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Generalizing the Breakdown of the Maximum Hardness and Minimum Polarizabilities Principles for Nontotally Symmetric Vibrations to Non-π-Conjugated Organic Molecules

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In previous works we have shown that certain π-conjugated organic molecules possess nontotally symmetric vibrations that break the maximum hardness (MHP) and minimum polarizability principles (MPP). We have also derived a set of simple rules to determine a priori without calculations whether a particular π-conjugated organic molecule violates these two principles. In the present work, we generalize these results, and we show that not only π-conjugated organic molecules but also other molecules without π-conjugated structure or even π-bonds can exhibit nontotally symmetric molecular distortions that do not follow these two principles. We have also found that the breakdowns of the MHP and the MPP are not necessarily connected, since the polarizability is not always proportional to the softness. Finally, we also introduced a methodology based on the diagonalization of the hardness Hessian matrix with respect to the vibrational normal coordinates to determine the nontotally symmetric molecular displacements that do not follow the MHP.

I. Introduction

During the past 15 years, the use of density functional theory (DFT)[1−6] has been gradually increased for the prediction of molecular properties and for the study of chemical reactivity in many areas of chemistry, especially in the field of organometallic and bioinorganic chemistry.[7] DFT methods incorporating gradient corrected (nonlocal) exchange and correlation functionals provide results that have accuracy comparable to and frequently even higher than results from ab initio correlated calculations, while using less computer time. In this sense, the computational side of the DFT must be considered as a story of a great success with only few documented exceptions.[8]

It is also well recognized that, apart from computational advantages, there is a very important conceptual side to DFT.[9] In this branch of the theory, the central quantities are the response functions. These functions are the response of the chemical system to perturbations in its number of electrons, N, and/or the external potential, $\nu(\vec{r})$, which is the potential acting on an electron at $\vec{r}$ due to the nuclear attraction plus such other external forces as may be present. Assuming differentiability of the electronic energy, E, with respect to N and $\nu(\vec{r})$, a series of response functions emerge, probably the most important being the electronic chemical potential, μ, and the hardness, η, defined as[1,9−13]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(\vec{r})} \tag{1}$$

and

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\vec{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{\nu(\vec{r})} \tag{2}$$

A three-points finite difference approximation leads to the following working definitions of these quantities:

$$\mu = -\frac{1}{2}(I + A) \tag{3}$$

and

$$\eta = I - A \tag{4}$$

where I and A are the first vertical ionization potential and electron affinity of the neutral molecule, respectively. Most response functions have been identified with quantities that correspond (or at least are related) to common chemical concepts. Thus, for instance, the negative of the electronic chemical potential in eq 3 is the electronegativity definition of Mulliken,[14] while the derivative in eq 2, which is a measure of the resistance of a chemical species to change its electronic configuration, turns out to be the chemical hardness.[10] Associated with this latter property there are two important chemical reactivity principles that have been rationalized within the framework of conceptual DFT: the hard and soft acids and bases principle (HSAB)[10,12] and the maximum hardness principle (MHP).[10,15−17] First proposed by Pearson,[10,15] the MHP states that, at a given temperature and external potential, molecular systems tend to a state of maximum hardness. On the basis of the MHP and the empirical inverse relationship between hardness and polarizability (α),[18,19] Chattaraj and Sengupta[20] have recently introduced the minimum polarizability principle (MPP). This principle states that any system evolves naturally toward a state of minimum polarizability. These two principles, the MHP and the MPP, have been applied to a number of different chemical processes with several successes[10,21−41] but also some reported failures.[28,33,36,40]

A formal proof of the MHP based on statistical mechanics and the fluctuation−dissipation theorem was given by Parr and Chattaraj[16] under the constraints that the chemical and the external potentials must remain constant upon distortion of molecular structure. There is no single chemical process that

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satisfies these two severe constraints. However, relaxation of these constraints has been found to be permissible in some internal rotations, vibrations, or chemical reactions.[10,21−41] Henceforth, we will refer to the generalized MHP (GMHP) or MPP (GMPP) as the maximum hardness or minimum polarizability principles that do not require the chemical and external potentials to stay constant during a molecular change. Recently, an alternative and simpler proof of the MHP has been given by Ayers and Parr.[42]

A consequence of the GMHP/GMPP turns out to be that the hardness/polarizability should be maximal/minimal at the equilibrium geometry for a distortion along a given nontotally symmetric vibrational mode. This kind of distortion is especially interesting because positive and negative deviations from the equilibrium structure along nontotally symmetric vibrational modes yield molecular configurations that have the same η, μ, α, and average potential of the nuclei acting on the electrons (ν_{en}).[22] Then, if Q represents a nontotally symmetric normal mode coordinate, it follows that $(\delta\mu/\delta Q) = 0$, $(\delta\eta/\delta Q) = 0$, $(\delta\alpha/\delta Q) = 0$, and $(\delta\nu_{en}/\delta Q) = 0$ at the equilibrium geometry. Hence, for small distortions along nontotally symmetric normal modes, μ and ν_{en}[43] are roughly constant, thus approximately following the two conditions of Parr and Chattaraj.[16]

Despite nontotally symmetric distortions being the most favorable case for the fulfillment of the MHP and MPP, we recently found that several π-conjugated organic molecules having bond length alternation (BLA) nontotally symmetric vibrational modes break these two principles, irrespective of the method of calculation used.[44,45] We established a set of simple rules to predict a priori, without calculations, the existence of vibrational modes for a given molecule that break these principles.[45] Briefly, we showed that systems that disobey the GMPP must be π-conjugated molecules having nontotally symmetric BLA vibrational modes.[45] Finally, we show that exceptions to the GMHP in some nitrogen heterocycles are caused by pseudo-Jahn−Teller coupling between the ground and the excited state along the nontotally symmetric modes that break the principle.[46]

The main goal of the present work is to show the existence of non-π-conjugated molecules exhibiting nontotally symmetric vibrations that disobey the GMHP and GMPP. One may consider the BLA vibrational mode in benzene that distorts the molecule from D_{6h} to D_{3h} symmetry. Because of the partial localization of the π-electrons in the latter system, one could envisage a decrease of the polarizability and an increase of the hardness along this distortion, as we illustrated computationally.[45] However, less expected is the generalization of this breakdown to non-π-conjugated or even non-π-bonded organic and inorganic molecules, as we will show in this paper. The result obtained is quite relevant since it is important to find out the conditions at which the GMHP and GMPP hold.

II. Computational Details

All geometry optimizations and hardness, polarizability, and frequency calculations have been carried out with the GAUSSIAN 98 package[47] at the Hartree−Fock (HF)[48] levels using the cc-pVTZ basis set,[49] except for the cyclohexane in its chair conformation, for which the Pople's 6-31+G* basis set[50] has been used. To analyze the effect of electron correlation, B3LYP/cc-pVTZ calculations[51] have been carried out for three selected systems.

Koopmans' theorem ($I \approx -\epsilon_H$ and $A \approx -\epsilon_L$)[52] allows one to write μ and η in terms of the energy of frontier HOMO (ϵ_H) and LUMO (ϵ_L) molecular orbitals of the reference species.[10] For closed shell species one obtains

$$\mu = \frac{1}{2}(\epsilon_L + \epsilon_H) \tag{5}$$

and

$$\eta = \epsilon_L - \epsilon_H \tag{6}$$

It is worth noting that because of the particular definition of μ and η given by eqs 1 and 2, all operational equations that provide μ and η values, and in particular, eqs 3−6 are approximate.[53] Finally, the isotropic average static polarizabilities have been obtained through eq 7:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{7}$$

To search for the nuclear displacements exhibiting a marked fulfillment or breakdown of the GMPP and GMHP, we have diagonalized the second derivative matrix of the polarizability (α'') and the hardness (η'') with respect to the nontotally symmetric normal coordinates. The components of these Hessian matrices are

$$\alpha_{kl}'' = \left(\frac{\partial^2\alpha}{\partial Q_k\,\partial Q_l}\right) \quad \text{and} \quad \eta_{kl}'' = \left(\frac{\partial^2\eta}{\partial Q_k\,\partial Q_l}\right) \tag{8}$$

with k and l running over the nontotally symmetric vibrational modes. The α_{kl} elements have been obtained by the first numerical differentiation of the analytical first derivatives of the polarizability with respect to the normal coordinates, α'.[45] η'' has to be calculated by numerical second differentiation of the hardness with respect to the normal coordinates. The hardness has been evaluated using Koopmans' approximation (eq 6). The magnitude of the displacement used for the numerical derivatives with respect to vibrational coordinates was 0.04 au. The stability of these derivatives was checked by repeating the calculation with displacements of 0.02 and 0.08 au. The validity of the eigenvalues sign obtained after diagonalization of the α'' and η'' Hessian matrices for those distortions that disobey the GMPP or the GMHP was verified by doing single-point isotropic polarizability and hardness calculations along postdiagonalization nuclear distortions.

In a previous work,[45] we already carried out calculations of α'' to establish the nuclear displacements that have a more marked GMPP or anti-GMPP character. Here, we compute η'' for the first time to determine the nontotally symmetric distortions that produce the largest hardness changes, which correspond to molecular distortions that have a more clear GMHP or anti-GMHP character than the original vibrational modes.

III. Results and Discussion

The whole set of molecules studied in this work are gathered in Figure 1. Because of their interest, we will concentrate our discussion in three selected systems: the hydrogen fluoride tetramer ($(HF)_4$), diborane (B_2H_6), and the anionic aluminum tetramer (Al_4^{2-}) that will be thoroughly analyzed in sections A−C. Other molecules considered in our study will be discussed in section D.

Table 1 collects the diagonal terms and eigenvalues of the polarizabilility (α'') and hardness (η'') Hessian matrices with respect to the nontotally symmetric modes, corresponding to

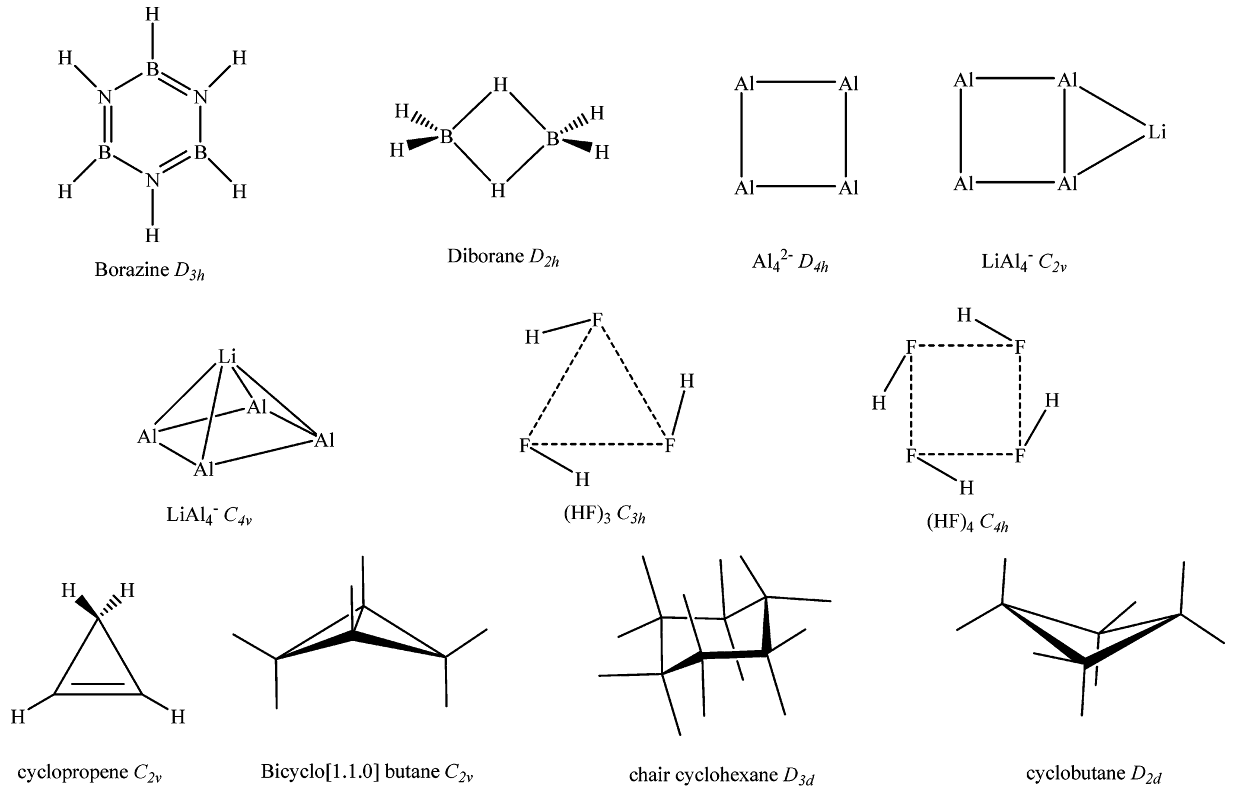

Figure 1. A schematic representation of the molecules studied in this work.

TABLE 1: HF/cc-pVTZ and B3LYP/cc-pVTZ Diagonal Terms and Eigenvalues of the Hessian Matrices of the Polarizabilility (α'') and Hardness (η'') with Respect to the Nontotally Symmetric Modes, Which Break the GMPP or GMHP for the Hydrogen Fluoride Tetramer, Diborane, and Al_4^{2-} (All Values Are Given in au)

molecules	level		diagonal α''	eigenvalues α''		diagonal η''	eigenvalues η''
tetramer HF (C_{4h})	HF	E_u	-2.2×10^{-3}	-7.8×10^{-3}	B_g	3.9×10^{-4}	4.4×10^{-4}
		B_g	-6.6×10^{-3}	-7.4×10^{-3}			
	B3LYP	E_u	-5.1×10^{-3}	-3.5×10^{-2}			
		B_g	-7.4×10^{-3}	-3.8×10^{-2}			
diborane (D_{2h})	HF	B_{3u}	-4.8×10^{-2}	-4.9×10^{-2}	B_{2u}		9.8×10^{-3}
		B_{2g}		-3.0×10^{-1}	B_{3g}	1.0×10^{-2}	1.0×10^{-2}
					B_{1u}	6.1×10^{-3}	1.3×10^{-2}
	B3LYP	B_{2g}		-1.2×10^{-1}	B_{2u}	3.9×10^{-3}	1.7×10^{-2}
					B_{3g}	1.9×10^{-2}	1.9×10^{-2}
					B_{1u}	6.3×10^{-3}	1.1×10^{-2}
Al_4^{2-} (D_{4h})	HF[b]	E_u	-4.7×10^{-1}	-4.7×10^{-1}	B_{1g}	2.8×10^{-5}	2.8×10^{-5}
					B_{2g}	3.2×10^{-4}	3.2×10^{-4}
					E_u	8.9×10^{-4}	8.9×10^{-4}
	B3LYP[a,b]	E_u	-5.2×10^{-3}	-5.2×10^{-3}	E_u	8.9×10^{-5}	8.9×10^{-5}

[a] The molecule in the equilibrium geometry presents degenerated HOMO orbital; therefore, the calculated hardness uses the average HOMO energies. [b] The molecule in the equilibrium geometry presents degenerated LUMO orbital; therefore, the calculated hardness uses the average LUMO energies.

the nuclear displacements that before or/and after diagonalization disobey the GMPP or GMHP for the hydrogen fluoride tetramer, diborane, and Al_4^{2-} evaluated at the HF and B3LYP levels. A schematic representation of selected vibrational normal coordinates, the so-called prediagonalization displacement vectors and postdiagonalization nuclear distortions (eigenvectors), which break the GMPP or/and GMHP at the HF level, are given in Figures 2 and 3. In particular, Figure 2 depicts the nuclear distortions having negative diagonal terms or negative eigenvalues of α'' for the hydrogen fluoride tetramer and trimer, diborane, borazine, and Al_4^{2-} species, while Figure 3 shows the nontotally symmetric distortions having positive diagonal terms or positive eigenvalues of η'' for the hydrogen fluoride tetramer, diborane, and cyclopropene species.

A. The Hydrogen Fluoride Tetramer. With respect to the hydrogen fluoride tetramer of C_{4h} symmetry, we have found at both the HF and B3LYP levels two vibrational modes with E_u and B_g symmetry (shown in Figure 2) that have negative diagonal terms of α and, therefore, that disobey the GMPP. Makov[24] demonstrated from symmetry considerations that molecular properties such as the hardness or the polarizability at the equilibrium geometry are an extremum, which could be either a minimum or a maximum, with respect to distortions along nontotally symmetric normal coordinates. Therefore, the positive/negative sign of the diagonal terms of matrix α'' tell us whether a certain nontotally symmetric vibrational mode has GMPP/anti-GMPP character. The eigenvectors obtained from diagonalization of the polarizability Hessian matrix give the linear combinations of nontotally symmetric vibrational modes (for a given eigenvector all implicated vibrational modes belong to the same symmetry species) that produce the largest polarizability changes. If an eigenvector has a negative eigenvalue,

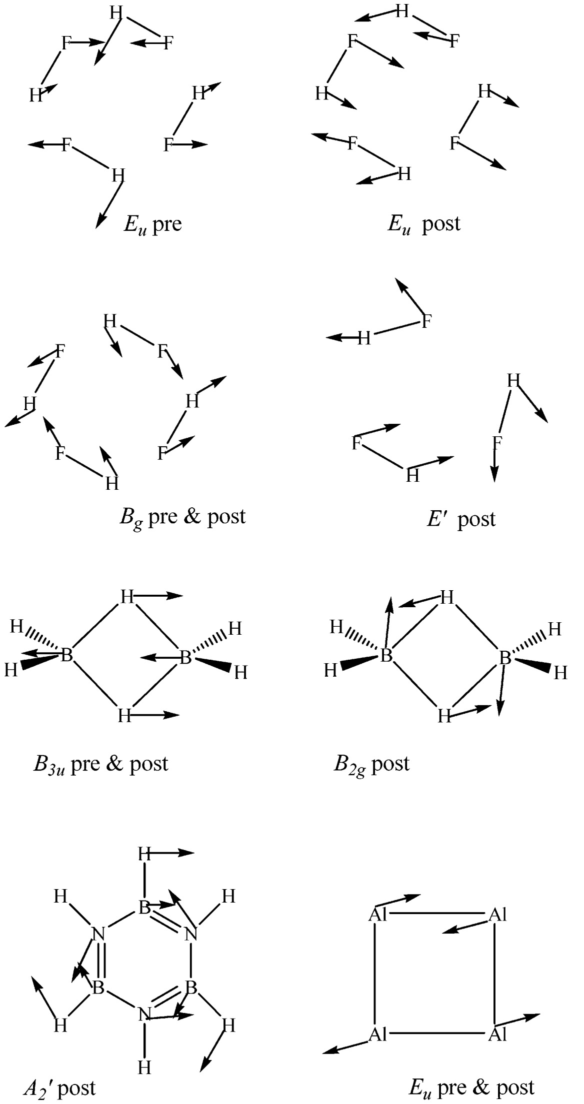

Figure 2. Schematic representation of the selected displacement vectors corresponding to the pre- and postdiagonalization nuclear distortions that break the MPP at the HF/cc-pVTZ level. In diborane, the depicted displacement vectors of the boron atoms are 10 times bigger than those of the hydrogen atoms.

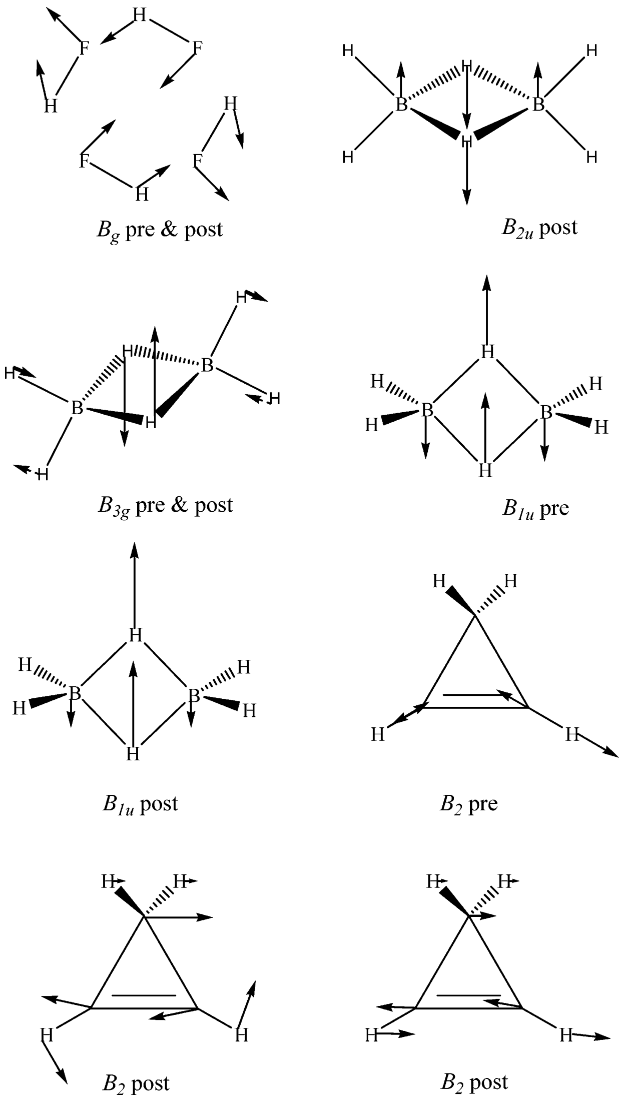

Figure 3. Schematic representation of the selected displacement vectors corresponding to the pre- and postdiagonalization nuclear distortions that break the MHP at the HF/cc-pVTZ level. In diborane and cyclopropene, the depicted displacement vectors of the boron and the carbon atoms are 5 and 10, respectively, times bigger than those of the hydrogen atoms.

the equilibrium structure will represent a maximum of polarizability along this distortion, which consequently does not fulfill the GMPP. Likewise, a positive/negative sign of the diagonal terms of matrix η'' tells us whether a certain nontotally symmetric vibrational mode has anti-GMHP/GMHP character. A positive eigenvalue in the diagonalization of η'' implies a breakdown of the GMHP along this distortion.

Diagonalization of the matrix α'' for the hydrogen fluoride tetramer does not lead to further distortions disobeying the GMPP, and only small changes can be appreciated comparing the E_u and B_g pre- and postdiagonalization nuclear distortions. Interestingly, the B_g mode that breaks the GMPP has a kind of BLA distortion that resembles that of π-conjugated molecules studied in our previous work.[45] However, the degenerate E_u mode does not possess this BLA movement.

At the HF level, calculation of η'' for the hydrogen fluoride tetramer shows that this molecule has a vibrational mode of B_g symmetry that disobeys the GMHP (see Figure 3). Diagonalization of η'' does not lead to significant changes. On the contrary, at the B3LYP level all the nontotally symmetric modes before and after the diagonalization of the hardness Hessian follow the GMHP. The difference between the HF and B3LYP results is due to a change in the order of the HOMO and HOMO-1 orbitals when going form HF to B3LYP. The HOMO at the HF level becomes the HOMO-1 with the B3LYP method, and vice versa. Interestingly, this molecule has more anti-GMPP than anti-MHP modes, thus being an exception to the usual finding that the GMPP is more restrictive than the GMHP.[45]

As mentioned above, the MPP was established from an empirical linear relationship between the polarizability[18] (or its cubic root)[19] and the softness (S), which is the inverse of the hardness. Given this direct relation between the MPP and MHP, one may wonder why the modes that break the GMPP and GMHP in the hydrogen fluoride tetramer do not coincide. In fact, Doerksen and Thakkar[41] already showed that the polarizability does not correlate well with the hardness evaluated using the eq 6 for 70 azaboracycles. To get some insight into the origin of the discrepancy, we have started our analysis from the exact expression of the isotropic static electronic polarizability derived from perturbation theory:[54]

$$\alpha = \frac{1}{3\hbar}\sum_{n\neq 0}\left[\frac{|\langle\psi_0|\hat{\mu}|\psi_n\rangle|^2}{\omega_n}\right] \tag{9}$$

In this equation, ψ_0 and ψ_n are the wave functions of the ground and nth excited states, respectively, and $\omega_n = (E_n - E_0)/\hbar$, where E_0 and E_n are the energy of the ground and nth excited states. Considering now that the only nonnegligible excited state in eq 9 corresponds to the HOMO to LUMO excitation, and making the assumption that the energy difference between the ground and this excited state equals the HOMO−LUMO gap, one finds that the static electronic polarizability is proportional to the softness, i.e.

$$\alpha \propto S = \frac{1}{\epsilon_L - \epsilon_H} \tag{10}$$

Since we have used eq 6 for the calculation of the hardness, if eq 10 were correct, then we should find the same anti-GMPP and anti-GMHP modes. However, for the hydrogen fluoride tetramer (and also for other systems analyzed in a previous work)[45] this is not the case, and therefore, at least for this example, the proportionality between the polarizability and the softness given by eq 10 does not hold. Less crude approximations are given by the following proportionality relationships:[55]

$$\alpha \propto \sum_{i=H-1}^{H}\sum_{j=L}^{L+1}\frac{1}{\epsilon_j - \epsilon_i} \tag{11}$$

and

$$\alpha \propto \sum_{i=1}^{H}\sum_{j=L}^{N}\frac{1}{\epsilon_j - \epsilon_i}. \tag{12}$$

In eq 11, one makes the hypothesis that all excited states that do not include HOMO-1 and HOMO to LUMO and LUMO+1 orbitals excitations can be neglected and that the $|\langle\psi_0|\hat{\mu}|\psi_n\rangle|^2$ term is identical for all selected excitations. The latter assumption is the only approximation considered in eq 12.

These considerations have been quantified in Table 2, which lists the changes in the exact static isotropic electronic polarizability, softness, and the approximations to the polarizability given by eqs 11 and 12 for ±0.04 au distortions along the normal vibrational modes that break the GMHP and GMPP in hydrogen fluoride tetramer and diborane. The positive/negative sign of the change in the exact static isotropic electronic polarizability indicates the GMPP/anti-GMPP character of the vibrations. The results show that neither the softness nor the approximation of eq 11 yields the correct sign to detect the GMPP/anti-GMPP character of the nontotally symmetric vibrations analyzed. The sign provided by the softness is always wrong, as expected from the fact that the anti-GMPP and anti-GMHP vibrational modes do not coincide for this molecule. However, eq 12 provides the correct signs for the hydrogen fluoride tetramer. These results cast serious doubts about the general validity of assuming the proportionality between polarizability and softness, which is the main assumption made in the formulation of the MPP.

B. Diborane. At the HF level, diborane with D_{2h} symmetry possesses a B_{3u} nontotally symmetric vibrational mode (Figure 2) that disobeys the GMPP. Besides, at both HF and B3LYP levels, diagonalization of the polarizability Hessian matrix leads to a B_{2g} nontotally symmetric distortion (Figure 2), as a result of a combination of vibrational modes with the same symmetry, which has a more marked anti-GMPP character than the previous nontotally symmetric distortion. This B_{2g} nuclear displacement has BLA character within the four bonds (or more precisely, two 3c−2e bonds) connecting the boron and the bridge hydrogen atoms in the molecule.

As far as the fulfillment of the GMHP is concerned, at the HF level diborane has two vibrational modes of B_{3g} and B_{1u} symmetry that do not comply with this principle (see Figure 3). At B3LYP level the same is true for the two modes with B_{3g} and B_{1u} symmetry and for a new mode with B_{2u} symmetry. After diagonalization of the hardness Hessian matrix both levels of calculation lead to three vibrational distortions with B_{3g}, B_{1u}, and B_{2u} symmetries that break the GMHP. Figures 2 and 3 contain the selected displacement vectors corresponding to the pre- and postdiagonalization nuclear distortions that break the MPP and MHP, respectively, at the HF level. The results obtained at the B3LYP level are very similar.

As found above for the hydrogen fluoride tetramer, the anti-GMPP and the anti-GMHP vibrations are also inconsistent in diborane. Here again, it is found that the sign of the change in the exact static isotropic electronic polarizability along a normal vibrational coordinate, which indicates the GMPP/anti-GMPP character of the vibrations, does not match with the sign of the change in softness for any of the vibrational modes having anti-GMPP or anti-GMHP character (see Table 2). The sign of the change in the quantities derived from eqs 11 and 12 agrees with the sign for two out of the three vibrational modes analyzed.

C. The Anionic Aluminum Tetramer. Since its discovery in 2001,[56] the D_{4h} molecule $(Al)_4^{2-}$ has become the prototypical inorganic aromatic system.[57] At both HF and B3LYP levels a unique vibrational mode with E_u symmetry (see Figure 2) breaks the GMPP. This mode, which does not possess the typical shape of a BLA displacement, is equivalent to the one found for triplet cyclobutadiene with D_{4h} symmetry in our previous study.[45,58] On the other hand, whereas at the HF level this molecule has, both before and after diagonalization, three nontotally symmetric vibrational modes that disobey the GMHP of B_{1g}, B_{2g}, and E_u symmetry, only this latter mode breaks the GMHP at the B3LYP level. As for the hydrogen fluoride tetramer, the difference between the HF and B3LYP results is due to a change in the orbital frontier orbitals. While at the HF level only the LUMO is degenerated, at the B3LYP level both the HOMO and LUMO orbitals are degenerated.

For this molecule at the HF level, the LUMO has E_u symmetry, and therefore it is degenerated. This makes the calculation of the hardness a little bit more difficult. Positive and negative deviations from the equilibrium structure along nontotally symmetric vibrational modes destroy the degeneracy by stabilizing the initial $1e_u$ or $2e_u$ orbital depending on the sign of the distortion. Therefore, the use of just the LUMO energy for positive and negative displacements results in an erroneous value for the hardness because the nature of the LUMO orbital changes for the two different displacements. Moreover, when the normal mode is degenerate, for the same positive and negative displacement a different value of the hardness is obtained; therefore, the first derivative is not zero (as it should be). We devised two possibilities for correctly calculating the hardness in this case. First, it is possible to obtain the hardness following always the same orbital (either $1e_u$ or $2e_u$), despite the fact that for a given sign of the displacement the orbital is not the LUMO but the LUMO + 1. Then one has to perform the average of the two hardness derivatives obtained following each orbital. Second, one can use the average of the

TABLE 2: HF/cc-pVTZ Changes in Static Isotropic Average Polarizabilities, Softness, and Two Crude Approximations of the Polarizabilility for the Molecular Distortions along the Normal Vibrational Modes that Break the GMHP and GMPP of the Hydrogen Fluoride Tetramer and Diborane (All Increments Are Given in au Relative to the Equilibrium Structure)

molecules		α	$1/(\epsilon_L - \epsilon_H)$	$\sum_{i=H-1}^{H}\sum_{j=L}^{L+1} 1/(\epsilon_j - \epsilon_i)$	$\sum_{i=1}^{H}\sum_{j=L}^{N} 1/(\epsilon_j - \epsilon_i)$
$(HF)_4$	B_g ± 0.04	5.3×10^{-6}	-5.0×10^{-7}	1.8×10^{-4}	1.3×10^{-4}
	E_u ± 0.04	-7.3×10^{-6}	1.6×10^{-5}	7.1×10^{-5}	-2.8×10^{-5}
	B_g ± 0.04	-2.1×10^{-5}	5.4×10^{-6}	7.3×10^{-4}	-1.6×10^{-4}
diborane	B_{3g} ± 0.04	2.6×10^{-3}	-2.5×10^{-5}	4.6×10^{-5}	5.0×10^{-3}
	B_{3u} ± 0.04	-1.6×10^{-4}	2.5×10^{-4}	1.0×10^{-3}	1.1×10^{-3}
	B_{1u} ± 0.04	2.8×10^{-3}	-1.5×10^{-5}	1.1×10^{-3}	1.1×10^{-3}

TABLE 3: HF/cc-pVTZ Diagonal Terms and Eigenvalues of the Hessian Matrices of the Polarizabilility (α″) and Hardness (*η*″) with Respect to the Nontotally Symmetric Modes, Which Break the GMPP or GMHP for the Hydrogen Fluoride Trimer, Borazine, and $LiAl_4^-$ Species (All Values Are Given in au)

molecules		diagonal α″	eigenvalues α″		diagonal *η*″	eigenvalues *η*″
trimer HF (C_{3h})[a]	E′		-4.3×10^{-3}			
borazine (D_{3h})[a,b]	A_2′		-7.3×10^{-2}	A_2′	1.4×10^{-3}	1.9×10^{-3}
					1.8×10^{-2}	2.0×10^{-2}
				E′		2.3×10^{-3}
					2.2×10^{-3}	2.5×10^{-3}
					5.9×10^{-3}	6.1×10^{-3}
$LiAl_4^-$ (C_{2v})	B_2	-4.8×10^{-1}	-6.4×10^{-1}	B_2	1.4×10^{-4}	5.4×10^{-5}
					5.1×10^{-4}	7.3×10^{-4}
$LiAl_4^-$ (C_{4v})	E	-5.7×10^{-2}	-4.6×10^{-2}	E	6.0×10^{-5}	1.1×10^{-2}
		-4.7×10^{-1}	-4.8×10^{-1}	B_2		4.5×10^{-6}

[a] The molecule in the equilibrium geometry presents degenerated HOMO orbital; therefore, the calculated hardness uses the average HOMO energies. [b] The molecule in the equilibrium geometry presents degenerated LUMO orbital; therefore, the calculated hardness uses the average LUMO energies.

TABLE 4: HF/cc-pVTZ Diagonal Terms and Eigenvalues of the Hardness Hessian Matrix (*η*″) with Respect to the Nontotally Symmetric Modes, Which Break the GMHP (All Values Are Given in au)

molecules		diagonal *η*″	eigenvalues *η*″
cyclopropene (C_{2v})	B_2	9.2×10^{-3}	4.2×10^{-3}
			1.0×10^{-2}
bicyclo[1.1.0]butane (C_{2v})	B_1		2.9×10^{-3}
	A_2		1.6×10^{-3}
	B_2		2.4×10^{-3}
cyclobutane (D_{2d})[a]	B_2		1.6×10^{-3}
	E		5.0×10^{-3}
chair cyclohexane (D_{3d})[a,b]	E_g		1.3×10^{-3}
			4.2×10^{-3}
			7.4×10^{-3}
	E_u	1.6×10^{-3}	8.2×10^{-3}
			3.4×10^{-3}
	A_{1u}		1.3×10^{-3}
	A_{2g}		4.5×10^{-3}

[a] The molecule in the equilibrium geometry presents degenerated HOMO orbital; therefore, the calculated hardness uses the average HOMO energies. [b] HF/6-31+G*.

LUMO and LUMO + 1 energies to obtain more realistic “LUMO” energy. Even though we have used this latter technique, we have checked that both approaches lead to the same result. At the B3LYP level, as both HOMO and LUMO orbitals are degenerated, the calculated hardness uses the average of HOMO and the average of LUMO energies.

D. Other Interesting Molecules. In this section we will briefly discuss the results obtained at the HF level for the hydrogen fluoride trimer, borazine, and two different geometries of the $Li(Al)_4^-$ complex. Finally, we will analyze the fulfillment of the GMHP for cyclopropene, bicyclo[1.1.0]butane, cyclobutane, and cyclohexane in its chair conformation.

As can be seen in Table 3, the hydrogen fluoride trimer does not possess vibrational modes that violate either the GMPP or the GMHP. Only after diagonalization it appears a molecular distortion of E′ symmetry, depicted in Figure 2, that disobeys the GMPP, showing the utility of the diagonalization of α″ to detect molecular distortions that break the GMPP. Borazine possesses pre- and postdiagonalization distortions that break the GMHP and only one postdiagonalization molecular displacement that disobeys the GMPP. Last, for two different isomers of the $Li(Al)_4^-$ complex with C_{2v} and C_{4v} symmetry, we have found pre- and postdiagonalization distortions that break both principles.

Although they are not *π*-conjugated organic species, all systems analyzed so far possess a certain degree of cyclic electron delocalization, even in the case of hydrogen-bonded species such as the hydrogen fluoride trimer and tetramer. Table 4 gathers the results obtained for a series of molecules having basically localized *σ* and *π* bonds. All nontotally symmetric pre- and postdiagonalization distortions in these molecules follow the GMPP. For this reason, we shall concentrate our discussion in this latter group of molecules exclusively in the analysis of the GMHP. In the bicyclo[1.1.0]butane and cyclobutane, diagonalization of the hardness Hessian matrix is necessary to find molecular distortions that do not follow the GMHP, thus displaying the usefulness of the diagonalization of *η*″ to discover this kind of molecular motions. In contrast, both cyclopropene (see Figure 3) and cyclohexane in its chair conformation exhibit pre- and postdiagonalization distortions that disobey the GMHP. Therefore, it is clear from these examples that electron delocalization is not a prerequisite for having nontotally symmetric distortions that refuse to comply the GMHP. Indeed, our experience shows that most molecules have nontotally symmetric distortions that violate the GMHP.

IV. Conclusions

In this work we have shown that not only BLA nontotally symmetric vibrational distortions in *π*-conjugated organic molecules break the GMHP and GMPP but also other organic and inorganic molecules without *π*-conjugated structure or even without *π*-bonds can exhibit nontotally symmetric molecular distortions with BLA and nonBLA character that do not follow these two principles. It is important to mention that the rules derived in our previous work[45] are still valid to predict whether a given π-conjugated organic system will have nontotally symmetric vibrational modes that disobey the GMPP. However, these rules apply only to organic π-conjugated species, while in this work we have found that the collection of molecules that violate the GMHP and GMPP is much larger. Indeed, we have identified some molecules with an almost completely localized electronic structure that do not follow the GMHP. This is a relevant result since it is important to know the applicability limits of the GMHP and GMPP. We have also found that the molecular distortions that disobey the GMPP are not necessary the same as those that break the GMHP. This result has been attributed to the fact that the proportionality between the polarizability (or its cube root) and the softness (the inverse of the hardness) does not always hold. We have also devised a method that allows to determine the nontotally symmetric molecular displacements with more marked GMHP or anti-GMHP character through diagonalization of the hardness Hessian matrix. Finally, we have derived a procedure to calculate the hardness derivatives when the HOMO and/or the LUMO are degenerated.

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