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Ab initio MO calculation in terms of localized orbitals of the ^{14}N electric field gradient in nitriles

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The contributions of each localized orbital of the CN group and of the molecular remainder to the N electric field gradient (EFG) were calculated for nitriles with R = H, F, CH_3, OH, NH_2, CCH, COH, NO, CN and the E and Z forms of iminoacetonitrile. The changes in the EFG introduced by substituents resulted mainly from the polarization and conjugation of the C—N bonds, with a small contribution from the N lone pair. The total EFG has a large and rather constant contribution from the N lone pair, which is modified by the contributions from the three C—N bonds and the molecular remainder. The resulting EFG is determined by the signs and magnitudes of the C—N bonds' contributions for each substituent and to a lesser degree by the molecular remainders. The asymmetry parameter of the EFG is mainly determined by the inequivalence of the C—N bonds with a very small contribution from the molecular remainder. The molecular remainder and the crystal field in solids contribute more to the largest component of the EFG than to the asymmetry parameter. All these results have allowed us to discuss the validity of the assumptions made in the Townes and Dailey theory when it is applied to nitriles.

Introduction

Information about the molecular charge distribution may be obtained from the study of the interaction between the nuclear quadrupole moment (Q) and the electric field gradient (EFG) produced by external charges [1]. The EFG reflects

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the local charge distribution and is very sensitivie to the changes introduced by substitution [2-5]. Components of the EFG are obtained from microwave and nuclear quadrupole resonance spectroscopy and are related to the population of the different valence orbitals and lone pairs through the theory of Townes and Dailey [4] (TD). However, only two independent components of the EFG are obtained [4] from most experiments and in nitriles, for example, the populations of two π, one σ and a lone pair orbital have to be determined in order to fully characterize the charge distribution around the N nucleus. Clearly approximations must be made [3, 4] in order to obtain information about the distribution responsible for the measured EFG. Most workers have assumed [3, 4] that in nitriles the N lone pair population is constant, and that either one of the π orbitals or the σ_{CN} orbital is not perturbed by the substitution.

The validity of these assumptions and the origin of the variations in the EFG upon substitution may also be studied by calculating the N EFG tensor in different nitriles using extended basis sets [1, 2]. Such a calculation would allow us to obtain the contribution of each orbital to the EFG and hence to determine the validity of some of the assumptions used in the TD theory. Moreover, the effects of substitution on each of the orbitals could also be obtained, and this in turn would allow us to determine how the resulting changes are reflected in the EFG components. Since the TD theory is based on a description of the electronic structure in terms of localized orbitals [4] such as bonds, lone pairs, etc., we use here the more intuitive localized orbitals [1] instead of molecular orbitals. In this way, the results may be more easily compared with those provided by the TD theory.

In the present work, we have calculated the MO—SCF wave functions of eleven nitriles with $R = H$, F, CH_3, OH, NH_2, CCH, COH, NO, CN and the *E* and *Z* forms of iminoacetonitrile [9] (IACN). We have localized the orbitals [6-8] and studied the validity of that approach for all the nitriles studied in this work. We have calculated (i) the changes in the local component of the electrical dipole moment, (ii) the electric field at the localized bonds and (iii) the orbital contribution to the N EFG from each of the bonds of the CN group, and then studied their correlations. We have found that the changes introduced by the substituents into the N EFG resulted mainly from variations in the C—N bonds. The N lone pair contribution to the EFG was only slightly perturbed by the substitution. We have found that the largest component of the total N EFG has a large and almost constant contribution from the lone pair that is modified by the C—N bond contribution. The contributions of the different localized orbitals of the CN group and of the molecular remainder to the other two diagonal components of the EFG tensor are also analyzed in this work. We have found that in general the molecular remainder makes a noticeable contribution to the largest diagonal component and a negligible contribution to the asymmetry parameter of the EFG.

Calculations

The canonical MOs were calculated with the GAUSSIAN 76 and HONDO 5 programs [10, 11] using 4-31G and 4-31G* basis set with standard exponents and scale factors [12]. Experimental bond lengths and bond angles were used when available. No structural information was known for R = COH, OH or for the IACNs, so we used the optimized geometry available (for R = OH, [13]; =COH, [14] and for the IACNs, [9]). The canonical MOs were localized with the PLOCAL subroutine of the GAUSSIAN 70 program using Boys' procedure [15]. In our study, the CN group is represented [6-8] by two inner shell orbitals, $1s_C$ and $1s_N$, An N lone pair and three C—N banana bonds. We have also used the neutral subgroup scheme where the CN group is represented [6-8] by (a) two inner shell orbitals, the $1s_C$ formed by 1s electrons of the C atom and two nuclear charges, and the $1s_N$ formed with the N 1s electrons and two nuclear charges; (b) an N lone pair, L_N, that contains two electrons and two nuclear charges, (c) three banana bonds, b_{CN}, that include six electrons and six nuclear charges. The CN group is bonded to the rest of the molecule by means of a single bond, b_{C-R}, that contains two electrons and one nuclear charge at the C site and another at the nearest atom of the substituent [6-8]. The contribution of each subgroup and the total contribution to the EFG, electric dipole moment and electric field were calculated with the subroutine PROPERTIES of the IBMOL V program [16]. The components of the EFG tensor were obtained, within the LCAO approximation, from

$$eq_{ii} = \sum_{j,k} P_{jk}\langle\Phi_j|(3i^2 - r^2)/r^5|\Phi_k\rangle + \sum_a [(3i^2 - r^2)/r^5]Z_a,$$

whee $i = x$, y, z, P_{jk} is the jk-th element of the density matrix, r is the distance between the charge under consideration and the center of the N nucleus, and Z_a is the charge of the nucleus "a". Similarly, the components of the dipole moment were obtained from

$$\mu_i = \sum_{j,k} P_{jk}\langle\Phi_j|i|\Phi_k\rangle + \sum_a Z_a i.$$

The calculations were made with the IBM 3083, 3033 and 370/158 computers.

Discussion

We have assumed that the localized orbitals represent a sufficiently realistic basis to describe the essential characteristics of a group as well as the intergroup interactions. In order to obtain these orbitals, we have employed Boys' procedure in its second version [15]. We know that this method leaves small "tails" on atoms of the molecule which do not correspond to the group where the orbital is mostly localized [17, 18]. Other localization procedures [19] give orbitals less prone to produce "tails", but they require more computational time. Following Tomasi and coworkers [7, 8], we have adopted Boys' procedure because it gives, with less computational effort, results similar to those obtained with more sophisticated methods [19].

The presence of "tails" may in Boys' procedure introduce ambiguities in the study of substituent effects so we have calculated the degree of localization of some of the orbitals in the molecules studied in this work. The degree of localization or mean square deviation [6–8] (DL) between an orbital λ_i and its main part $\bar{\lambda}_i$ is $DL = 2(1 - \langle \lambda_i | \bar{\lambda}_i \rangle)$. In this definition, the main part represents the portion of the orbital obtained after neglecting [6–8] the "tails". Because the DL does not change much with the basis set, we report here only the results obtained with the 4-31G set [6–8]. Table 1 shows the results obtained for the CN orbitals in different nitriles. We see that substitution has little effect on the DL of the b_{CN} and L_N orbitals although it noticeably changes the localization of the b_{C-R} orbital. On the other hand, when R is not symmetric, the local symmetry around the b_{CN}s is perturbed. We therefore report in Table 1, the DL for each one of the b_{CN} orbitals. We see that in this case the changes produced by substitution in the DL are relatively small for the banana bonds.

The N lone pair provides the largest contribution to the EFG and for that reason, we have calculated their DL values in the nitriles studied in this work. We have found that the localization of the L_N orbital is about 94% around the N atom with a small "tail" in the C atom of the CN group. We have checked this result by eliminating from the L_N orbital all the contributions arising from the basis orbitals located at R and by recalculating the DL of the L_N. In Table 1, it is seen that with this new definition, the localization has increased, showing the presence

Table 1. Mean square deviation (or degree of localization) (DL) between the orbital λ_i and its main component $\bar{\lambda}_i$ for the localized orbitals of the —CN group. Values within parentheses correspond to the degree of localization of L_N obtained without considering the "tails" located in the substituents

Substituent	DL(b_{CN})	DL(L_N)	DL(b_{CR})
—H	0.0170	0.0591 (0.0030)	0.0061
—F	0.0116	0.0857 (0.0039)	0.0161
—CH_3	0.0107	0.0506 (0.0070)	0.0238
—OH	0.0119 0.0124 0.0187	0.0738 (0.0047)	0.0177
—NH_2	0.0168 0.0130 0.0130	0.0593	0.0175
—NO	0.0110 0.0106 0.0107	0.0690 (0.0037)	0.0406
—CCH	0.0135	0.0401 (0.0458)	0.0048
—COH	0.0105 0.0105 0.0055	0.0584 (0.0045)	0.0378
—CN	0.0119	0.0550 (0.0119)	0.0079
E—IACN	0.0108 0.0108 0.0065	0.0532 (0.0061)	0.0293
Z—IACN	0.0102 0.0102 0.0068	0.0545 (0.0059)	0.0345

of small "tails" of the N lone pair in the neighboring C atom. The fact that the contribution of these "tails" to the DL values remained very small and constant led us to conclude that the N lone pair was well represented by the localized orbital obtained by Boys method [15]. The presence of such "tails" led us to study the DL of the lone pairs located close to the CN group as in R = F, NH_2, OH and NO. In Table 2 the DL and the gross atomic population [6-8], P_{CN}, of the lone pairs of these substituents at the CN group are shown. The P_{CN} for $-NH_2$ is much larger than in the other nitriles, even when the OH has two and the F has three lone pairs. The most delocalized lone pair is that of the NO even though its P_{CN} value is the lowest. A calculation of the population of that orbital in other atoms showed that the L_N orbital of the NO delocalizes towards the O atom whereas the lone pairs in NH_2, OH, and F tend to delocalize toward the CN group in the order $NH_2 \gg F > OH$.

In order to study the changes in the charge distribution produced by substitution [6-8] as a function of the variation of the local dipole moments and the electric fields acting in the localized orbitals, (LOs) [6-8], we have partitioned the total molecular electric dipole moment, μ_z, into orbital components with the aid of the neutral subgroups [6-8]. In particular, the dipole moment of the CN group becomes the sum of the dipole moment of the L_N orbital, $(\mu)L_N$, and of the three b_{CN} orbitals, $(\mu)b_{CN}$. The local dipole moments were calculated taking the C—N direction as the z axis and placing the origin at the N atom. We found that the y and x components were negligible when compared with μ_z so we did not list them here. We also calculated the changes in the z component of the electric field, ΔE_z acting on each localized orbital taking HCN as the reference molecule. We have found (see Fig. 1) an excellent correlation (with $r = 0.972$) between the changes in the local dipole moment, $\Delta(\mu_z)$, and the ΔE_z's for both types of LOs in the charge centroids. The large difference in the slope for the b_{CN} and L_N orbitals shows again [6-8] that the banana bonds are significantly more polarizable than the lone pair in nitriles. In order to study the effect of the "tails" in this correlation, we have calculated $\Delta\mu_z$ by using only the main part of the localized orbitals and have found that the correlation is lowered ($r = 0.946$) and that the points with the larger deviations are those corresponding to OH, NH_2, and F. This result is not surprising because we have found that there are

Table 2. Degree of localization (DL) of each lone pair present in the substituents and its population P_{CN} at the —CN group. The values of $(P_{CN})_{Tot}$ correspond to the total population of lone pairs of the substituents present at the —CN group. Values within parentheses are the DL obtained without considering the "tail" present at the C atom of the —CN group

Substituent	λ_i	DL	P_{CN}	$(P_{CN})_{Tot}$
—F	L_F	0.0155	0.024	0.072
—OH	L_O	0.0270 (0.0131)	0.023	0.046
$-NH_2$	L_N	0.0266 (0.0002)	0.117	0.117
—NO	L_N	0.0657 (0.0342)	−0.035	−0.035

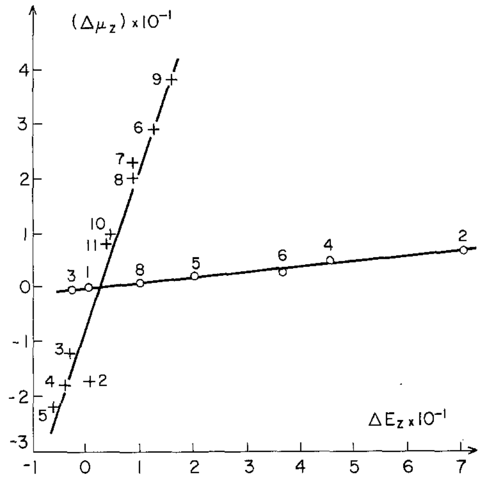

Fig. 1. Variation of the z component of the orbital electric dipole moment $\Delta(\mu_z)$ vs the variation of the z component of the electric field (ΔE_z) for several nitriles. The crosses correspond to the values of the b_{CN} orbitals while the circles to the L_N orbital. The notation is such that —H = 1, —F = 2, —CH_3 = 3, —OH = 4, —NH_2 = 5, —NO = 6, —CCH = 7, —COH = 8, —CN = 9, *E* form of iminoacetonitrile = 10 and *Z* form of iminoacetonitrile = 11, *1*: H; *2*: F; *3*: CH_3; *4*:NH_2; *5*: CCH; *6*: NO.

non-negligible "tails" at the C atom in the CN group and it is known that such "tails" influence correlations involving the dipole moment [8]. When these groups are neglected in the plot, r has the value 0.996 when the "tails" are included and changes to 0.991 when they are not.

The electric field gradient

The EFG is highly sensitive even to minute changes in the charge distribution around the nucleus [4]. The EFG is a second rank tensor which is symmetric and traceless [4]. Its principal axes are chosen so that $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. In general, one determines experimentally [4] the nuclear quadrupole coupling constant, $e^2q_{zz}Q/h$ (NQCC), and the asymmetry parameter of the EFG, $\eta = |(q_{yy} - q_{xx})/q_{zz}|$. Additionally, in single crystals [4], the three Euler angles which relate an external frame of reference to the principal axes of the EFG tensor may be also measured. The value of η reflects the deviation of the EFG tensor from axial symmetry [4]. Table 3 shows the values of eq_{zz} reported by several authors using different basis sets and those obtained in this work. The values of eq_{zz} calculated with the 4-31G and the 4-31G* basis sets showed excellent correlation with those obtained with the Dunning basis set [20] ($r = 0.999$) and with an extended near Hartree-Fock basis set ($r = 0.994$ for the 4-31G* and $r = 0.947$ for the 4-31G set). The above results show that even though the absolute values of eq_{zz} vary slightly with the basis set, the changes produced by substitution are well represented by the sets used in this work. Further support for the above conclusion is obtained from a comparison between measured and calculated values of the NQCC in R = H, F, CH_3, NH_2, CCH and NO where an excellent correlation was also found (see Fig. 2).

For all the nitriles (except for R = NH_2), the principal z axis of the EFG tensor was found to be directed along the C—N bond. The maximum deviation for

Table 3. Calculated *zz* component of the electric field gradient (eq_{zz}) and asymmetry parameter η at the N atom in the —CN group. (Values are in a.u. = $9.717\ 10^{21}$ V/m^2). (a) Values obtained with the 4-31G basis set. (b) Values obtained with the 4-31G* basis set. (c) Bonaccorsi R, Scrocco E, Tomasi J (1969) J Chem Phys 50:2940. (d) Barber M, Hayne SM, Hinchliffe A (1980) J Mol Struct 62:207

—R	$-eq_{zz}$		$-eq_{zz}$		η	
	(a)	(b)	(c)	(d)	(a)	(b)
—H	0.950	(0.998)	1.120	1.195	0.00	
—F	0.539	(0.593)	0.695	0.711	0.00	
—CH_3	0.852	(0.908)	1.009	—	0.00	
—OH	0.613	(0.664)	—	—	0.50	(0.44)
—NH_2	−0.681	(0.720)	—	—	0.91	(0.92)
—NO	0.879	(0.922)	—	—	0.60	(0.55)
—CCH	0.915	(0.950)	—	1.094	0.00	
—COH	0.966	(1.020)	—	—	0.28	(0.29)
—CN	0.948	(1.017)	1.137	1.191	0.00	
E—IACN	0.912	(0.972)	—	—	0.11	(0.10)
Z—IACN	0.929	(0.983)	—	—	0.06	(0.07)

R ≠ NH_2 was found for R = NO (3.3°), while for cyanamide (R = NH_2), a drastic change was found in the *z* axis direction when the 4-31G basis set was employed. However, when the 4-31G* basis set was used, the *z* axis returned to the orientation found in all the other nitriles. The values of eq_{zz} and eq_{yy} are very close in cyanamide so that only a small variation results upon interchange of the *z* and *y* principal axes. The origin of this peculiar behavior may be found in the delocalization of the N lone pair of the —NH_2 towards the —CN group in cyanamide as is seen in Table 2. Such a delocalization increases the charge density at the N atom of the —CN group mainly in a plane that bisects the —HNH

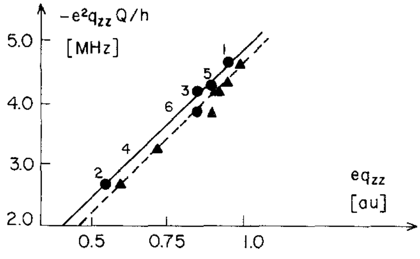

Fig. 2. Experimental values of the nuclear quadrupole coupling constant (e^2qQ/h) vs the calculated values of the *zz* components of the electric field gradient ($eq_{zz} = eq$) at the *N* atom in the —CN group. Circles correspond to values obtained with the 4-31G basis set while the triangles to those obtained with the 4-31G* basis set. The lines were drawn as visual aids. The experimental values of e^2qQ/h were obtained for HCN from Bhattacharya BN, Gordy W (1960) Phys Rev 119:144; for CH_3CN from Witanowsky H, Webb GA (19873). In: Nitrogen NMR, Plenum Press, London for NH_2CN from McDonald JN, Taylor D, Tyler JK, Sheridan J (1968) J Mol Struct 26:285; for ONCN from Dickinson, R Kirby GW, Sweeny JG, Tyler JK (1978) Faraday Trans II, 74:1393, for FCN and HCCN from Tyler JK, Sheridan J (1963) Trans Faraday Soc 59:2661

angle, thus delocation decreases eq_{xx} and increases the value of eq_{yy}, since the charge distribution is now less symmetric around the C—N bond. This is in contrast to the other nitriles where delocalization does not occur. These changes of eq_{yy} and eq_{xx} in cyanamide produce a large increase in η compared with the values found in the other nitriles. Table 3 shows that the η value of cyanamide is the highest for the nitriles studied in this work. The value of η calculated for cyanamide agrees very well with the results obtained in dimethyl- and diethylcyanamide where values of η of about 0.90 were measured [21]. Clearly, the delocalization of the lone pair of the amino N atom produces significant changes in the symmetry of the EFG present at the N atom of the —CN group in cyanamides. The sensitivity of the orientation of the EFG axes found in cyanamide shows that the dimension of the basis set is important in determining the correct orientation of the EFG axes when η is close to one.

The separate contributions of each LO, and of the molecular remainder, to the N eq_{zz} for several nitriles are shown in Table 4. We have found that the molecular remainder contributes from 8-26% of the total value of eq_{zz}. In the TD theory, the eq_{zz} values are considered to arise only from the contribution of the orbitals of the atom containing the quadrupolar nucleus [4]. The above result shows that eq_{zz} also contains a sizeable contribution from the molecular remainder which must be taken into account when making comparisons even between closely related molecules such as the nitriles studied here. It is clear that the contribution of the molecular remainder cannot be neglected *a priori* as is done in the TD theory. Its neglect should be based on an estimate of its relative value. The orbital populations extracted from the TD theory[4] therefore contain a contribution from the molecular remainder, so that interpretations based solely in terms of "through-the-bonds" mechanisms are open to question [4]. From Table 4, it is seen that the values of eq_{zz} are determined by contributions having different signs: one produced by the L_N orbital, which is dominant and constant within ±4% of the average value, and another (about 55% of the L_N orbital contribution) produced

Table 4. Separate orbital contributions to the *zz* components of the electric field gradient (eq_{zz}) at the N atom in the —CN group. Values within parentheses were calculated with a 4-31G* basis set

—R	$(eq_{zz})b_{CN}$	$(eq_{zz})L_N$	$(eq_{zz})_{Rem}$
—H	0.803 (0.765)	−1.827 (−1.835)	0.074 (0.072)
—F	0.949 (0.928)	−1.627 (−1.656)	0.139 (0.135)
$—CH_3$	0.861 (0.815)	−1.804 (−1.816)	0.091 (0.093)
—OH	0.936 (0.927)	−1.675 (−1.706)	0.126 (0.115)
$—NH_2$	−0.041 (0.916)	0.864 (−1.747)	−0.142 (0.111)
—NO	0.750 (0.721)	−1.729 (−1.743)	0.100 (0.100)
—CCH	0.750 (0.721)	−1.789 (−1.806)	0.124 (0.128)
—COH	0.743 (0.705)	−1.797 (−1.811)	0.088 (0.086)
—CN	0.706 (0.658)	−1.779 (−1.795)	0.125 (0.120)
E—IACN	0.798 (0.754)	−1.806 (−1.819)	0.105 (0.090)
Z—IACN	0.785 (0.628)	−1.809 (−1.822)	0.120 (0.207)

by the contributions of the b_{CN} banana orbitals and the molecular remainder. Information about the substituent effects on the EFG may be obtained if we choose a simple nitrile as a reference molecule [6–8, 22]. Figure 3 shows the different orbital contributions of the substituents with respect to the HCN molecule [22]. In this case, for R = CH$_3$; OH, and F, the contributions of L_N and b_{CN} orbitals to the EFG are both of the same sign so that these substituents produce an increase in eq_{zz} with respect to that found in HCN. For R = NO, CCH, COH, CN, *E*- and *Z*-IACN, we have found that these substituents produce orbital contributions to the EFG of opposite signs so that the total values of the eq_{zz}'s are either similar to or lower than those in HCN, depending on the magnitude of the banana bond and the molecular remainder contribution (BMR). These results show that the variation in the sign of the BMR contribution, which depends upon the type of substituents, may explain the rather random behavior of the N NQCC found in nitriles [3, 4]. As mentioned above, the total EFG for each substituent reflects the addition or substraction of the BMR contribution to or from that of the lone pair orbital. Through this mechanism, the effects of substitution are reflected in the N EFG and quite different values of the coupling constant may be obtained depending on the type of BMR contribution produced by the substituent under consideration.

The changes in the charge distribution around the N nucleus upon substitution are also reflected in the position of the charge centroids of the different orbitals and in μ_z. We have found that $\Delta(\mu_z)L_N = -0.323\ \Delta(eq_{zz})L_N + 0.002$, $(r = 0.949)$

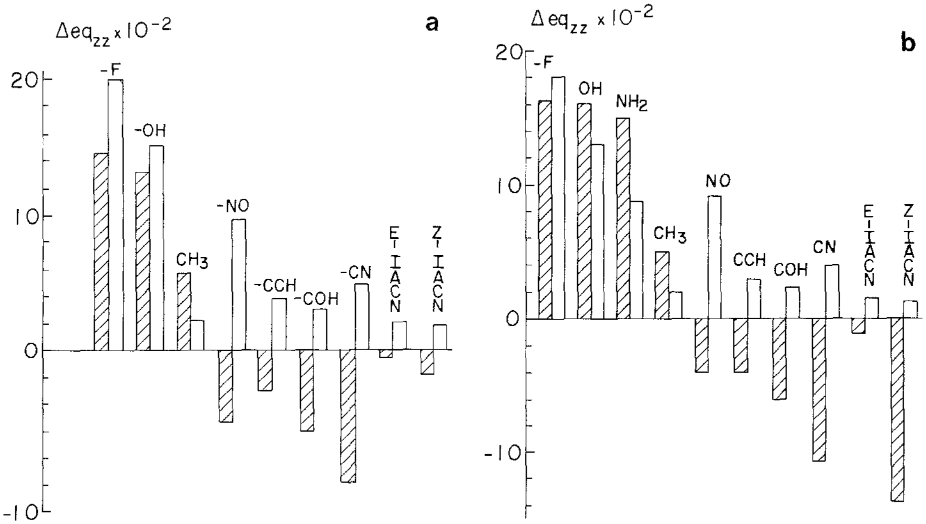

Fig. 3a,b. Changes in the orbital contributions to the *zz* components of the electric field gradient (eq_{zz}) of several nitriles with respect to HCN. The *shadowed bars* correspond to the contribution of the b_{CN} orbitals while the empty bars represent the contribution of the L_N orbital to eq_{zz}. **a** Results obtained with the 4-31G basis set; **b** Results obtained with the 4-31G* basis set. In **a**, the results corresponding to NH$_2$CN are omitted because the anomalous orientation of the principal axes of the field gradient (see text) found with the 4-31G basis set for that nitrile

Table 5. Orbital contributions to the *yy* components of the electric field gradient (eq_{yy}) at the N atom in the —CN group. Values within parentheses were calculated with a 4-31G* basis set

—R	$(eq_{yy})b_{CN}$	$(eq_{yy})L_N$	$(eq_{yy})_{Rem}$
—OH	−0.321 (−0.323)	0.837 (0.853)	−0.055 (−0.053)
$—NH_2$	0.949 (−0.145)	−1.727 (0.876)	0.122 (−0.039)
—NO	−0.110 (−0.103)	0.866 (0.873)	−0.055 (−0.056)
—COH	−0.231 (−0.201)	0.899 (0.906)	−0.050 (−0.047)
E—IACN	−0.339 (−0.317)	0.903 (0.910)	−0.059 (−0.057)
Z—IACN	−0.356 (−0.327)	0.905 (0.911)	−0.058 (−0.056)

Table 6. Orbital contributions to the *xx* components of the electric field gradient (eq_{xx}) at the N atom in the —CN group. Values within parentheses were calculated with a 4-31G* basis set

—R	$(eq_{xx})b_{CN}$	$(eq_{xx})L_N$	$(eq_{xx})_{Rem}$
—OH	−0.615 (−0.605)	0.837 (0.853)	−0.068 (−0.063)
$—NH_2$	−0.807 (−0.771)	0.863 (0.871)	0.079 (−0.072)
—NO	−0.640 (−0.619)	0.863 (0.870)	−0.043 (−0.047)
—COH	−0.511 (−0.505)	0.898 (0.905)	−0.037 (−0.037)
E—IACN	−0.459 (−0.437)	0.903 (0.910)	−0.037 (−0.037)
Z—IACN	−0.431 (−0.419)	0.905 (0.911)	−0.036 (−0.037)

and that $\Delta(\mu_z)b_{CN} = 2.282\,\Delta(eq_{zz})b_{CN} - 0.102$, $(r = 0.960)$. We see, from these equations, that the variation in eq_{zz} is mainly determined by the charge rearrangement produced in the banana bonds, with only a small contribution of opposite sign arising from the N lone pair.

The rather small changes found in the contribution of L_N orbital to the EFG, gives support to the assumption that its population may be taken as constant in the TD analysis of the experimental data [4]. Similar assumptions regarding the C—N bond population are clearly not valid unless symmetry reasons prevent certain orbital interactions, as in benzonitriles [3]. In addition, the large and almost constant contribution of the L_N orbital to the EFG, may explain the relative constancy of the N EFG in such different compounds as potassium ferricyanide [23] and HCN [4]. Clearly, as long as the L_N orbital is not involved directly in bonding, the value of the N EFG is only slightly perturbed by the substituents.

Tables 5 and 6 show the separate contributions from each localized orbital to eq_{yy} and eq_{xx} respectively. For R = H, F, CH_3, CN and CCH, we have that $eq_{xx} = eq_{yy} = (eq_{zz})/2$ and $\eta = 0$, as expected from the symmetry of the molecules[4]. We may explain the finite values of η found in asymmetric nitriles as a consequence of the interactions between the substituents and some of the banana bonds [1, 4]. The value of the asymmetry parameter reflects: (a) the inequivalence of the conjugation between different C—N banana bonds and neighboring orbitals

[1, 4], (b) any unequal polarization of the banana bonds caused by the lack of molecular symmetry and (c) an asymmetry in the contribution to the *xx* and *yy* components arising only from the molecular remainder. From Tables 5 and 6, it is seen that the contributions from the molecular remainder to eq_{yy} and eq_{xx} are both of the same sign and of approximately the same order of magnitude; thus, these contributions to η almost cancel each other. This means that the separate contribution of the molecular remainder to the asymmetry parameter is small or negligible in most nitriles, whereas for eq_{zz} it may become important depending on the values taken by the orbital contributions. Consequently, in the solid state, where distances between neighboring molecules are similar to most of the intergroup distances within a molecule, the effect of the direct crystal field contribution could be more important in the coupling constant than in the asymmetry parameter value.

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