this comparison is nearer to l_N than to β_{CN}'s, the changes in the shape of l_N are somewhat emphasized. However it becomes evident that even this test, on the whole, proves that the β_{CN} orbitals have changes of shape larger than the l_N ones.

4. Analysis of the Substituent Effects on the −CN Group

What we have shown in the preceding section permits us to focus this analysis on the group of the three β_{CN} orbitals. The results of similar analyses on the l_N orbitals will be summarized at the end of this section.

As a test of the perturbation produced by the substitution on the β_{CN} orbitals group we shall use the electric field E generated by all the other charges of the molecule, nuclei and electrons.[5]

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[4] The electrostatic potential calculated at this distance from the N nucleus is the molecular quantity which gives, according to Kollman *et al.* [24], the best correlation with the strength of a hydrogen-bonded complex between our molecules and a proton donor.

[5] The numerical values of the E components displayed in the figures also include the contributions from the electrons described by $1s_C$, $1s_N$ and l_N. Since these LO's are relatively insensitive to the substitution, the correlation between the properties of β_{CN} and E along our set of molecules does not significantly depend on the contribution to E given by such LO's.
The electric field operator matrix elements have been calculated by using the formulas given by Matsuoka [25].

To permit comparisons based on simple numerical quantities, we have selected the z component (the z axis runs along the CN direction) of $\boldsymbol{E}$ calculated at the position of the charge center of the three β_{CN}'s.

We plot, in Fig. 1, the mean value of ΔE_z at these three points against $\Delta(Q_N - Q_C)_{\beta_{\mathrm{CN}}}$ and, in Fig. 2 and Fig. 3, ΔE_z against $\Delta\mu_z(\beta_{\mathrm{CN}})$: this last quantity refers to the z component of the neutral subunit composed of six β_{CN} electrons and six nuclear charges which we have defined in the preceding section.

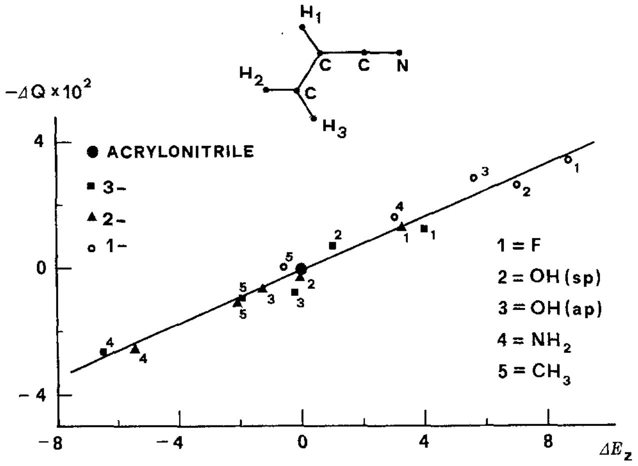

Fig. 1. Correlation between the changes of the difference of the gross populations of N and C $[\Delta(Q_N - Q_C)]$ and the changes of the z component of the electric field generated by the charges of the molecular remainder. The ΔE_z values are given in arbitrary units (1 arb. unit = 27360 c.g.s.)

The electric dipole operator unduly emphasizes distant contributions, such as those deriving from the tails of the LO's. To show more clearly that in the present case these tails do not cause serious problems for our analysis, we give in Figs. 2 and 3 two different versions of the correlation between ΔE_z and $\Delta\mu_z(\beta_{\mathrm{CN}})$: in the first (Fig. 2) the $\mu_z(\beta_{\mathrm{CN}})$'s have been calculated directly from the LO's "with tails", in the second the dipole moments have been calculated from the main portion of the β_{CN}'s (i.e. from LO's renormalized after the deletion of the tails). The graphs of Figs. 1, 2 and 3 look similar: the local dipole and the difference of the subtotal gross populations can be considered, in this context, as roughly equivalent tests of the response of the group to the perturbation. On the whole, the correlations look fairly good and make manifest that the changes in the target group can be explained to a large extent in terms of classical polarization effects.

A more careful examination of the graphs of Figs. 2 and 3 shows that the correlation for the orbital with tails is of the same quality wherever the substituent is placed (correlation coefficient = 0.993), while for orbitals without tails the correlation is better in the cases where the substituent is in position 2 or 3 (correlation coefficient = 0.993) than in the cases where the substituent is in position 1 (correlation

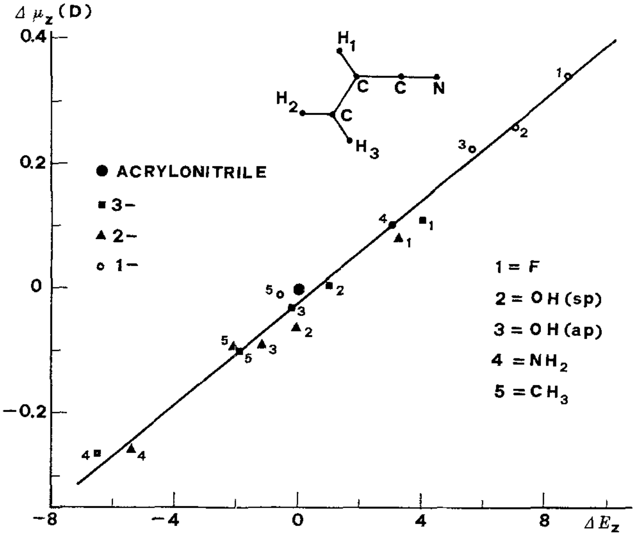

Fig. 2. Correlation between the changes of the z component of the dipole moment of the three CN banana bonds and the changes of the z component of the electric field of the molecular remainder. The dipole moments refer to localized orbitals "with tails"

coefficient for the whole set = 0.970). A better correlation for compounds with substituent in position 1 could be obtained by changing the coefficient of proportionality between ΔE_z and $\Delta\mu_z(\beta_{CN})$ and by adding to this linear relationship a constant. This indicates that there are other minor effects hidden beneath the simple and straightforward correlations reported in Figs. 2 and 3.

As we have said above, the correlations given in Figs. 1 and 2 represent a résumé of more detailed analyses, taking into consideration also the other components of

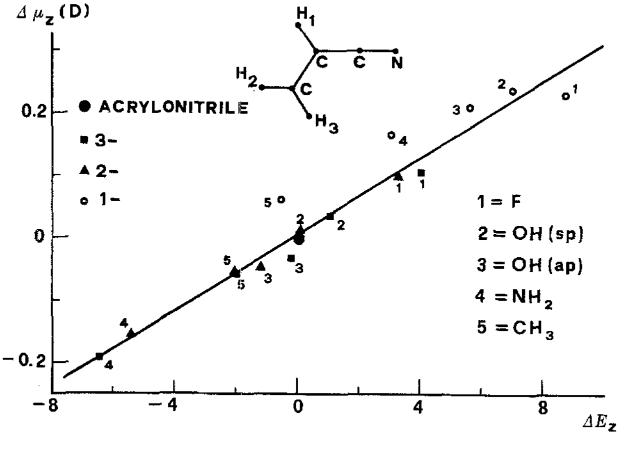

Fig. 3. As Fig. 2 but with dipole moments calculated on localized orbitals "without tails"

$\Delta \boldsymbol{E}$ calculated on the charge centers of the β_{CN} or concerning the calculation of $\Delta \boldsymbol{E}$ at other points of the space. We may dispense with reporting here quite a large amount of numerical results, as it is sufficient to note that all such analyses confirm that the relationship between changes of $\boldsymbol{E}$ and displacement of the β_{CN} charge clouds is not due to an incidental numerical compensation valid only for a specific component of $\boldsymbol{E}$ calculated at a single specific point.

A more detailed examination of $\Delta \boldsymbol{E}$ may however be of some advantage in order to clarify better some details of the change of the electronic distribution in the –CN group. As an example we may consider the differential effects related to the lack of axial symmetry with respect to the C–N axis. This asymmetry can be measured by the value of the μ_x(CN) component (see Table 6). We show in Fig. 4a a map giving the trend of ΔV and ΔE (both referred to the molecular remainder) for compound XIII in the molecular plane: the full lines are the isopotential curves generated by the difference in the charge distribution between I and XIII (ΔV curves) and the corresponding force lines are represented by broken lines with arrows indicating the direction of the force driving a *negative* probe charge.[6] It appears evident that such forces push on the whole the six β_{CN} electrons towards negative x values ($\Delta\mu_x > 0$, as shown in Table 6), with only a small displacement along the z axis. Both displacements are well correlated with the mean value of the $\Delta \boldsymbol{E}$ components calculated at the charge center positions of the three banana bonds.

In Fig. 4b we present a similar map, relative to compound XIV. In this molecule the situation is practically the reverse of the preceding one. The electrostatic net force due to the substitution pushes the β_{CN} electrons towards positive x values ($\Delta\mu_x < 0$).

To give an idea of the different combination of effects one may find even in such a limited set of compounds, we give in Fig. 4c a third example of ΔV map which looks quite different from the preceding ones; it refers to compound XV. In this case the ΔE_x component is smaller than for compound XIII and there is a net displacement of the β_{CN} electrons towards positive z values. These three molecules are those which present larger positive (or negative) deviations from axial symmetry. In spite of the smallness of such effects the value of ΔE_x calculated at the β_{CN} charge center positions correlates fairly well with $\Delta\mu_x(\beta_{CN})$ (the correlation coefficient is 0.947 for the whole set and 0.994 for the set of 3-substituted compounds which presents the largest variations of ΔE_x). The corresponding graph is given in Fig. 5.

A more detailed description of the substitution effects which makes distinction between direct and indirect effects can be obtained by resorting to a decomposition of $\Delta \boldsymbol{E}$ into group contributions. The decomposition we have employed here has been obtained by resorting directly to the LO's without any further manipulation.

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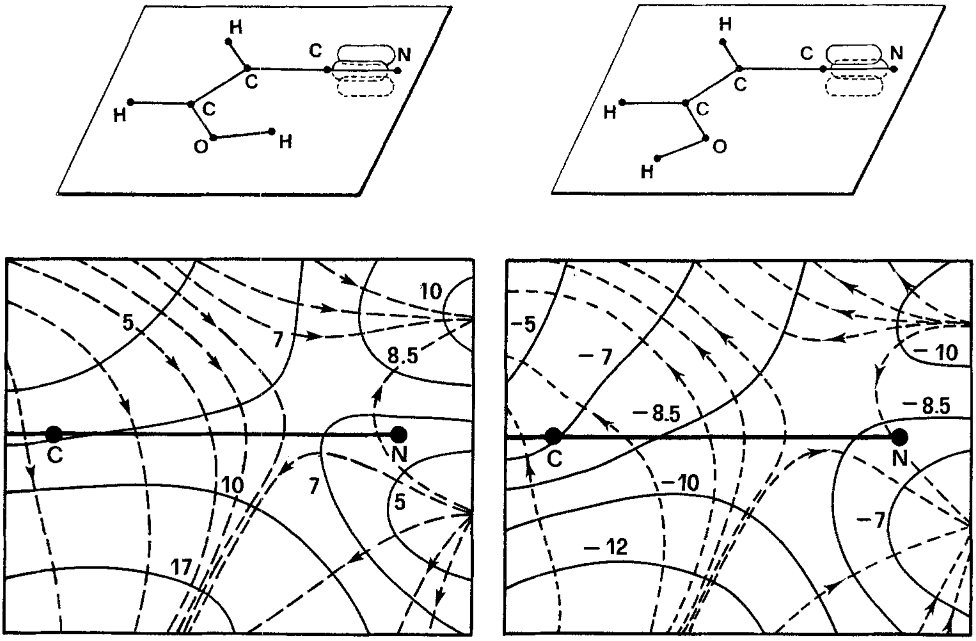
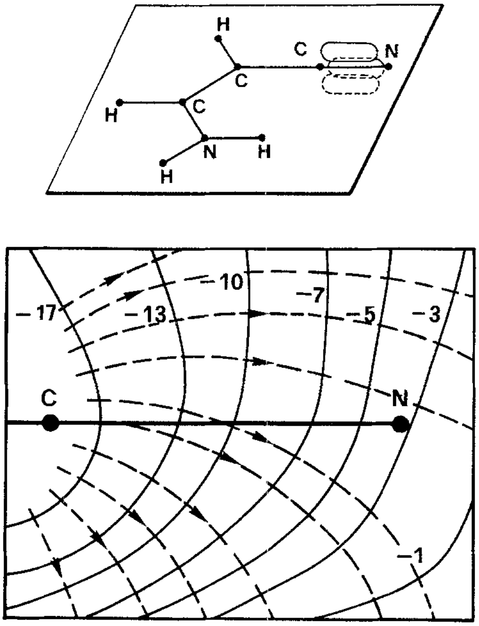
[6] Because of the plotting programme we have employed, there is no connection in this figure between the density of the force lines and the field strength, which can be appreciated by the separation of the isopotential lines.



(a)

(b)



(c)

Fig. 4. Maps giving the change of the electrostatic potential of the molecular remainder (full lines) in a region of the molecular plane containing the N and C nuclei.

a) difference between 3, OH(sp)-acrylonitrile (XIII) and acrylonitrile (I).

b) difference between 3, OH(ap)-acrylonitrile (XIV) and (I).

c) difference between 3, NH_2-acrylonitrile (XV) and (I).

The ΔV values are given in kcal/mole. In these figures there are reported also a few force lines (broken lines) with arrows indicating the direction of the force driving a negative probe charge

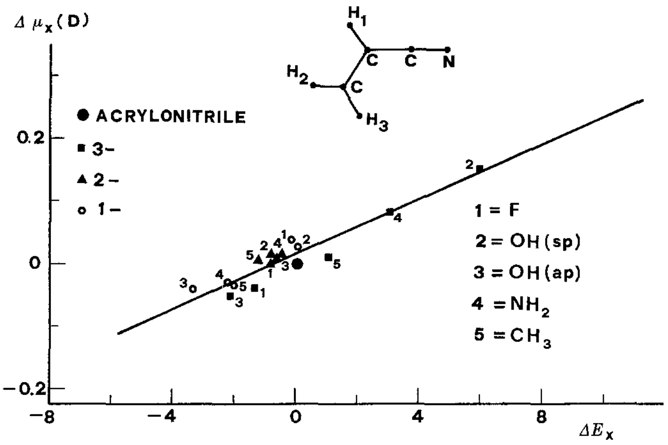
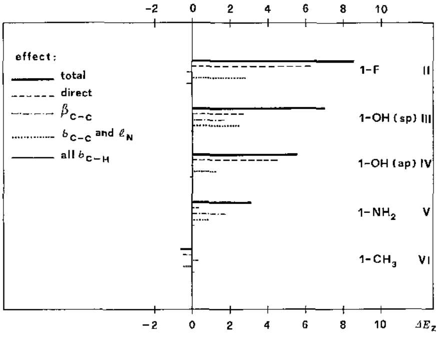
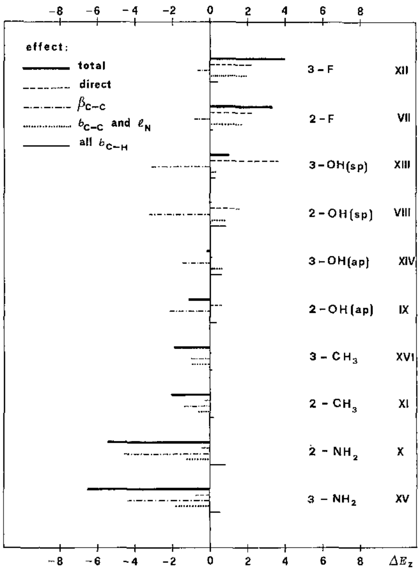


Fig. 5. Correlation between the changes of the x component of the dipole moment of the three banana bonds ("with tails") and the corresponding component of the changes of electric field of the molecular remainder

We report in Fig. 6 the value of ΔE_z (averaged on the three centers of the β_{CN}'s), together with its partition into: a) a "direct" component (i.e. the contribution due to the replacement of a hydrogen with the substituent group), b) the contribution of the two $\beta_{C=C}$ orbitals, c) a term which collects the contributions of the adjacent σ_{CC} bond and l_N, d) a term collecting the contributions of the two remaining σ_{CH} bonds. The nuclear charges are partitioned in such a way as to ensure electroneutrality to each group (with this partition the contribution to ΔE of the inner shell orbitals is negligible).



(a)



(b)

Fig. 6. A decomposition of the ΔE_z a) for 1-substituted acrylonitriles; b) for 2- and 3-substituted compounds. The ΔE_z values are given in arbitrary units (see Fig. 1)

For a given substituent R, the direct effect is larger when R is placed in position 1, because this position is closer to the target group. The only exception is given by the 3, OH(sp)-acrylonitrile (compound XIII) where direct, through space, effects are particularly effective. The conformational influence on the OH group direct effect is in any case evident, even if more modest, also in the other compounds. On the whole the magnitude of the direct effects is, in general, in the order $F > OH > NH_2 > CH_3$, the effect of the first two groups being constantly that of attracting the β_{CN} electrons towards the C end of the CN group.

The direct effect is the dominant term only for F substitutions: in the other cases there are different combinations of effects which must be described in more detail.

In the compounds having the R group in position 1 the indirect substitution effects deriving from changes in the β_{CC} LO's are larger in compounds (III) and (V), i.e. in those compounds which have an X–H bond syn-periplanar with respect to the C=C group. A similar relationship is evident also in the 2, and 3, substituted compounds: the changes in the C=C group are larger in compounds VIII and XIII (which both have an OH bond *sp* to C=C) than in compounds IX and XIV (which have both an OH bond *ap* to C=C) and are even larger in compounds X and XV (which have an NH bond *sp* to the C=C group). It seems evident that the changes in the β_{CC}'s are particularly sensitive to direct, through space, effects of this kind rather than to changes in the conjugation effect. This subject will be developed in more detail in a forthcoming paper where the analysis will be centered on the substitution effects on the C=C group.

The indirect contributions of the two β_{CC}'s are of some interest also in a different context. For a given substituent, the contribution to ΔE_z given by C=C is practically the same if the substituent is placed either at positions 2 or 3 (compare the couples VII–XII, VIII–XIII, IX–XIV, X–XV, XI–XVI). In fact the two positions are equivalent with respect to the C=C group, and the occurrence of nearly equal contributions to ΔE_z indicates that the second order effects, due to the differential modifications of the R group by the asymmetrical group H–C–C≡N, are of no great importance. To demonstrate this observation more clearly we report in Table 8 the distance $\langle r \rangle$ from the O nucleus of the charge centers of the σ_{OH} bond orbital and of one of the two O lone pairs (after the localization procedure the two O lone pairs are represented by two equivalent l_O orbitals symmetrically placed with respect to the molecular plane). The constancy of the $\langle r \rangle$ values reflects the fairly good conservation of the shape of the corresponding LO's, especially remarkable for the lone pair orbitals.

Table 8. Distance $\langle r \rangle$ from the O nucleus of the charge centers of some LO's of the OH group (in Å)

Compound	$\langle r \rangle_{OH}$	$\langle r \rangle_{l_O}$	$\langle r \rangle_{CO}$
1, OH(sp)-Acrylon.	0.522	0.302	0.537
1, OH(ap)- „	0.523	0.307	0.538
2, OH(sp)- „	0.523	0.299	0.530
2, OH(ap)- „	0.524	0.303	0.529
3, OH(sp)- „	0.515	0.298	0.532
3, OH(ap)- „	0.525	0.304	0.530

As a last observation on the indirect C=C effect we may note that such an indirect effect is larger than the direct one for all R with exception of F and that this term is the dominant one when R is NH_2 or CH_3 (we have already pointed out that the dissection of the substituent effects for OH depends heavily on the relative orientation of such group). This remark can be considered as our contribution to the long debated question on the relative importance of the direct and the through bonds transmission of substitution effects.

In this analysis we have not taken into explicit consideration the N lone pair and the σ_{CC} bond connecting CN to the remainder. The low sensitivity of l_N to the substitution effects makes the straight line correlating $\Delta\mu_z(l_N)$ to ΔE_z nearly parallel to the ΔE_z axis. The N lone pair is a little more sensitive to fields acting in a direction perpendicular to the C–N axis (see Table 5): in this case too there is a good correlation between ΔE_x and $\Delta\mu_x(l_N)$.

The σ_{CC} bond has been considered as a part of the molecular remainder: it is to some extent a question of definition whether to consider such a group as a part of CN or of the molecular skeleton. We have seen that this bond has an appreciable polarizability, but we consider it more convenient to postpone a discussion on the substituent effects of this bond to another occasion when it will be possible to compare the changes in this bond with the changes of other σ bonds directly connected to a carbon skeleton.

5. Concluding Remarks

We have limited the examination of the influence of the substituent on the characteristics of the –CN group in acrylonitriles simply to an analysis of the results of the mutual interplay of electron interactions, ruled by the quantum mechanical laws, without any attempt to provide models for these interactions. This analysis has been based exclusively on the knowledge of the molecular first order density function, with the introduction of only one supplementary concept, that of a first partition of the electronic density into group contributions by means of a transformation of the canonical orbitals into localized ones.

A critical point with regard to the possibility of using LO's in the description of chemical groups is raised by the presence in the LO's of tails spread on the other atoms of the molecule. As remarked above, LO tails could be included in transferable models of chemical groups [14], but in our analysis their occurrence did not produce great problems. We have reported some numerical tests showing that the LO's of CN are well localized and that it is possible to get correlations between substituent effects and changes in the characteristics of the CN group whether one takes into account or disregards such tails. Also the main features of the dissection of the substitution effects are not altered by the tails.

Another feature of the LO's which deserves some discussion is the presence of a large local overlap between two localized orbitals having an atom in common [9]. In some cases this presence could perhaps produce difficulties in the definition of a group, and a finer dissection procedure should be adopted, but, in the present case, where the substitutions are made at least at a bond away from the target group, there are no particular ambiguities in the determination of the substitution effects on the CN group.

It has been shown that the CN group is a quite well-defined entity, with limited differential charge transfers in our set of molecules, and that changes in the electronic distribution inside this group are due, for the largest part, to the polarization of the LO's describing the bond between C and N, the lone pair being decidedly less polarizable.

The partition of the substituent effects shows that the direct effect of the substituent is the dominant term for substitutions in position 1, while for substitutions in positions 2 and 3 it remains the most important term only when the substituent is F; for the other cases the dominant term is represented by the indirect, through bonds, effect involving the C=C group.

In our opinion, the most interesting result of the present analysis is that classical electrostatics seem to provide an aid in interpreting the substitution effects. This conclusion is drawn from an analysis performed on groups subjected to mutual interactions which are taken into account by rigorous quantal SCF calculations, but we have mentioned in the preceding section that the mutual group interplay produces only minor changes in the characteristics of R. This was only a side observation which deserves further testing, but which could represent the basis for an approximate modelling of the electronic distribution of a group in a given molecular environment. Let us suppose, for example, that the investigation regards the properties of a group G; there is perhaps the possibility of introducing an intermediate level of approximation between a zeroth order approximation consisting of the juxtaposition of rigid group models (including G too) and a complete SCF description of the whole molecule. This intermediate level could derive from a classical (i.e. without exchange terms) description of the modifications of G in the field of the other groups.[7] It must be remarked that even the zeroth-order approximation can give acceptable results, as we have shown in a preceding paper [11] and that the partition of the whole molecule into a target group, described more accurately, and a remainder, can represent an interesting step towards the theoretical analysis of the reactivity characteristics of large molecules.

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[7] A transformation of the AO basis in a hybrid basis, as suggested e.g. in Ref. [14] could be of some help for practical computations at this intermediate level.

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