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The Effect of Substitution on the Properties of a Chemical Group

II. An Analysis of the SCF Description of Changes in the C=C group in Monosubstituted Ethylenes and Acrylonitriles

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The effect of the substituent R(R = F, OH, NH_2, CH_3) on the electron distribution of the C=C group of ethylene and acrylonitrile may be fairly well represented in terms of classical interactions between the σ and π components of this group and the molecular remainder. A distinction between direct and indirect effects is made, and an estimate of the relative importance of conjugative versus inductive effects is done.

This analysis has been performed on a set of 22 SCF wavefunctions calculated with the 4-31G basis set.

Key words: Chemical substitution effects – Intramolecular interactions.

1. Introduction

The analysis of the changes in the properties of a given chemical group induced by substitution of other groups in the same molecule constitutes a basic step in the interpretation of chemical phenomena.

In a preceding paper [1] (paper I of this series) we have presented a simple method of analysis which exploits SCF wavefunctions of a set of related compounds to obtain a description of the charge distribution of the chemical group under examination (the target group). The differences in the charge distribution of the target group along the set of molecules are brought into relation with the differences in the electric field produced by the molecular remainder, i.e. from the

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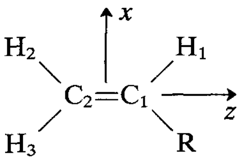
molecular framework which remains constant in the set of molecules and from the chemical group which changes in the various compounds.

The quantities under examination, charge distribution and one-electron properties of the target, and charge distribution and electric field of the remainder are obtained by rigorous *ab initio* quantal calculations (in the SCF approximation), but the emphasis in the analysis is given to classical effects.

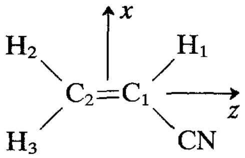
This approach has been tested with some success in paper I on a set of monosubstituted acrylonitriles, with —CN as target group. In the present paper we deal with the analysis of the substitution effects on the C=C group in monosubstituted ethylenes and acrylonitriles. In the previous case the target and the substituent were separated by one or two bonds of the molecular framework, while in the present one target and substituent are directly connected; this different topological arrangement should permit shedding more light on the limits of validity of an approach relying on classical effects.

2. The Molecular Wavefunctions under Analysis

The wavefunctions we have employed in our analysis refer to fixed standard geometries [2] (see Table 1 of paper I) and have been calculated with the GAUSSIAN 70 program [3] on a 4-31G basis set [4]. The numbering of atoms and the orientation of Cartesian axes are reported in schemes (1) and (2).



(1)



(2)

In substituted acrylonitriles the group R can substitute atoms H_1, H_2, H_3 giving origin to *vicinal*, *trans* and *cis* compounds which will be denoted accordingly.

In both sets the substituents are F, OH, NH_2 and CH_3. For the OH containing compounds we considered two different geometrical conformations, with the O–H bond syn-periplanar (sp) or anti-periplanar (ap) to C=C.[1]

The NH_2 group is planar and the CH_3 group has in all cases a C—H bond syn-periplanar to $>C=C<$.

We report in Table 1 the energies and the dipole moments of these wavefunctions.

As starting point for the analysis we have performed a localization of the canonical orbitals according to the Boys' technique [5]. We consider it more instructive to

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[1] This choice of two different conformations for the OH-compounds has been performed only to give an example of the importance of the orientation of substituents. The question of the influence of actual internal motions on the electronic distribution of the target group will not be considered in this paper.

Table 1. Total energy and dipole moment components

Molecule	E	μ_{tot}	μ_x	μ_z
Ethylene	−77.9207	0	0	0
F-Ethylene	−176.6461	0.7634	0.6715	0.3631
OH-Ethylene (sp)	−152.6611	0.6140	0.0562	0.6115
OH-Ethylene (ap)	−152.6604	0.9680	0.7444	−0.6188
NH_2-Ethylene	−132.8704	0.5634	−0.1983	−0.5274
CH_3-Ethylene	−116.9022	0.1457	0.0182	−0.1446
Acrylonitrile	−169.5133	4.3207	3.4402	−2.6141
1,F-Acrylontrile	−268.2292	3.5072	1.3433	−3.2398
1,OH-Acrylonitrile (sp)	−244.2456	4.9849	3.1053	−3.8996
1,OH-Acrylonitrile (ap)	−244.2471	0.6390	0.5276	−0.3605
1,NH_2-Acrylonitrile	−224.4581	4.0790	3.9040	−1.1817
1,CH_3-Acrylonitrile	−208.4952	4.2691	3.6802	−2.1636
2,F-Acrylonitrile	−268.2357	2.3526	1.6594	−1.6676
2,OH-Acrylonitrile (sp)	−244.2549	1.4748	1.4001	−0.4636
2,OH-Acrylonitrile (ap)	−244.2558	4.7994	1.8076	−4.4459
2,NH_2-Acrylonitrile	−224.4713	6.3720	4.5663	−4.4443
2,CH_3-Acrylonitrile	−208.4949	4.9755	3.8637	−3.1349
3,F-Acrylonitrile	−268.2344	5.2851	5.0206	−1.6509
3,OH-Acrylonitrile (sp)	−244.2562	3.6033	3.4567	−1.0174
3,OH-Acrylonitrile (ap)	−244.2536	6.8645	5.2491	−4.4237
3,NH_2-Acrylonitrile	−224.4726	5.2984	2.9842	−4.3781
3,CH_3-Acrylonitrile	−208.4949	4.4600	3.2097	−3.0966

report here results obtained with separate localizations of the σ and π electronic subsystems which permit one to look more directly at the separation of inductive and conjugative effects. Some results of these localizations will be displayed later.

3. The Influence of the Substituents on the Polarization of the C=C group

As it was done in paper I, we may recur, for a first rough measure of the polarization of the π and σ subunits of the C=C group, to the partial gross atomic charges on atoms C_1 and C_2 related to the localized orbitals $\sigma_{C=C}$ and $\pi_{C=C}$. The relevant data are reported in Tables 2 and 3.

Table 2. Differences between the partial atomic gross charges of C_1 and C_2 in the ethylene series as a measure of the group polarization[a]

Compound	$[Q(C_1)-Q(C_2)]\pi_{CC}$	$[Q(C_1)-Q(C_2)]\sigma_{CC}$
Ethylene	0	0
F-Ethylene	−0.094	0.069
OH-Ethylene (sp)	−0.287	0.104
OH-Ethylene (ap)	−0.152	0.171
NH_2-Ethylene	−0.335	0.172
CH_3-Ethylene	−0.073	0.058

[a] The values are given in e units ($1e = 4.80298 \times 10^{-10}$ esu)

Table 3. Differences between the partial atomic gross charges of C_1 and C_2 in the acrylonitrile series[a]

Compound	$\Delta[Q(C_1)-Q(C_2)]\pi_{CC}$	$\Delta[Q(C_1)-Q(C_2)]\sigma_{CC}$
Acrylonitrile	0	0
1,F-Acrylonitrile	−0.085	0.072
1,OH-Acrylonitrile (sp)	−0.275	0.100
1,OH-Acrylonitrile (ap)	−0.141	0.163
1,NH_2-Acrylonitrile	−0.321	0.166
1,CH_3-Acrylonitrile	−0.068	0.060
2,F-Acrylonitrile	0.092	−0.057
2,OH-Acrylonitrile (sp)	0.302	−0.109
2,OH-Acrylonitrile (ap)	0.168	−0.174
2,NH_2-Acrylonitrile	0.370	−0.187
2,CH_3-Acrylonitrile	0.079	−0.043
3,F-Acrylonitrile	0.093	−0.039
3,OH-Acrylonitrile (sp)	0.317	−0.084
3,OH-Acrylonitrile (ap)	0.172	−0.166
3,NH_2-Acrylonitrile	0.387	−0.183
3,CH_3-Acrylonitrile	0.096	−0.056

[a] The values for acrylonitrile are respectively 0.186 and 0.102*e*.

The polarization of the group under the effect of a specific substituent R is remarkably constant in the ethylene and acrylonitrile series and it is not affected in this last series by the position of R with respect to —CN. Conformational effects (see the couples of OH-substituted compounds) are on the contrary quite remarkable. Polarization of σ and π electrons are of opposite sign, as many other analyses have demonstrated, and the charge shift is, in general, larger for π electrons.

Population analysis cannot give more than the main features of the electronic distribution, and a better visualization of the changes in the electronic distribution may be obtained by examining difference maps of the LO in question (an example

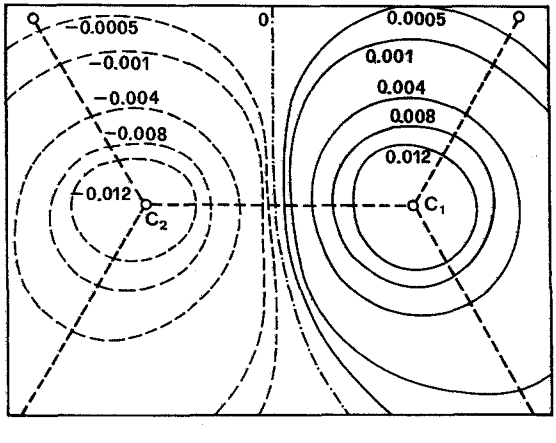

Fig. 1. Electron density difference map for the π_{CC} group of 2, NH_2-acrylonitrile. This map is calculated as difference between the charge density of the π_{CC} LO in the substituted compound and the charge density of π_{CC} in acrylonitrile. It refers to a plane parallel to the molecular one, at a distance of 0.3 Å. Isodensity values are in *e* units

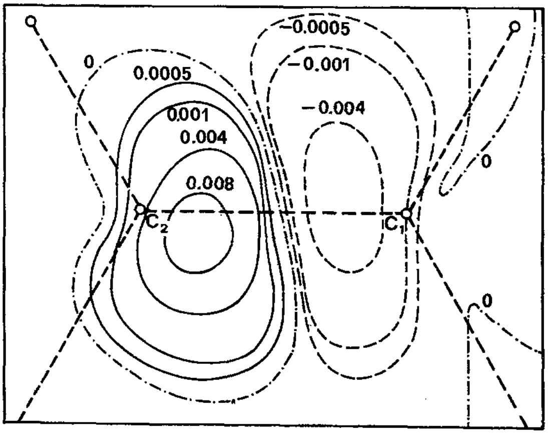

Fig. 2. Electron density difference map for the σ_{CC} group of 2, NH_2-acrylonitrile. Same remarks as for Fig. 1

is given in Figs. 1 and 2). These maps are not appropriate, however, to quantify the changes in the target group which we try to correlate with the effect of the substituent. To this end we choose a different numerical quantity related to a one-electron observable, viz. the LO contribution to the molecular dipole moment.

The electric dipole is in fact sufficiently sensitive to changes in electron distribution and not too biased towards long range (or short range) contributions to the observable [6]. The LO components of $\boldsymbol{\mu}$ refer to neutral subunits, composed of two negative electron charges occupying the LO in question and of an appropriate fraction of nuclear charges ($+e$ on both C nuclei for π_{CC} and σ_{CC}) [6, 7].

To illustrate the classical polarization effects of the substituent on C=C we correlate the changes in $\boldsymbol{\mu}^{\lambda}$ (λ stays for π_{CC} or σ_{CC}) with the changes in the electric field $\boldsymbol{E}^{\lambda}$ generated by all the other components of the molecule and measured in an appropriate point $\boldsymbol{r}_i$ where the electron density of λ is sufficiently large. $\boldsymbol{\mu}^{\lambda}$ as well as $\boldsymbol{E}^{\lambda}$ being vectorial quantities, we may proceed to a somewhat more detailed analysis, considering separately each component of this couple of vectors.

We give in Tables 4 and 5 the $\Delta\mu_z^{\pi}$ and ΔE_z^{π} values, which are graphically presented also in Fig. 3. The values are given as differences with respect to the parent compounds, ethylene and acrylonitrile.

The quality of correlation is not too different from that found in paper I for the —CN group (correlation coefficient $r = 0.952$). It should be remarked that the best correlation line does not pass through the origin (R = H) and that the —CH_3 compounds have a noticeable deviation. This is probably due to the differential polarization effects of the σ_{CC} group which will be discussed later.

In Fig. 4 we report a decomposition of ΔE_z^{π} into a direct component (i.e. the contribution due to the substitution of H with R) and indirect components due to changes in the intrinsic properties of the other subunits (σ_{CC}, CH, CN), present in the molecule, induced by chemical substitution. All subunits are electrically

Table 4. Changes of the z component of the dipole moment of the π_{CC} and σ_{CC} groups[a]

Molecule	$\Delta\mu_z^\pi$	$\Delta\mu_z^\sigma$	Molecule	$\Delta\mu_z^\pi$	$\Delta\mu_z^\sigma$
Ethylene	0	0			
F-Ethylene	0.1527	−0.1581	2,F-Acrylonitrile	−0.1448	0.1188
OH-Ethylene (sp)	0.7300	−0.1539	2,OH-Acrylonitrile (sp)	−0.7974	0.1530
OH-Ethylene (ap)	0.3069	−0.1619	2,OH-Acrylonitrile (ap)	−0.3563	0.1509
NH_2-Ethylene	0.8547	−0.1604	2,NH_2-Acrylonitrile	−0.9908	0.1746
CH_3-Ethylene	0.1648	−0.0355	2,CH_3-Acrylonitrile	−0.1698	0.0301
Acrylonitrile	0	0			
1,F-Acrylonitrile	0.1468	−0.1953	3,F-Acrylonitrile	−0.1591	0.1372
1,OH-Acrylonitrile (sp)	0.7174	−0.1260	3,OH-Acrylonitrile (sp)	−0.8443	0.1515
1,OH-Acrylonitrile (ap)	0.3093	−0.1531	3,OH-Acrylonitrile (ap)	−0.3789	0.1590
1,NH_2-Acrylonitrile	0.8494	−0.1301	3,NH_2-Acrylonitrile	−1.0472	0.1766
1,CH_3-Acrylonitrile	0.1549	−0.0224	3,CH_3-Acrylonitrile	−0.2355	0.0430

[a] The values are given as difference with respect to the parent compounds ethylene ($\mu_z^\pi=\mu_z^\sigma=0$) and acrylinotrile ($\mu_z^\pi=-0.5820$, $\mu_z^\sigma=-0.0709$). All values are given in Debyes.

neutral entities defined in terms of the corresponding LO's. It may be remarked that the total value of ΔE_z^π derives from a compensation between contributions having opposite sign and different absolute values. In particular it is not possible to correlate the changes of μ_z^π (i.e. the polarization of the π_{CC} group) with the direct contribution to ΔE_z^π alone: the substitution produces significant changes in all the groups. We have not considered it necessary to report separately the components of ΔE_z^π deriving from each CH and C—CN group; it may be remarked however that the contribution of changes in the C—CN group to polarization of π_{CC} is roughly equivalent to that deriving from a CH group. The constancy of the

Table 5. Values of the z component of the electric field generated by all the molecular subunits, with the exception of π_{CC} (E_z^π) or σ_{CC} (E_z^σ) and measured in points where the electronic charge density of π_{CC} and σ_{CC} respectively is high[a]

Molecule	ΔE_z^π	ΔE_z^σ	Molecule	ΔE_z^π	ΔE_z^σ
Ethylene	0	0			
F-Ethylene	−6.05	−39.30	2,F-Acrylonitrile	5.10	40.23
OH-Ethylene (sp)	14.05	−39.30	2,OH-Acrylonitrile (sp)	−17.65	40.63
OH-Ethylene (ap)	4.95	−37.95	2,OH-Acrylonitrile (ap)	−8.85	39.53
NH_2-Ethylene	24.35	−39.15	2,NH_2-Acrylonitrile	−31.20	41.14
CH_3-Ethylene	2.60	−9.35	2,CH_3-Acrylonitrile	−4.60	9.91
Acrylonitrile	0	0			
1,F-Acrylonitrile	−7.00	−36.29	3,F-Acrylonitrile	5.80	39.57
1,OH-Acrylonitrile (sp)	13.95	−37.16	3,OH-Acrylonitrile (sp)	−18.60	40.98
1,OH-Acrylonitrile (ap)	3.55	−34.34	3,OH-Acrylonitrile (ap)	−7.70	38.75
1,NH_2-Acrylonitrile	23.50	−37.13	3,NH_2-Acrylonitrile	−31.45	41.38
1,CH_3-Acrylonitrile	3.40	−8.03	3,CH_3-Acrylonitrile	−4.85	10.01

[a] All values are in arbitrary units (1 ar. un. = 27360 esu cm^{-2}) and refer to differences with respect to the parents compounds (acrylonitrile: $E_z^\pi=-19.90$, $E_z^\sigma=-6.17$)

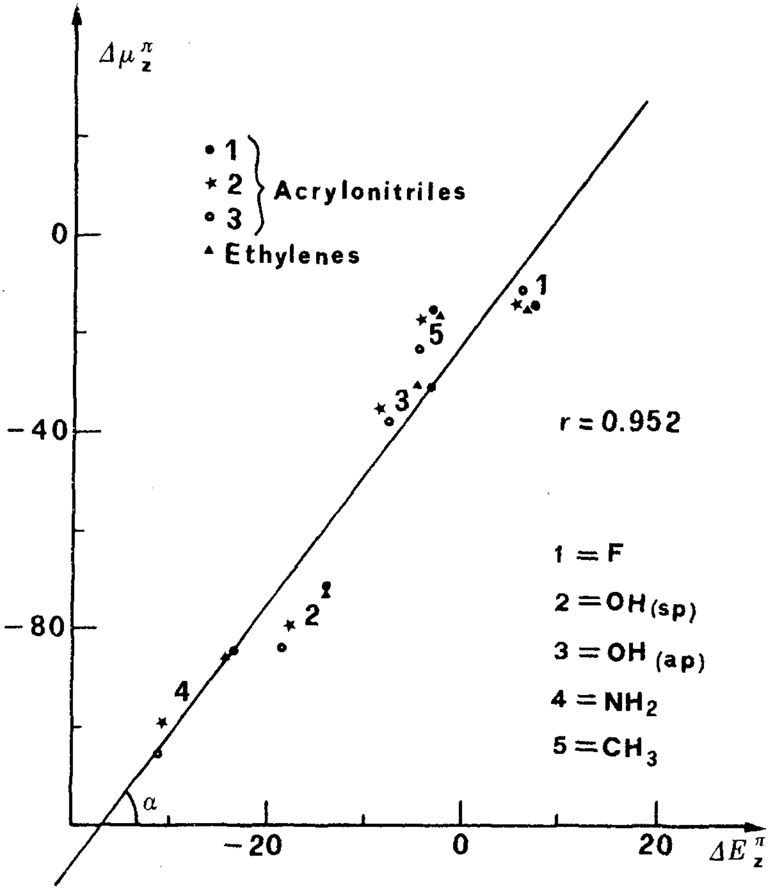

Fig. 3. Correlation between the changes in the z component of the dipole moment of the π_{CC} group (μ_z^π) and the changes in the z component of the electric field of the molecular remainder (E_z^π). The μ_z values are given in Debyes and the E_z^π values in arbitrary units (1 arbitr. un. = 27360 esu cm^{-2}). Ethylenes and 1-acrylonitriles are plotted with orientation of the z axis opposite to the choice displayed in schemes (1) and (2)

collective contributions of CH and C—CN groups for a given R indicates that these indirect effects of substitution do not depend on the position of R and suggests that they are only slightly affected by the molecular framework.

The contribution deriving from changes in the σ_{CC} group does parallel neither the direct contribution nor the total final value of ΔE_z^π; it may be noticed that this contribution is large and practically constant for all R containing a heteroatom and decidedly smaller for R = CH_3. We have already observed that the values of the unsubstituted compound as well as the CH_3 substituted ones are not well correlated by the same regression line correlating the $\Delta\mu_z$ and ΔE_z values of the other compounds. This could be an indication that a linear correlation between electric field and changes in electronic distribution only represents a first approximation, acceptable when the differential effects are of moderate magnitude as in a

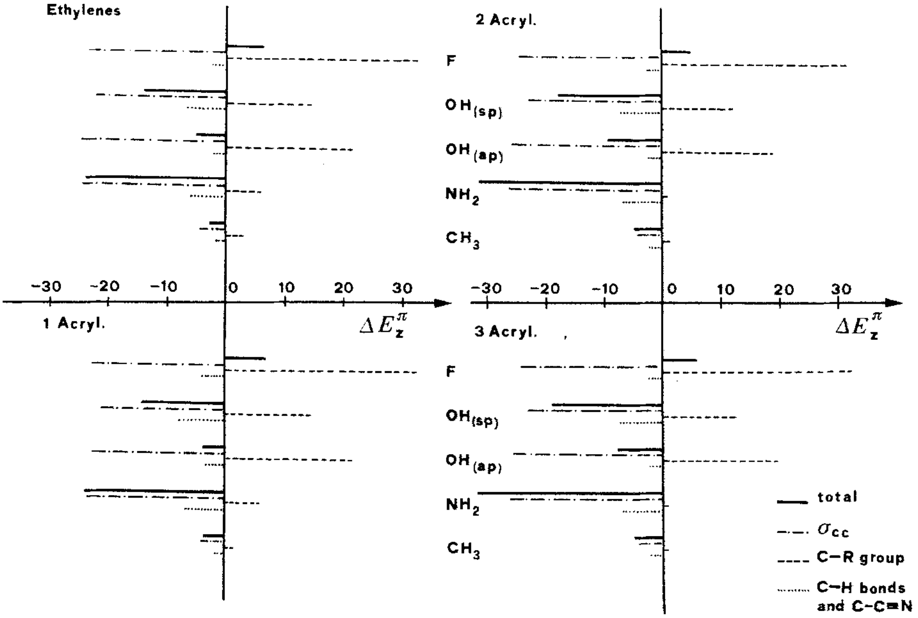

Fig. 4. A decomposition of ΔE_z^π into direct and indirect components (see the text)

series where all R groups have a heteroatom, etc., and higher terms are necessary in other cases. This topic however deserves further examinations.

The direct contribution to ΔE_z^π has only a modest dependence on the molecular environment. The comparison of the values for (ap) and (sp) OH compounds indicates that the direct contribution heavily depends on through-space effects, a conclusion which agrees with what was remarked in paper I as a conclusion of the analysis of the indirect contribution of the C=C group to $\Delta \boldsymbol{E}$ acting on CN.

Direct and indirect contributions to $\boldsymbol{E}^\pi$ are not affected by the molecular framework. To make this conclusion more evident, which is of some interest because of its practical implications, we graphically compare in Fig. 5 the value of E_z^π for the R-acrylonitriles (REtCN) with the sum of the values of E_z^π in acrylonitrile (EtCN) and in the corresponding R-ethylene (REt).

The values of ΔE_z^π we have employed in these analyses require some further comments. The values of $\Delta \boldsymbol{E}^\pi$ have been calculated at a point corresponding to the position of the charge centre of the π_{CC} localized orbital but displaced by 0.32 Å in the y direction. This displacement has been suggested by the necessity of probing the electric field in a point where the electronic density of π_{CC} is sufficiently large. The quality of the correlation between $\Delta\boldsymbol{\mu}$ and $\Delta \boldsymbol{E}^\pi$ does not depend on the actual value of the shift along the y coordinate: we have tested different values of y corresponding to the interval $0.1 \leq y \leq 0.4$ Å without observing appreciable changes in the correlation. Also the position of the point $\boldsymbol{r}$ along the z coordinate is not particularly critical, the ΔE_z^π values being practically

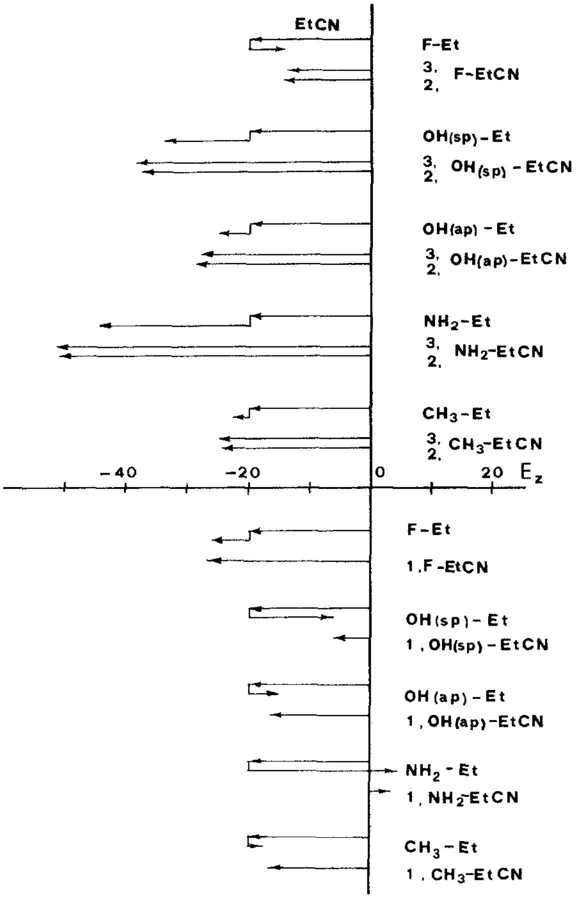

Fig. 5. A graphical comparison of the E_z^π values of R-acrylonitriles (REtCN) with the sum of the E_z^π values of R-ethylenes (REt) and unsubstituted acrylonitrile (EtCN)

constant in an interval of 0.4 Å along the z coordinate. It must be stressed however that the ΔE_z values employed in this paper are not to be confused with a mean value of the electric field of the molecular remainder.

The basic data for the analysis of the substitution effects on the σ_{CC} group are reported in Tables 4 and 5. The correlation between $\Delta\mu_z^\sigma$ and ΔE_z^σ is given in Fig. 6. It appears evident that the polarization of the σ_{CC} subunit is lower than that of the π_{CC} group. The values of ΔE_z^σ for all cases in which R contains a heteroatom are practically constant, and consequently the points corresponding to the correlation between $\Delta\mu^\sigma$ and ΔE_z^σ are collected in two clusters, the second pertaining to the molecules having $R = CH_3$ (regression coefficient = 0.936).

The dissection of the ΔE_z^σ values, analogous to that previously reported for the ΔE_z^π values, is given in Fig. 7. It may be noticed that the direct and the π_{CC} contributions to ΔE_z^σ are in this case of the same sign, the direct terms having a

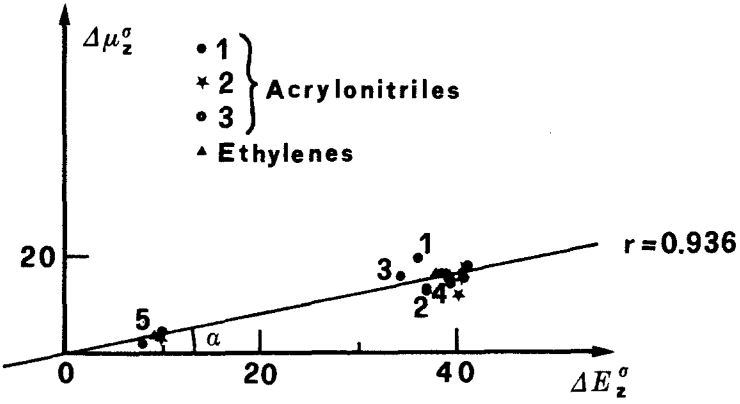

Fig. 6. Correlation between the changes in the z component of the dipole moment of the σ_{CC} group and the changes in the z component of the electric field due to the molecular remainder. For other remarks see Fig. 3

good correlation with the electronegativity of R, as for the ΔE_z^π, while the π_{CC} terms are overwhelming for R = NH_2, OH, although the case of the couples of (ap) and (sp) OH-compounds indicates that the through-space influence of the substituent on the polarization is not negligible. The direct term is not sufficient to reproduce the trend of ΔE_z^σ, whose actual value depends on the reorganization after the substitution of all the subunits more directly connected to the target (the

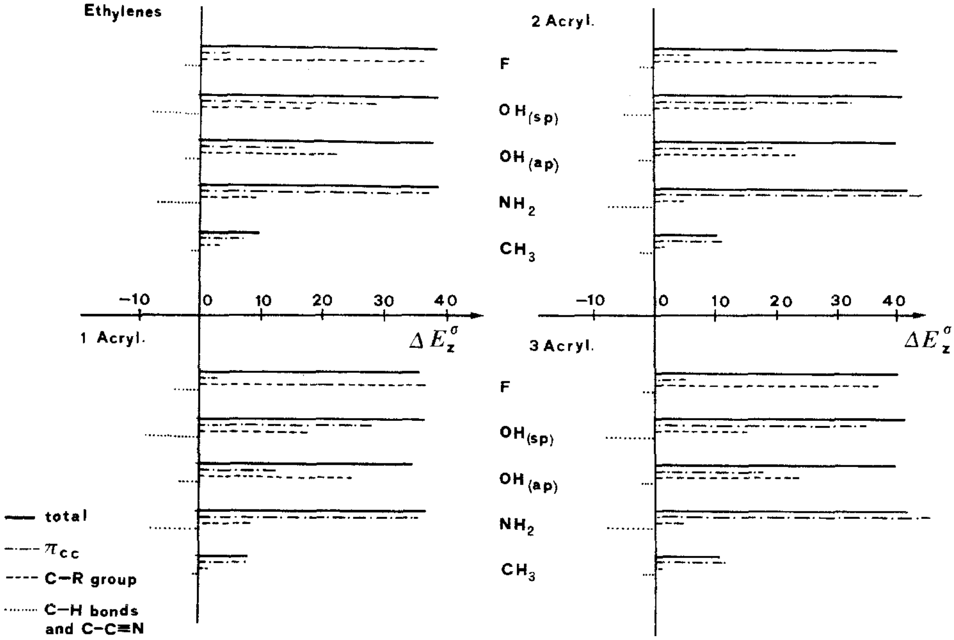

Fig. 7. A decomposition of ΔE_z^σ into direct and indirect components

terms deriving from changes in the CH groups and in CN are of lesser importance). In this case again the different contributions are not affected by changes in the molecular skeleton or by the position R has in acrylonitriles. These conclusions are in the line with what deduced from the dissection of ΔE_z^{π} given above and from the dissection of ΔE_z^{CN} given in paper I.

4. Comments

The analysis of the effects of a substituent R on the properties of the C=C group we have presented in this paper relies on the comparison of the polarization of the target in its SCF LO description with the classical electric field produced by the molecular remainder. To quantify this comparison we have employed the correlation between the z components of the dipole of the target $\boldsymbol{\mu}^t$ and of the electric field $\boldsymbol{E}^t$, this last calculated at a suitably chosen point $\boldsymbol{r}$. We have not presented the correlation between the x components on $\boldsymbol{\mu}^t$ and $\boldsymbol{E}^t(\boldsymbol{r})$ because it gives quite similar results (the y component of $\boldsymbol{\mu}$ is zero).

The selection of these two quantities, $\boldsymbol{\mu}^t$ and $\boldsymbol{E}^t(\mathbf{r})$, requires some additional comments. The dipole moment of the neutral target group is a quantity sufficiently good to illustrate the main features of the charge shift produced by chemical substitution, and it is at the same time not too complex to reduce the readability of this simple analysis. Further details could be derived by the examination of other quantities related to the electric charge distribution, like the electric quadrupole components (see paper I). The electric field produced by the molecular remainder and acting on the whole target charge distribution is simply represented by the value assumed at a given point; in other words the two quantities brought into correlation are not homogeneous, the first being a mean value, the second a local value. We have preferred to adopt this simple definition of the probe measuring the effects of the remainder rather than others more sophisticated, because it seems to us to satisfy sufficiently well the conditions of simplicity and immediacy we have put as prerequisites of this analysis.

We have tried to consider the C=C as composed by two subunits, the σ and the π one. The LO's of these two subunits are in fact described by exclusive subspaces, but their spatial overlap is quite remarkable [8] and a picture of intramolecular interactions given in terms of separate electronic distributions which interact according to the laws of classical electrostatics must be considered with some precaution. This separation of C=C in π and σ components has been performed for heuristic reasons because the largest part of empirical considerations on substitution effects separately considers σ and π subsystems. The results presented here substantially confirm the general feeling about the different behaviour of σ and π groups under the effect of substitution, but such separation introduces some shortcomings which are evident in different points of the present analysis, e.g. in the results displayed in Fig. 3. It must be stressed however that separation into σ and π components is not inherently tied to the interpretation of substitution effects in classical terms we are examining in this series of papers. We have considered also the alternative description in terms of two banana bonds: the two subunits present a slightly lower spatial overlap and the correlation of each banana bond with the field produced by the rest of the molecule is of a slightly better quality of that obtained for the σ-π description of C=C. In paper I we considered the multiple bond of C—N as a whole and probably in the practical applications of the results of these analyses, which are at present under investigation, it will be convenient to consider C=C as a unique group.

Another point which deserves further comment is the question concerning the importance of conjugation in the molecules we have considered. The evaluation of conjugation effects rests on the consideration of relative weights resonant structures, the most important being in the ethylene series those given in schemes (3) and (4):

$$\underset{(3)}{C_2{=}C_1{-}R} \qquad \underset{(4)}{\bar{C}_2{=}C_1{-}R^+}$$

which cannot be extracted without additional assumptions from the SCF description of the first-order density function. In the LO description of the electron distribution the role of local subunits is emphasized, even for π electrons[2], and in this schematization the question of electron delocalization (which is generally considered to be the cause of conjugative effects) is translated in an analogous question concerning the importance of the tails of the LO's. We have checked the correlations we have found with analogous comparisons concerning but the normalized main portion of the π_{CC} LO. We do not present here the results of such analyses because they would represent nothing more than a duplication of those already examined, the correlation between $\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{E}(\mathbf{r})$ being practically insensitive to the tails. The interested reader is referred to paper I where a comparison of this kind is reported.

The question of the distinction between conjugative and inductive effects has been however of such historical importance in the elucidation of the electronic structure of molecules to deserve an attempt to obtain an estimation of their actual weights. This may be tentatively done by comparing the π charge distribution in the molecule with that of a reference system composed of $H_2C{=}CH_2$ and HR (this last with the geometry present in the actual molecule) and by assuming that all the electron flow from R to the atom C_2 is due to conjugation. If this flow is measured on the LO describing the R group one obtains the values reported in Table 6. On the other hand the total π electron transfer to C_2 is due to both conjugative and inductive effects. It turns out that the relative weight of conjugation is restricted in the range 3–9%. This estimate is rather approximate and open to many criticisms, but it is in good agreement with different estimates, all suggesting that polarization is the main factor influencing the charge shift due to substitution.

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[2] For a comprehensive and accurate description of π systems in terms of localized orbitals, see England and Ruedenberg [9].

Table 6. Evaluation of the exceeding π charge on atom C_2 (column A) and of its portion pertinent to the R group (column B). Column C gives an estimate of the percent weight of conjugative effects

Compound	A	B	C(%)
F-Ethylene	0.0578	0.0052	9.0
OH-Ethylene (sp)	0.1581	0.0070	4.4
OH-Ethylene (ap)	0.0925	0.0078	6.4
NH_2-Ethylene	0.1879	0.0095	5.1
CH_3-Ethylene	0.0442	0.0015	3.3

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