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The Effect of Substitution on the Properties of a Chemical Group

III. An Analysis of the SCF Description of Changes in the C—H Groups in Monosubstituted Ethylenes and Acrylonitriles

Caterina Ghio, Eolo Scrocco and Jacopo Tomasi

Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento, 35, I-56100 Pisa, Italy

The differences in the charge distributions of the C—H bonds in monosubstituted ethylenes and acrylonitriles can be fairly well interpreted in terms of classical interactions between the C—H group and the molecular remainder. The position of the C—H bond with respect to the substituent rules the relative importance of direct effects, due to the substituent, with respect to the indirect ones, due to changes in the other groups induced by substitution.

Inspection of the analytical form of the localized orbitals in the set of molecules under examination indicates that changes in the charge distribution could be approximated by a description based on rigid generalized atomic hybrids.

Key words: Chemical substitution effects–Intramolecular interactions.

1. Introduction

In two preceding papers [1, 2] – I and II of this series respectively – we have presented and employed a method to analyze the substitution effects in SCF *ab initio* molecular wavefunctions. The analysis aims at assessing what are the limits of a classical description of the substitution effects which try to explain the changes in the electron distribution of a given group (the target) in terms of changes in the electric field $\boldsymbol{E}^t$ produced by all the other groups of the molecule. When a substitution (H → R) occurs in a given molecular framework the field $\boldsymbol{E}^t$ acting on the target changes both because a group is changed (CH → CR, direct effect) and

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because there appear displacements in the electron distribution of the other groups induced by substitution (indirect effects).

In paper I it was shown that there actually exists a correlation between changes in the electronic distribution of the CN group present in monosubstituted acrylonitriles and the corresponding changes in $\boldsymbol{E}^{CN}$. In addition it was shown that the effects of the substituent on the CN group mainly concern the triple bond electrons, the N lone pair being somewhat insensitive to perturbations.

The target considered in paper II was the C=C group and the analysis was carried out over a fairly large set of monosubstituted ethylenes and acrylonitriles. A separation of this group into its σ and π components has been attempted and appropriate correlations between changes in electron distribution and changes in electric field have been observed for both components; the π components being more sensitive to substitution effects.

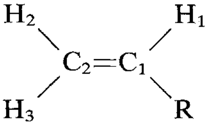
In both papers a dissection of the changes of $\boldsymbol{E}^t$ into direct and indirect components (see above) was presented. This dissection brings out the relative importance of the through-space versus the through-bond transmission of the substitution effects and, at the same time, demonstrates the fairly good transferability of all the components of $\boldsymbol{E}^t$.

In the present paper we analyze the effect of the substituent on the C—H group using again the same techniques. The molecular systems we have considered are the same ethylenes and acrylonitriles employed in paper II, to which reference is made for better specifications about basis set and geometry. Attention will be especially turned to the examination of finer effects due to the different location of each C—H group in the molecule with respect to R and to the presence (or absence) of a further group, the CN one, discriminating between ethylenes and acrylonitriles.

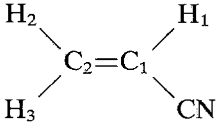
In addition we try to look more deeply into the effect produced by substitution on the mathematical expression of the group molecular orbitals. This kind of analysis, which might seem rather numerological, in contrast with the preceding one aiming a heuristic physical interpretation of the effect, is motivated by the possibility, given by the classical representation of substitution effects, of reducing the computation times for the calculation of the properties of a group in different molecular environments.

2. The Substitution Effects on the C—H Groups

In the set of 22 molecular wavefunctions corresponding to ethylene, acrylonitrile and the substitution compounds obtained by replacing one H atom by F, OH (in two different conformations, syn-periplanar and anti-periplanar with respect to C=C), NH_2 and CH_3, there are 49 CH groups which differ among themselves for either the position they have with respect to the substituent R or the nature of the substituent itself or the presence of a CN group. They constitute the subject of the present analysis. For their identification we adopt the same numbering of the atoms employed in paper II and reported here in the schemes (1) and (2). We shall employ local axes, the z one in the C—H direction (from C to H) and the x one on the molecular plane with positive values always in the half-plane containing the C=C group.



(1)



(2)

The description of the groups present in a molecule is given, as in the preceding papers, in terms of localized orbitals (LO's) obtained from the SCF wavefunction via the Boys localization procedure [3]. In the present case there are not particular problems about this description of the target group, because it is well known that the C—H LO's have only moderate tails on the other atoms of the molecule [4].

The substitution produces changes in the electronic distribution of each CH which can be roughly appreciated by examining the subtotal gross charges Q of the pertinent LO. The subtotal gross charge of an atom X related to the orbital λ, $(Q_X)_\lambda$, is obtained as the difference between the orbitalic gross atomic charge on X and an appropriate fraction of the nuclear charge of X, which is equal to $+e$ for both nuclei C and H when λ is the CH LO. We give in Table 1 for the ethylene and acrylonitrile series the values of the sum of the subtotal atomic charges $(Q_C+Q_H)_{CH}$ and of their difference $(Q_C-Q_H)_{CH}$.

The magnitude of the tails of the LO's is generally measured by the mean square deviation between the LO, λ, and its main portion, $\bar{\lambda}$, renormalized to unity: m.s.d. $= 2(1-\langle\lambda|\bar{\lambda}\rangle)$ [5, 6]. In this case we prefer to give the quantity $(Q_C+Q_H)_{CH}$ as an indirect index of the magnitude of the tails[1], because this value is more directly comparable to $(Q_C-Q_H)_{CH}$ which gives an approximate idea of the polarization inside the LO.

The $\Delta(Q_C+Q_H)$ and $\Delta(Q_C-Q_H)$ values, reported in Table 2, practically only depend on the nature of R and on the position the CH group has with respect to R. In other words the presence and the position of the CN group does not greatly affect the substitution effects on the CH groups.

In general the changes of (Q_C-Q_H), being related, as above said, to the variations of polarization inside the bond, are decidedly higher than the corresponding changes in (Q_C+Q_H), the only notable exception being presented by the CH groups *trans* to R for which the two indexes are of the same order of magnitude.

The charge shifts $\Delta(Q_C-Q_H)_{CH}$ and $\Delta(Q_C+Q_H)_{CH}$ give obviously only a rough representation of the electron distribution rearrangement inside the localized orbital λ_{CH}. We give in Fig. 1 an example of the maps of the difference charge distribution $\Delta\rho^{CH}$ (the charge distribution of λ_{CH} in the substituted compound

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[1] The population of the tail of λ_{CH} is $-(Q_C+Q_H)$ electrons.

Table 1. Comparison among the sum and the difference in gross atomic charges on C and H for each kind of C—H bond

H vicinal to R

	Ethylene (Q_C+Q_H)	3,Acryl. (Q_C+Q_H)	2,Acryl. (Q_C+Q_H)	Ethylene (Q_C-Q_H)	3,Acryl. (Q_C-Q_H)	2,Acryl. (Q_C-Q_H)
H	0.0513	0.0452	0.0514	0.3077	0.3741	0.4050
F	0.0570	0.0601	0.0604	0.3751	0.4470	0.4764
OH (*sp*)	0.0476	0.0486	0.0524	0.4230	0.4932	0.5183
OH (*ap*)	0.0510	0.0508	0.0499	0.3313	0.4050	0.4362
NH_2	0.0457	0.0424	0.0454	0.3634	0.4398	0.4654
CH_3	0.0478	0.0430	0.0509	0.3215	0.3913	0.4238

H cis with respect to R

	Ethylene (Q_C+Q_H)	1,Acryl. (Q_C+Q_H)	2,Acryl. (Q_C+Q_H)	Ethylene (Q_C-Q_H)	1,Acryl. (Q_C-Q_H)	2,Acryl. (Q_C-Q_H)
H	0.0513	0.0452	0.0319	0.3077	0.3741	0.4562
F	0.0442	0.0419	0.0203	0.3669	0.4291	0.5017
OH (*sp*)	0.0489	0.0386	0.0264	0.2778	0.3329	0.4075
OH (*ap*)	0.0484	0.0451	0.0103	0.3509	0.4142	0.4865
NH_2	0.0553	0.0495	0.0231	0.2650	0.3280	0.3982
CH_3	0.0539	0.0488	0.0322	0.2984	0.3607	0.4383

H trans with respect to R

	Ethylene (Q_C+Q_H)	1,Acryl. (Q_C+Q_H)	3,Acryl. (Q_C+Q_H)	Ethylene (Q_C-Q_H)	1,Acryl. (Q_C-Q_H)	3,Acryl. (Q_C-Q_H)
H	0.0513	0.0514	0.0319	0.3077	0.4050	0.4562
F	0.0339	0.0322	0.0066	0.3294	0.4234	0.4771
OH (*sp*)	0.0358	0.0340	0.0132	0.3273	0.4121	0.4685
OH (*ap*)	0.0415	0.0416	0.0136	0.2945	0.3928	0.4447
NH_2	0.0432	0.0430	0.0157	0.2785	0.3737	0.4229
CH_3	0.0493	0.0507	0.0267	0.2929	0.3879	0.4420

minus the charge distribution in the parent molecule). This example shows what complex pattern of small rearrangements is hidden under the charge shifts of Table 2.

We may however try to get a heuristic interpretation of changes in the electronic distribution by correlating a quantity related to it with the changes in the classical electric field $\boldsymbol{E}^{CH}$ produced by all the other groups of the molecule. As was done in papers I and II, we choose as quantity related to $\Delta\rho^{CH}$ the changes in the LO contribution to the molecular dipole, $\Delta\boldsymbol{\mu}^{CH}$, and as quantity related to changes in the electric field $\boldsymbol{E}^{CH}$, the value of $\Delta\boldsymbol{E}^{CH}$ calculated at the charge centre of the C—H LO. This choice of the numerical index related to the electric field experienced by λ_{CH} focusses the attention on the charge shifts occurring in the

Table 2. Comparison among the differences with respect to the parent compound in the quantities reported in Table 1

H vicinal to R

	Ethylene $\Delta(Q_C+Q_H)$	3,Acryl. $\Delta(Q_C+Q_H)$	2,Acryl. $\Delta(Q_C+Q_H)$	Ethylene $\Delta(Q_C-Q_H)$	3,Acryl. $\Delta(Q_C-Q_H)$	2,Acryl. $\Delta(Q_C-Q_H)$
F	0.0057	0.0149	0.0090	0.0674	0.0729	0.0714
OH (*sp*)	−0.0037	0.0034	−0.0015	0.1153	0.1191	0.1133
OH (*ap*)	−0.0003	0.0056	0.0010	0.0236	0.0309	0.0312
NH_2	−0.0056	−0.0028	−0.0060	0.0557	0.0657	0.0604
CH_3	−0.0035	−0.0022	−0.0005	0.0138	0.0172	0.0188

H cis with respect to R

	Ethylene $\Delta(Q_C+Q_H)$	1,Acryl. $\Delta(Q_C+Q_H)$	2,Acryl. $\Delta(Q_C+Q_H)$	Ethylene $\Delta(Q_C-Q_H)$	1,Acryl. $\Delta(Q_C-Q_H)$	2,Acryl. $\Delta(Q_C-Q_H)$
F	−0.0071	−0.0033	−0.0116	0.0593	0.0550	0.0455
OH (*sp*)	−0.0024	−0.0066	−0.0216	−0.0299	−0.0412	−0.0487
OH (*ap*)	−0.0029	−0.0001	−0.0055	0.0432	0.0401	0.0303
NH_2	0.0040	0.0043	−0.0088	−0.0427	−0.0461	−0.0580
CH_3	0.0026	0.0036	0.0003	−0.0093	−0.0134	−0.0179

H trans with respect to R

	Ethylene $\Delta(Q_C+Q_H)$	1,Acryl $\Delta(Q_C+Q_H)$	3,Acryl. $\Delta(Q_C+Q_H)$	Ethylene $\Delta(Q_C-Q_H)$	1,Acryl. $\Delta(Q_C-Q_H)$	3,Acryl. (Q_C-Q_H)
F	−0.0174	−0.0192	−0.0253	0.0217	0.0184	0.0209
OH (*sp*)	−0.0155	−0.0174	−0.0183	0.0204	0.0071	0.0123
OH (*ap*)	−0.0098	−0.0098	−0.0187	−0.0132	−0.0122	−0.0115
NH_2	−0.0081	−0.0084	−0.0162	−0.0292	−0.0313	−0.0331
CH_3	−0.0020	−0.0007	−0.0052	−0.0148	−0.0171	−0.0142

main portion of the LO, which, as we have seen, are the most important consequences of the substitution.

We report in Table 3 and 4 the numerical values of the z components of $\Delta\boldsymbol{\mu}^{CH}$ and $\Delta\boldsymbol{E}^{CH}$ respectively. It may be remarked that the values of the different $\boldsymbol{\mu}^{CH}$'s refer to neutral subunits (the two electrons of λ_{CH} and two positive $+e$ charges on C and H nuclei) and that their numerical values are in the range 1.80–1.95 Debyes, in agreement with what found in other series of molecules (see, e.g. Bonaccorsi et al. [4]) with this definition of the CH subunit.

In Fig. 2 we report the correlation we have found between the z components of $\Delta\boldsymbol{\mu}^{CH}$ and $\Delta\boldsymbol{E}^{CH}$. Analogous correlations hold also for the x components, although the absolute values of the numerical quantities are smaller: to save space we do not report here these supplementary data.

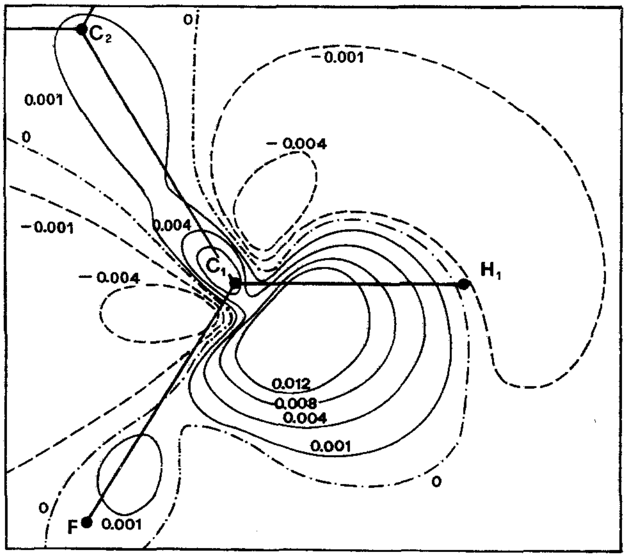

Fig. 1. Map of the difference of electron charge density of the localized orbital corresponding to the C_1—H_1 bond in F-ethylene with respect to the same bond in ethylene. The map refers to the molecular planes. Isodensity values are given in *e* units

The best correlation line (regression coefficient $r = 0.964$) does not pass through the origin. This fact is not surprising because there are surely other factors, of minor weight, hidden under the assumed classical relationship between perturbing influence of substituent and charge shifts. Another reason for such a behaviour derives, in our opinion, from the approximations specific of the simple numerical test we have selected to point out the classical relationship. In fact we are comparing here an integral quantity ($\Delta\mu_z^{CH}$), which depends on changes of the whole LO charge distribution, with a local quantity (ΔE_z^{CH}), calculated at a single point. In the preceding papers we did remark that the choice of the point where ΔE^X is calculated, the quality of the correlation being practically unaltered if this point is displaced in a rather wide region around the LO charge centre. This remark also holds in the present case, but it is evident that the index gives better results if it refers to more similar cases, e.g. the changes of E^{CH} within the subset of heterosubstituted compounds, and worse indications for the parent compounds.

An indirect evidence that the charge distribution of the molecular skeleton reacts in quite an analogous manner to perturbations in substituted and unsubstituted ethylenes and acrylonitriles can be obtained by analyzing the response of these molecules to an external perturbator. A detailed examination of these tests could support the classical interpretation of the deformations of the charge distribution, but such a topic deserves a separate discussion, being not directly related to substitution effects.

Table 3. Changes of the z component of the dipole moment of the C—H groups[a]

H vicinal to R

	Ethylene $\Delta\mu_z$	3,Acryl. $\Delta\mu_z$	2,Acryl. $\Delta\mu_z$
F	0.1818	0.1871	0.1787
OH (*sp*)	0.1772	0.1808	0.1789
OH (*ap*)	0.0968	0.0838	0.0873
NH_2	0.1087	0.1059	0.1036
CH_3	0.0185	0.0177	0.0168

H cis with respect to R

	Ethylene $\Delta\mu_z$	1,Acryl. $\Delta\mu_z$	2,Acryl. $\Delta\mu_z$
F	0.0691	0.0675	0.0597
OH (*sp*)	−0.0483	−0.0472	−0.0537
OH (*ap*)	0.0462	0.0465	0.0265
NH_2	−0.0640	−0.0627	−0.0916
CH_3	−0.0190	−0.0226	−0.0375

H trans with respect to R

	Ethylene $\Delta\mu_z$	1,Acryl. $\Delta\mu_z$	3,Acryl. $\Delta\mu_z$
F	0.0323	0.0305	0.0570
OH (*sp*)	0.0168	0.0041	0.0201
OH (*ap*)	−0.0173	−0.0147	−0.0004
NH_2	−0.0483	−0.0498	−0.0435
CH_3	−0.0211	−0.0252	−0.0130

[a] The values are given as difference with respect to the parent compounds ethylene ($\mu_z^{CH} = -1.9064$) and acrylonitrile ($\mu_z^{C_1H_1} = -1.6967$, $\mu_z^{C_2H_2} = -1.8076$, $\mu_z^{C_2H_3} = -1.7800$). All values are given in Debyes

Going back again to the set of ΔE_z^{CH} values employed in Fig. 2, we give in Fig. 3 a decomposition of these indexes into direct component, i.e. the contribution due to the substitution of a C—H bond with C—R, and indirect components which are due to the changes in the intrinsic properties of the other groups present in the molecules induced by chemical substitution.

Widely different are the results on CH groups placed in *vicinal*, *cis* or *trans* position with respect to the site where substitution occurs. On the *vicinal* CH's the substitution field is practically due to the direct contribution alone, the other contributions representing only minor corrections. The relative weight of the direct contribution decreases in the *cis* and *trans* cases, where the most important

Table 4. Changes of the z component of the electric field of the C—H groups[a]

H vicinal to R

	Ethylene ΔE_z	3,Acryl. ΔE_z	2,Acryl. ΔE_z
F	27.80	26.60	22.23
OH (*sp*)	25.40	24.00	19.15
OH (*ap*)	15.00	13.60	9.43
NH_2	13.20	12.65	8.12
CH_3	3.20	2.65	−2.48

H cis with respect to R

	Ethylene ΔE_z	1,Acryl. ΔE_z	2,Acryl. ΔE_z
F	1.80	2.20	1.85
OH (*sp*)	−13.70	−13.60	−13.90
OH (*ap*)	−0.90	−0.20	−1.05
NH_2	−13.70	−13.40	−14.30
CH_3	−4.30	−4.40	−5.15

H trans with respect to R

	Ethylene ΔE_z	1,Acryl. ΔE_z	3,Acryl. ΔE_z
F	−1.20	−6.00	−0.40
OH (*sp*)	−4.40	−10.14	−5.25
OH (*ap*)	−6.10	−10.78	−5.90
NH_2	−11.30	−15.63	−11.10
CH_3	−2.80	−8.58	−3.60

[a] The values are given as difference with respect to the parent compounds ethylene ($E_z^{CH} = 678.00$) and acrylonitrile ($E_z^{C_1H_1} = 704.20$, $E_z^{C_2H_2} = 694.35$, $E_z^{C_2H_3} = 702.70$) all values are given in arbitrary units (see Fig. 2)

term is the one transmitted through the C=C group. We have not considered it necessary to give a more detailed dissection of this contribution into σ and π components, which are of opposite sign, because a detailed discussion of the results of this separation has been already given in paper II.

A comparison of these dissections within each set of CH groups indicates that the substitution of a C—H group with C—CN does not produce appreciable changes. This fact confirms the impression pointed out in paper II that the inclusion of CN groups in the ethylene skeleton does not significantly affect the response of the group to substitution.

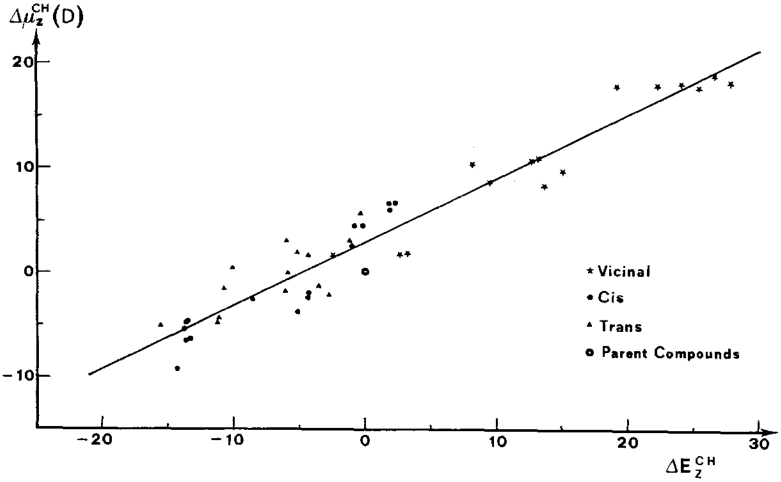

Fig. 2. Correlation between the changes in the z component of the dipole moment of the C—H groups (μ_z^{CH}) and the changes in the electric field of the molecular remainder (E_z^{CH}) calculated at the charge centre of the C—H LO. The dipole values are given in Debyes and the field values in arbitrary units (1 ar. un. = 27360 esu cm^{-2})

3. The Effects of Substitution on the Analytic Expression of the Target Group

The electronic portion of the target groups A–B we have considered both in this paper and in the preceding one is described by a single LO, whose analytical expression in the LCAO expansion can be written:

$$\lambda_{AB} = c_{AB}\bar{\lambda}_{AB} + c_T\bar{\lambda}_T. \tag{1}$$

The main portion of the LO, $\bar{\lambda}_{AB}$, is defined over the subset of atomic basis orbitals centred on atoms A and B, while the portion concerning the tails, $\bar{\lambda}_T$, is defined over the complementary subset of atomic orbitals. This partition has been widely employed in the abundant literature over the tails of the LO's (for a short review see Bonaccorsi et al. [4]) and has been also exploited in this set of papers.

We shall now adopt the same technique of projection of a LCAO expression over appropriate functional subspaces to get an expression of $\bar{\lambda}_{AB}$ in terms of generalized atomic hybrids:

$$\bar{\lambda}_{AB} = N_A h_A + N_B h_B \tag{2}$$

($\bar{\lambda}_{AB}$, h_A, and h_B are all normalized).

The question we want to consider concerns the effect of substitution on the quantities of Eq. (2): do the changes in $\bar{\lambda}_{AB}$ more heavily affect the coefficients c_A and c_B or the form of the hybrids h_A and h_B? To get an answer we may consider the set of C—H LO's which we have examined in the preceding section from a different point of view. The changes in the coefficients and in the hybrids can be quantified in different ways, because according to definition (2) they can be

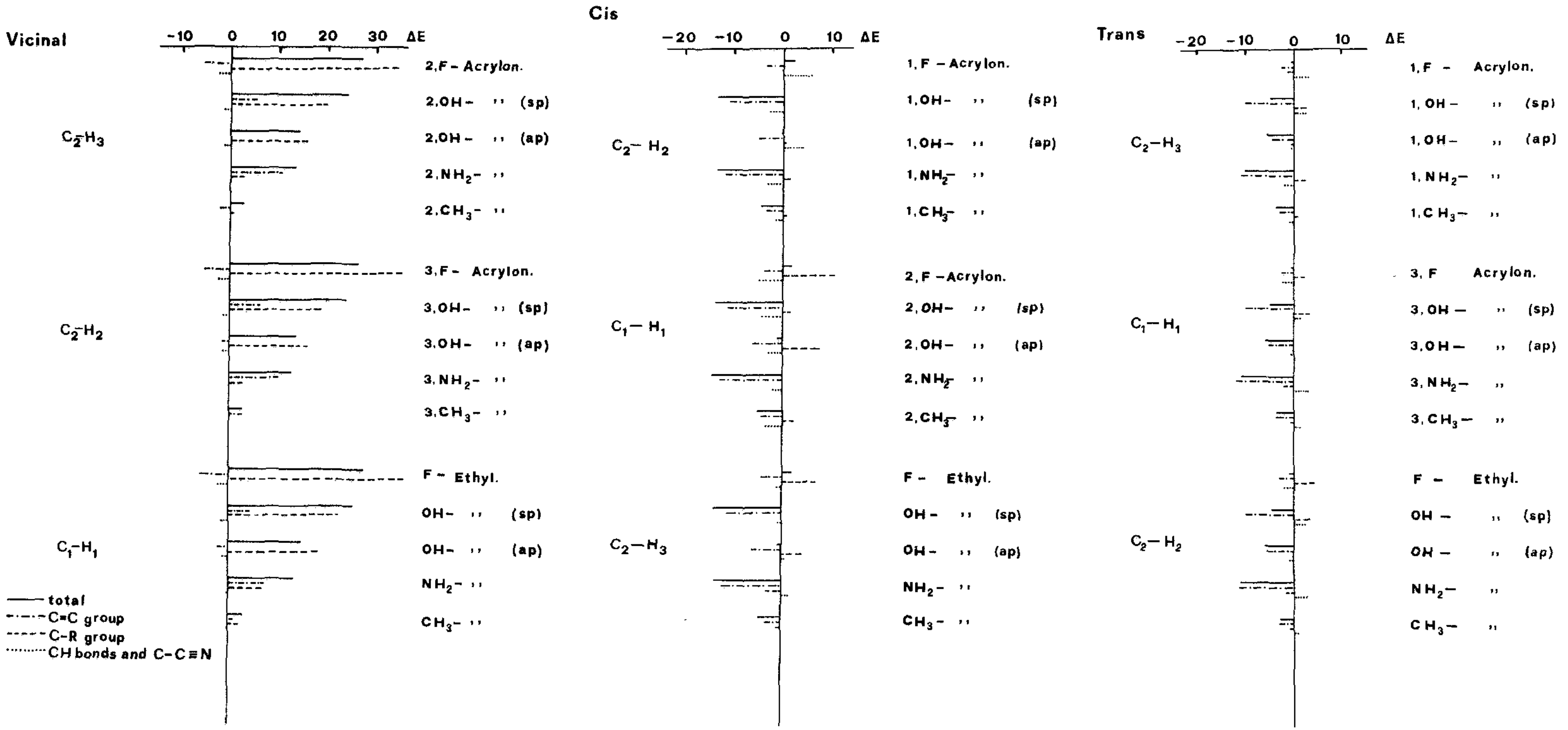

Fig. 3. A decomposition of the ΔE_z^{CH} values into direct and indirect contributions

Table 5. Contribution to the z component of the dipole moment of the C—H bonds in the ethylene series due to variations in coefficients (Charge Transfer) and in hybrids (Hybrid Deformation)

	Vicinal		Cis		Trans	
	C.T.	H.D.	C.T.	H.D.	C.T.	H.D.
F	0.1182	0.0613	0.0859	0.0177	0.0297	0.0019
OH (*sp*)	0.1924	−0.0051	−0.0443	−0.0040	0.0277	−0.0109
OH (*ap*)	0.0597	0.0370	0.0623	−0.0160	−0.0224	0.0050
NH_2	0.1032	0.0055	−0.0642	0.0002	−0.0464	−0.0020
CH_3	0.0301	−0.0112	−0.0136	−0.0053	−0.0227	0.0016

directly obtained from the localized expression of the SCF orbitals, but perhaps the test more directly related to the analyses given in the preceding section is the one reported in Table 5. In this Table we give the contributions to $\Delta\mu_z^{CH}$ due to changes in coefficients and to changes in the hybrids, respectively. The total value of $\Delta\mu_z^{CH}$ does not exactly correspond to the value given in Table 3 because the contributions of Table 5 refer to a first order expansion of $\Delta\mu$.

From these data it appears that the main effect of substitution is due to changes in the coefficients. In a first approximation, the substitution seems to be representable as a charge transfer between the two atoms performed over local entities, the hybrids, which are not greatly affected by the substitution. It may be remarked that this trend is valid also for C—H orbitals *vicinal* to the C—R group, in other words that the substitution does not produce noticeable deformation in the shape of the h_C hybrid involved in the C—H bond of the same C atom which bears the substituent.

This analysis could be refined by reporting data concerning other parameters, like the x component of $\Delta\boldsymbol{\mu}^{CH}$, but, in spite of the interest this discussion could have, we prefer to examine other groups from the same point of view. To this end we give in Table 6 the mean square deviation between the hybrid h_C in the parent compound and the same hybrid in the substituted molecule for the set of C—H bonds in ethylenes. These values, the meaning of which can be deduced from the discussion we have just made, can be used as reference for the examination of the m.s.d. of the carbon hybrids in the C=C groups between parent and substituted compounds which we report in Table 7. We have adopted here a representation of

Table 6. Mean square deviation $[2(1-\langle h_C^{eth}|h_C^{sub}\rangle)]$ between the hybrid h_C in the C—H bond of ethylene and the same hybrid of the substituted compounds

	Vicinal	Cis	Trans
F	0.00918	0.00024	0.00055
OH (*sp*)	0.00257	0.00303	0.00005
OH (*ap*)	0.01113	0.00015	0.00070
NH_2	0.00619	0.00171	0.00004
CH_3	0.00124	0.00030	0.00005

	h_{C_1}	h_{C_2}
F	0.00354	0.00099
OH (*sp*)	0.00611	0.00431
OH (*ap*)	0.00290	0.00396
NH_2	0.00634	0.00775
CH_3	0.00068	0.00059

Table 7. Mean square deviation of the hybrid h_C in one of the banana bonds of C=C in ethylene and the same hybrid in the substituted compounds

the C=C group in terms of banana orbitals and the data of the Table refer to the hybrid pertaining to one of the two bananas. (For the other one the data are of course equivalent). It turns out that the m.s.d.'s for these hybrids of C are of the same order of magnitude than those obtained for the hybrid involved in the C—H bonds, and, as a consequence, one may deduce that also for the C=C group the effects of substitution could be approximated by a description leaving the shape of h_C invariant and changing only the corresponding coefficient N_C.

Finally, we show in Table 8 the m.s.d. for the fourth hybrid of C, involved in the C—X bond. (Notice that in the LO description, which we have employed here, the four C hybrids are generalized sp^3 hybrids). The m.s.d.'s are a little larger than in the preceding case, but the changes in the hybrid remains smaller than the corresponding changes in the coefficient N_C (see Eq. 2).

It is not convenient to go any farther on the basis of an analysis of a set of SCF wavefunctions, but the results here presented seem to us interesting enough to justify further investigations directed to verify if these characteristics of the analytical expression of an LO can be exploited in a method of direct evaluation of substitution effects.

4. Conclusions

In this paper we have terminated the exposition of an analysis of SCF wavefunctions for a set of related molecules bearing different substituents. The analysis aimed at verifying to what extent classical effects only are able to explain the effects induced by the substituent in the charge distribution of an LO, assumed as a target. The answer seems, on the whole, positive, and may constitute the basis for more refined intuitive criteria to justify substitution effects, and, perhaps, the starting point for the implementation of computational methods which couple the positive qualities of the *ab initio* methods with the chemical evidence. The

	hybrid
F	0.12419
OH (*sp*)	0.07405
OH (*ap*)	0.11140
NH_2	0.04557
CH_3	0.00015

Table 8. Mean square deviation between the hybrid h_C, involved in the C—H bond of ethylene and the same hybrid in the C—R bond of substituted compounds

properties of substituted molecules can be derived, to a good extent, from those of the parent molecule and of the substituent group.

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