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AN AB INITIO STUDY OF THE ELECTRIC FIELD INFLUENCE ON THE ELECTRON DISTRIBUTION OF H-CN, CH₃-CN, CH₂=CH-CN, AND CH₂=C-(CN)₂

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To assess the role of the monomer polarizability in the course of electropolymerization reactions, an ab initio study of the influence of an intense electric field (10^9 V m^{-1}) on the dipole moment and total atomic charges of HCN, CH₃CN, CH₂CHCN, CH₂C(CN)₂ and CH₂CHCCH has been developed at the STO-3G, 3-21G and 6-31G* levels. The calculated polarizabilities of the three vinylic molecules are high, the induced dipole moment being 10% of the permanent one. The decrease of the atomic charge observed on the vinylic CH₂ group is insufficient for it to be solely responsible for the increase in its electrophilic character.

1. Introduction

Cathodic electropolymerization has been reported for various vinylic monomers: acroleine [1], acrylonitrile [2,3] and parachlorostyrene [4]. Polyacrylonitrile (PAN), which has been the subject of most studies, can be grafted as thin films on various metallic surfaces [5]. To explain the electropolymerization process, one considers [5] the role played by the electric field created at the metal-electrolyte interface by the double layer of particles with opposite signs. This electric field, whose generally accepted intensity [6] is of the order of 10^9 V m^{-1} , is supposed to affect directly the monomer in two ways: (a) orient the molecule on its path toward the reactive site, which should be an important process owing to the large dipole moment [7] ($12.91 \times 10^{-30} \text{ C m}$ or 3.87 D) due to the cyano group in acrylonitrile, and (b) increase the polarization of its electronic distribution and thus enhance the reactive ability of the monomer, in particular the electrophilic character of the terminal vinylic CH₂ group.

In view of possible implications in the selection of other monomers for cathodic electropolymerization,

it is important to assess the contribution of this polarization effect on the synthesis of the material. In an attempt to contribute to this question, the double-layer influence has been simulated by a homogeneous electric field. The effects of the field on the electronic distribution of acrylonitrile has been assessed by considering Mulliken net atomic charges, the induced dipole moment, and the electric polarizability. Three additional cyano molecules, H-CN (hydrogen cyanide), CH₃-CN (cyanomethane or acetonitrile) and CH₂=C(CN)₂ (1,1-dicyanoethylene), were studied in parallel with acrylonitrile in order to identify the role of the C=C bond of the vinylic moiety in the changes in the electronic distribution induced by the externally applied electric field. For reference, we have also considered the isoelectronic vinylacetylene, CH₂=CH-C≡CH, because it corresponds to the basic conjugated repeat unit, H[-CR₁=CR₂-C≡C-]_xH, found in polydiacetylenes which are presently the subject of numerous investigations in connection with their interesting non-linear optical properties [8].

2. Methodological aspects

Results reported in this Letter have been obtained at the Hartree-Fock level using the GAUSSIAN 80 series of programs [9], to which code for the finite-field steps has been added [10]. In this method, a term $-\boldsymbol{\mu} \cdot \mathbf{E}$ is added to the molecular Hamiltonian, where $\boldsymbol{\mu}$ is the dipole moment of the molecule and \mathbf{E} the applied electric field. The components of the electric polarizability tensor α can be defined as $\alpha_{ij} = (\partial \mu_i / \partial E_j)_0$ and are in practice obtained numerically as [11]

$$\alpha_{ij} = [\mu_i(E_j) - \mu_i(-E_j)] / 2E_j.$$

Computed values of physical properties such as the dipole moment and polarizability are known to depend on the basis set. To gain at least partial information on this dependence, we have run the computations for three basis sets [12]: the minimal (economical) STO-3G basis, the split-valence 3-21G basis and the 6-31G* split-valence basis including polarization functions on heavy atoms.

Dipole moments and especially electric polarizabilities are sensitive to structure and thus, for the sake of consistency, they have been calculated with the equilibrium geometry of the corresponding basis set. Gradient optimization techniques [13,14] have been employed to optimize fully the geometries of all the molecules with the following requirements: 10^{-10} au for the two-electron cutoff, 10^{-6} for the requested convergence on the density matrix elements, and 4.5×10^{-4} hartree bohr $^{-1}$ as the maximal residual force for the Cartesian component of the gradient of the energy. We checked that the geometries are basically unchanged when subjected to the field intensities considered in this work (up to 2.0×10^9 V m $^{-1}$). This is in agreement with literature information [15-18] on molecules under the influence of external electric fields; it has been shown that electric field intensities of the order of 10^{10} V m $^{-1}$ are needed to induce noticeable structural changes in molecules, e.g. of the order of 0.01 Å for bond length and some degrees for bond angles [18]. Accordingly, all reported results in this work correspond to the zero-field equilibrium geometries.

3. Results and discussion

The molecular structures are shown in fig. 1 together with the notation used for the geometrical parameters, the direction of the permanent dipole moments and the Cartesian frame; all molecular planes have been chosen to coincide with the (z, x) plane. The z axis has been chosen along the molecular bond closest to the permanent dipole moment.

Total energies and optimized geometrical parameters of interest for the three basis sets and corresponding experimental data are given in table 1. These are in agreement with previously published theoretical equilibrium geometries; relevant references to previous work are indicated in the table. Trends in theoretical geometries compare qualitatively with experimental data (table 1), although systematic deviations are observed. For instance the C≡N and C=C distances are underestimated while the C-CN bond length is systematically too large as expected owing to the neglect of electron correlation.

The non-zero components of the permanent dipole moment $|\boldsymbol{\mu}_0|$, its absolute value and the non-zero components of the induced dipole moment $|\boldsymbol{\mu}_i|$ for three values of the intensity of a homogeneous electric field oriented along the z axis, are listed in table 2. Dipole moments are expressed in D (1

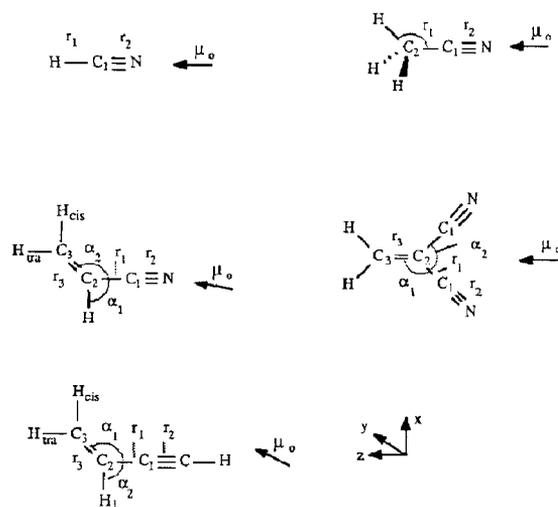


Fig. 1. Structures of the five molecules studied together with the notation used for the geometrical parameters, the direction of the dipole moments and the Cartesian frame.

Table 1

Total energy and optimized geometrical parameters at the STO-3G, 3-21G, and 6-31G* level and corresponding experimental data for HCN, CH₃CN, CH₂=CH-CN, CH₂=C(CN)₂ and CH₂=CH-CCH

Molecule		STO-3G	3-21G	6-31G*	Exp. [19]
HCN ^{a)}	r_1	1.070	1.050	1.059	1.063
	r_2	1.153	1.137	1.132	1.153
	E_T	-91.675209	-92.354084	-92.875197	
CH ₃ -CN ^{b)}	r_1	1.486	1.457	1.467	1.458
	r_2	1.154	1.139	1.135	1.157
	α	109.94	110.13	109.82	109.45
	E_T	-130.271542	-131.191802	-131.927534	
CH ₂ =CH-CN	r_1	1.460	1.427	1.443	1.426
	r_2	1.157	1.140	1.136	1.164
	r_3	1.315	1.319	1.320	1.339
	α_1	122.89	122.69	122.14	122.61
	α_2	115.46	115.57	115.82	115.66
	E_T	-167.627271	-168.820397	-169.768006	
CH ₂ =C-(CN) ₂	r_1	1.465	1.43	1.445	
	r_2	1.157	1.139	1.135	
	r_3	1.324	1.324	1.325	
	α_1	121.92	121.76	121.56	
	α_2	116.15	116.48	116.88	
	E_T	-258.171645	-260.027725	-261.490533	
CH ₂ =CH-CCH	r_1			1.439	
	r_2			1.188	
	r_3			1.322	
	α_1			123.71	
	α_2			115.96	
	E_T			-153.707874	

^{a)} Previous work on the same systems can be found in refs. [20,21].

^{b)} Previous work on the same systems can be found in ref. [22].

$D = 3.33 \times 10^{-30}$ C m). The field intensities considered are 0.001, 0.002, 0.004 au, namely 0.514×10^9 , 1.028×10^9 and 2.056×10^9 V m⁻¹, respectively, for $k = 1, 2$ and 3 . Fig. 2 shows for the cyano molecules the variation of $|\mu|$ with respect to electric field intensity calculated at the 6-31G* level.

Table 3 gives the values of the diagonal components α_{ii} ($i = x, y$ and z) of the polarizability tensor α and the mean polarizability $\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ (expressed in 10^{-41} F m²). Table 4 reports the Mulliken atomic charges (expressed in units of the electronic charge) on the atoms of all the molecules at zero field and for the highest value of the applied external field at the 6-31G* level.

The analysis of the data given in table 2 shows that the dipole moment increases with the quality of the basis set. A basis set of at least double-zeta quality

is necessary to provide values in agreement with experiment. The remaining difference between experimental and calculated values may be attributed to both a residual basis set deficiency and the neglect of electronic correlation effects. Trends between STO-3G, 3-21G and 6-31G* results are the same.

The permanent dipole moments of all the cyano molecules are high and are directed along the CN group from N to C, except for acrylonitrile where it is slightly tilted (7°) from that direction because of the presence of the vinylic bond. Comparing HCN and CH₃CN, substitution of the hydrogen atom by a methyl group increases the dipole moment by about 26%. However, substituting the methyl by a vinyl group does not lead to a substantial increase of the dipole moment; methyl and vinyl groups have practically the same effect on the resulting dipole mo-

Table 2

Non-zero components of the permanent dipole moment $|\mu_0|$ and non-zero components of the induced dipole moment $\mu_i(E_k)$ (in D) for three intensities (0.514×10^9 , 1.028×10^9 and 2.056×10^9 V m⁻¹, respectively for $k=1, 2, 3$) of a homogeneous electric field directed along the z axis

Molecule		STO-3G	3-21G	6-31G*	Exp. [7]
HCN	$ \mu_0 = \mu_{0z}$	2.4557	3.0426	3.2088	2.98
	$\mu_{iz}(E_1)$	0.0305	0.0462	0.0496	
	$\mu_{iz}(E_2)$	0.0610	0.0922	0.0991	
	$\mu_{iz}(E_3)$	0.1219	0.1842	0.1981	
CH ₃ -CN	$ \mu_0 = \mu_{0z}$	3.0961	3.8835	4.0422	3.92
	$\mu_{iz}(E_1)$	0.0484	0.0761	0.0808	
	$\mu_{iz}(E_2)$	0.0968	0.1502	0.1616	
	$\mu_{iz}(E_3)$	0.1938	0.3004	0.3233	
CH ₂ =CH-CN	μ_{0x}	0.3574	0.4950	0.5098	3.87
	μ_{0z}	3.1982	4.0004	4.2259	
	$ \mu_0 $	3.2181	4.0309	4.2565	
	$\mu_{ix}(E_1)$	0.0166	0.0235	0.0235	
	$\mu_{ix}(E_2)$	0.0332	0.0470	0.0470	
	$\mu_{ix}(E_3)$	0.0664	0.0939	0.0940	
	$\mu_{iz}(E_1)$	0.0788	0.1168	0.1241	
	$\mu_{iz}(E_2)$	0.1576	0.2335	0.2482	
	$\mu_{iz}(E_3)$	0.3151	0.4667	0.4963	
CH ₂ =C-(CN) ₂	$ \mu_0 = \mu_{0z}$	3.7069	4.6645	4.8365	
	$\mu_{iz}(E_1)$	0.0934	0.1364	0.1445	
	$\mu_{iz}(E_2)$	0.1868	0.2726	0.2886	
	$\mu_{iz}(E_3)$	0.3734	0.5440	0.5729	
CH ₂ =CHC=CH	μ_{0x}			0.1744	
	μ_{0z}			0.4424	
	$ \mu_0 $			0.4755	
	$\mu_{ix}(E_1)$			0.0273	
	$\mu_{ix}(E_2)$			0.0546	
	$\mu_{ix}(E_3)$			0.1091	
	$\mu_{iz}(E_1)$			0.1587	
	$\mu_{iz}(E_2)$			0.3175	
	$\mu_{iz}(E_3)$			0.6349	

ment. Thus, the net dipole moment is essentially dictated by the -CN contribution. The dipole moment of 1,1-dicyanoethylene is not much higher than that obtained by adding the contribution of each nitrile group.

The permanent dipole moment of vinylacetylene is low due to the absence of a heteroatom and its orientation is not along the triple bond, but tilted by about 20°, because of the higher delocalization of the electrons along the carbon skeleton.

As seen in table 2 and fig. 2, for the range of field intensities used in this work, $|\mu(E)|$ exhibits a linear response in the field. For systematic studies of $|\mu(E)|$ for systems analogous to the compounds

considered here, it seems justified (for the range of field intensities used in this work) to limit the classical power series expansion of $\mu(E)$ to the first two terms, i.e. $\mu(E) \approx \mu_0 + \alpha \cdot E$. This requires a calculation of the polarizability tensor of the molecules instead of computing $\mu(E)$ for a large number of values of the field.

For the cyano molecules, the induced dipole moment calculated for the highest value of the field varies from 5% of the permanent dipole for HCN and CH₃CN, to 10% for CH₂CHCN and CH₂C(CN)₂. The difference clearly comes from the vinylic bond. This is particularly clear in the case of acrylonitrile where the x component for μ for a field in the z di-

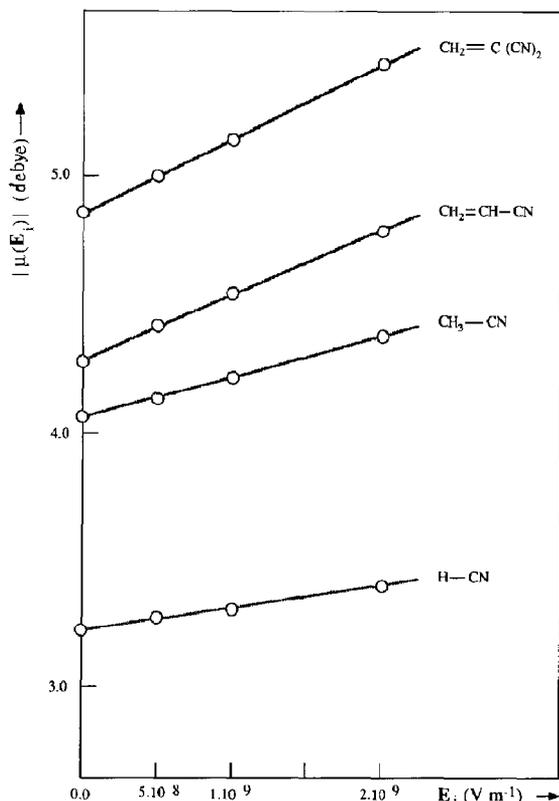


Fig. 2. Evolution of the total dipole moments of the cyano molecules with the intensity of a field oriented along the z axis (at the 6-31G* level).

rection (i.e. in the CN direction) has a non-negligible value. Thus in this case, the Cartesian frame does not correspond to the principal polarizability axes of the molecule. It is also the case for CH_2CHCCH but not for the other molecules owing to their symmetry.

For CH_2CHCN , we have performed a diagonalization of the polarizability tensor in the (x, z) plane and obtained for the principal longitudinal axis a direction tilted about 24° from the CN bond (the exact values are $24^\circ 04'$ at the STO-3G level, $24^\circ 57'$ at 3.21G and $24^\circ 15'$ at 6.31G*). So, the longitudinal axis is not directed along the permanent dipole direction, showing the ability of the C=C bond compared to CN to respond to the field. In this sense acrylonitrile behaves differently from vinylacetylene: for this latter molecule diagonalization of the polarization tensor leads to a tilt of $18^\circ 07'$ (at the 6-31G* level) and the longitudinal axis is close to

the permanent dipole direction. The electrons of a non-polar triple bond are more delocalizable than those of a polar one.

For the components of the polarizability tensor (table 3) calculated from the dipole moments, the influence of the basis set is the same, the addition of polarization atomic orbitals giving a correction of only 10%. For CH_2CHCN and CH_2CHCCH , the eigenvalues in the (x, z) plane are given in parentheses.

In the case of CH_3CN experimental polarizabilities measured at various wavelengths are available [23] and can be used to compare with our theoretical estimates. A factor of 1.37 is observed between the experimental, 49.6 (measured at $\lambda = 632.8$ nm), and the theoretical, 36.1, values for the average polarizability. There is still a significant quantitative difference between theory and experiment. This is not unexpected since polarizability is sensitive to the basis set. Previous studies suggest, however, that trends among similar compounds are qualitatively correct [11,24] and we assume a similar feature for the compounds studied in this work.

The polarizability is sensitive to substitution. From HCN to CH_3CN , $\langle \alpha \rangle$ is doubled showing that the methyl group acts like an electron reservoir. From HCN to CH_2CHCN , $\langle \alpha \rangle$ is tripled due to the conjugation effect between the C=C double bond and the C=N triple bond. We can classify the vinylic molecules according to their polarizability in the following order: $CH_2CHCN < CH_2CHC=CH < CH_2C(CN)_2$. As discussed above, it is not surprising that the vinylacetylene is more polarizable than acrylonitrile. The largest response is found as expected for dicyanoethylene owing to the twin nitrile groups and the increased molecular size.

Out-of-plane polarizabilities α_{yy} are three times smaller than the in-plane α_{xx} and α_{zz} values. This is a well known basis set effect [25]: small basis sets and even basis sets with polarization functions poorly fit experimental out-of-plane polarizabilities of planar molecules.

Finally α and μ are global quantities characteristic of the electronic distribution of each molecule. To get a better view of this distribution, we have considered the atomic charges as defined by Mulliken [26]. We observe a linear response with the electric field intensity in all bases considered. Owing to the above discussion on the basis set influence on α and

Table 3

Diagonal components of the polarizability tensor in the Cartesian frame defined in fig. 1 and mean polarizability values expressed in 10^{-41} F m². In parentheses are given the eigenvalues for CH₂CHCN and CH₂CHCCH (see text)

Molecule		STO-3G	3-21G	6-31G*	Exp. [23] ^{a)}
HCN	α_{xx}	4.545	9.600	12.312	
	α_{yy}	4.545	9.725	12.312	
	α_{zz}	19.786	29.937	32.182	
	$\langle \alpha \rangle$	9.625	16.420	18.935	
CH ₃ -CN	α_{xx}	13.098	24.895	27.974	41.3
	α_{yy}	13.098	24.895	27.974	41.3
	α_{zz}	31.386	48.699	52.403	66.2
	$\langle \alpha \rangle$	19.194	32.829	36.117	49.6
CH ₂ =CH-CN	α_{xx}	31.843 (27.036)	50.199 (43.120)	53.656 (46.793)	
	α_{yy}	7.931	17.400	23.515	
	α_{zz}	51.100 (55.906)	75.792 (82.871)	80.567 (87.430)	
	$\langle \alpha \rangle$	30.291	47.797	52.579	
CH ₂ =C-(CN) ₂	α_{xx}	55.977	82.163	89.929	
	α_{yy}	11.862	24.903	32.757	
	α_{zz}	60.654	88.590	93.749	
	$\langle \alpha \rangle$	42.831	65.219	72.145	
CH ₂ =CHC=CH	α_{xx}			54.819 (49.034)	
	α_{yy}			23.872	
	α_{zz}			103.004 (108.789)	
	$\langle \alpha \rangle$			60.565	

^{a)} Experimental data at $\lambda = 632.8$ nm.

$\mu(E)$, we limit our discussion to 6-31G* results. The values calculated for zero field and the highest field along z (fig. 1) are reported in table 4.

Only small changes in the atomic charges occur on varying the field intensity from 0 to 2.056×10^9 V m⁻¹. These modifications are small if one compares

Table 4

Values of the Mulliken atomic charges (expressed in units of the electronic charge) on the atoms of all the molecules at zero-field and for $E_z = 2.056 \times 10^9$ V m⁻¹ obtained with the 6-31G* basis set

Molecule		$E=0$	$E=E_3$	Molecule		$E=0$	$E=E_3$
HCN	q_N	7.380	7.404	CH ₂ =C-(CN) ₂	q_N	7.421	7.435
	q_C	5.934	5.924		q_{C1}	5.696	5.694
	q_H	0.687	0.672		q_{C2}	5.955	5.971
CH ₃ -CN	q_N	7.454	7.480	q_{C3}	6.315	6.302	
	q_{C1}	5.699	5.693	q_H	0.748	0.735	
	q_{C2}	6.531	6.535	CH ₂ =CHC=CH	q_H	0.711	0.733
	q_H	0.772	0.764		q_C	6.473	6.500
CH ₂ =CH-CN	q_N	7.449	7.476		q_{C1}	5.891	5.867
	q_{C1}	5.720	5.714		q_{C2}	6.171	6.181
	q_{C2}	6.173	6.182	q_{C3}	6.361	6.354	
	q_{C3}	6.336	6.331	q_{H1}	0.784	0.775	
	q_{Hcis}	0.777	0.781	q_{Hcis}	0.798	0.801	
	q_{Htra}	0.789	0.769	q_{Htra}	0.810	0.788	
q_H	0.756	0.747					

with those induced by different chemical environments. For example, the value of q_{C3} is equal to 6.336 for CH_2CHCN and to 6.315 for $CH_2C(CN)_2$, i.e. a difference of 0.021, while the variation of q_{C3} with the field ($q_{C3}(E_3) - q_{C3}(E_0)$) is equal to -0.005 for CH_2CHCN . This decrease of q_{C3} corresponds, as expected, to an increase of the electrophilic character of the $H_2C=$ terminal carbon but appears too weak to induce a significant modification of the reactivity of the monomer. An interesting result is the large shift in electron density out of the trans CH bond (collinear with the electric field), which suggests that appropriate substitution in that position may influence reactivity.

4. Conclusion

The results show that while large basis sets are needed to give dipole moments close to experimental values, the minimal STO-3G basis set provides reliable trends. It is thus not unrealistic to consider using minimal basis sets for systematic studies on larger molecules.

Our calculations of dipole moments and polarizabilities provide an estimate of the response of the electronic density to an applied electric field in a series of CN-containing molecules. They indicate non-negligible polarizabilities but the induced dipole moments remain weak compared to the permanent dipole moment for the field intensity range studied. A first analysis of the atomic charges points to a net charge transfer within the vinylic bond; however the magnitude of this effect does not provide a definite answer to the question of an increased electrophilic character of the CH_2 terminal group in acrylonitrile when subjected to the influence of the electric field intensities assumed to exist during electropolymerization.

A more detailed analysis of the changes induced in the electronic density function at these electric field intensities and stronger ones is planned to obtain a better picture.

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