

## On the Validity of the Maximum Hardness and Minimum Polarizability Principles for Nontotally Symmetric Vibrations

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The maximum hardness (MHP)<sup>1,2</sup> and the minimum polarizability (MPP)<sup>3</sup> principles are among the most widely accepted electronic structure principles of chemical reactivity. First proposed by Pearson, the MHP asserts that molecular systems at equilibrium tend to the state of maximum hardness ( $\eta$ ). More recently, on the basis of an inverse relationship between hardness and polarizability ( $\alpha$ ),<sup>4</sup> Chattaraj and Sengupta<sup>3</sup> introduced the MPP. This principle states that the natural evolution of any system is toward a state of minimum polarizability. Both principles have been applied successfully to the study of molecular vibrations,<sup>2,5–8</sup> internal rotations,<sup>9,10</sup> excited states,<sup>11,12</sup> aromaticity,<sup>13</sup> and different types of chemical reactions.<sup>14–25</sup>

A formal proof of the MHP was given by Parr and Chattaraj<sup>26</sup> under the constraints that the chemical potential ( $\mu$ ) and the so-called external potential ( $\nu(\mathbf{r})$ ) must remain constant upon distortion of molecular structure. Here  $\nu(\mathbf{r})$  is the potential acting on an electron at  $\mathbf{r}$  due to the nuclear attraction plus such other external forces as may be present. These are two severe constraints that are usually not fulfilled. However, relaxation of these constraints seems to be permissible, and in particular, it has been found that in most cases the MHP still holds even though  $\mu$  and  $\nu(\mathbf{r})$  vary during molecular vibration, internal rotation, or along the reaction coordinate.<sup>5–25</sup> Hereafter, we will refer to the

**Table 1.** Molecular Distortions of Pyridine along the B<sub>2</sub> normal Vibration Mode at 1304.4 cm<sup>-1</sup>

displacement <sup>a</sup>	$\epsilon_{\text{H}}^b$	$\epsilon_{\text{L}}^b$	$-2\mu^b$	$2\eta^b$	$\alpha^c$
-0.16	-0.26355	-0.03843	0.30198	0.22511	61.040
-0.04	-0.26439	-0.03954	0.30393	0.22485	61.301
eq.	-0.26444	-0.03961	0.30406	0.22483	61.320
0.04	-0.26439	-0.03954	0.30393	0.22485	61.301
0.16	-0.26355	-0.03843	0.30198	0.22511	61.040

<sup>a</sup> The distortion is given in bohrs. <sup>b</sup> Values are given in au of energy (hartrees). <sup>c</sup> Calculated as  $1/3(\alpha_{\text{xx}} + \alpha_{\text{yy}} + \alpha_{\text{zz}})$  and given in au.

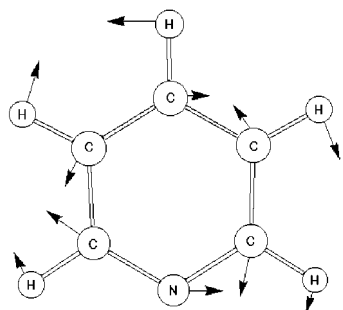
generalized MHP or MPP as the maximum hardness or minimum polarizability principles that do not require the constancy of  $\mu$  and  $\nu(\mathbf{r})$  during molecular change. The generalized versions of these principles have not been proved, and in fact failures of the generalized MHP and MPP in some chemical reactions<sup>18,21,25</sup> and excited states<sup>12</sup> have been reported. In most of these cases it has been shown that  $\mu$  and  $\nu(\mathbf{r})$  change noticeably. Therefore, these observations do not violate the strict MHP because this principle is rigorously valid only under constant  $\mu$  and  $\nu(\mathbf{r})$ .

The structural distortions taking place during molecular vibrations along the vibrational symmetry coordinates have been studied for several systems to analyze the validity of the generalized MHP<sup>2,5–7</sup> and MPP.<sup>8</sup> Pearson and Palke<sup>5</sup> (PP) showed that variations in hardness along totally symmetric and nontotally symmetric distortions are completely different. For nontotally symmetric vibration modes, PP showed that positive and negative deviations from the equilibrium produce molecular configurations that have the same  $\eta$ ,  $\mu$ , and average potential of the nuclei acting on the electrons ( $\nu_{\text{en}}$ ).<sup>5</sup> Then, if  $Q$  represents a nontotally symmetric normal mode coordinate, it follows that  $(\delta\mu/\delta Q) = 0$  and  $(\delta\nu_{\text{en}}/\delta Q) = 0$  at the equilibrium geometry. Hence,  $\mu$  and  $\nu_{\text{en}}$  are roughly constant for small distortions along nontotally symmetric normal modes, thus approximately following the two conditions of Parr and Chattaraj.<sup>26</sup> In contrast, for totally symmetric distortions, near the equilibrium geometry the hardness keeps increasing steadily as the nuclei approach each other. Indeed, neither  $\eta$  nor  $\mu$  or  $\nu_{\text{en}}$  shows any sign of a maximum or a minimum at the equilibrium geometry.

Makov<sup>7</sup> 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 modes. According to the generalized MHP and MPP, the equilibrium hardness must be a maximum, and the polarizability a minimum, for any nontotally symmetric distortion along vibrational symmetry coordinates. To our knowledge, all numerical calculations of hardness and polarizability along the nontotally symmetric normal modes confirm this point.<sup>2,5–8</sup> The object of the present work is to show for the first time the existence of nontotally symmetric vibration modes that break the generalized versions of the MHP and MPP. In contrast to the examples of a breakdown of the generalized MHP and MPP reported to date,<sup>12,18,21,25</sup> this is an example of a failure of these principles for the most favorable case in which  $\nu(\mathbf{r})$  and  $\mu$  keep almost constant, indicating that the strict version of the MHP cannot be straightforwardly generalized.

Table 1 collects the values of the HOMO and LUMO energies, chemical potential, chemical hardness, and polarizability corresponding to the equilibrium structure of pyridine and to structures obtained from positive and negative displacements along the B<sub>2</sub> mode depicted in Figure 1. In this Figure it is clearly seen that this B<sub>2</sub> vibrational mode has the characteristic atomic displacements of bond length alternation (BLA) modes. All geometry optimizations, polarizability, and frequency calculations have been

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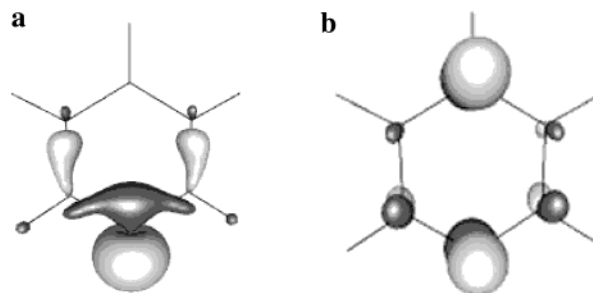


**Figure 1.** Schematic representation of the displacement vector corresponding to the  $B_2$  normal vibration mode at  $1304.4\text{ cm}^{-1}$ .

performed at the B3LYP level,<sup>27</sup> using the standard 6-31++G\*\* basis set<sup>28</sup> with the Gaussian98 package.<sup>29</sup> The calculated B3LYP//6-31++G\*\* geometry of pyridine is close to the experimental one,<sup>30</sup> the largest differences in bond lengths and angles being  $0.4\text{ pm}$  and  $0.3^\circ$ , respectively. The polarizability for the equilibrium structure in Table 1 is within a few percent of the experimental value of  $64.3^{31}$  and the best calculated value of  $63.95\text{ au}$ .<sup>32</sup> The chemical potential and the hardness have been calculated from the energy of frontier HOMO ( $\epsilon_H$ ) and LUMO ( $\epsilon_L$ ) molecular orbitals using the following approximate expressions:<sup>2,33</sup>

$$\mu = \frac{1}{2}(\epsilon_L + \epsilon_H); \quad \eta = \frac{1}{2}(\epsilon_L - \epsilon_H) \quad (1)$$

The values of hardness in Table 1 show that the equilibrium structure is a minimum of hardness in contradiction to the generalized MHP. The increase in the hardness value is due to a larger destabilization of the LUMO than that of the HOMO. The destabilization of the HOMO is expected in a nontotally symmetric displacements and leads usually to a decrease of the HOMO–LUMO gap and hardness. The destabilization of the LUMO is somewhat unexpected and can be understood by observing the shape of this orbital (Figure 2b) and the BLA distortion of the  $B_2$  vibrational mode (Figure 1). The increase in the LUMO energy is basically produced by the interaction between the lobe on N and the lobes on the C atoms adjacent to the N atom as the molecule vibrates. The increase in the



**Figure 2.** Representation of the B3LYP/6-31++G\*\* isosurfaces  $0.1$  (gray) and  $-0.1$  (black) au of the (a) HOMO and (b) LUMO.

antibonding interaction when the N atom and an adjacent C atom approach is more important than the reduction of the same antibonding interaction as the other adjacent C atom and N move away. As a result the LUMO is destabilized, and the hardness increases in contradiction with the generalized MHP. As expected from the inverse relationship between hardness and polarizability,<sup>4</sup> it is found that the polarizability value diminishes during the  $B_2$  displacement from the equilibrium structure, in disagreement with the MPP.

The strict version of the MHP is not disobeyed since neither  $\mu$  nor  $\nu(\mathbf{r})$  are constant during the vibration. At first view, one may attribute the breakdown of the generalized MHP and MPP in this normal mode to the fact that  $\mu$  and  $\nu(\mathbf{r})$  change significantly during this vibration. However, this is not the case, and we have found that variations in  $\mu$  and  $\nu(\mathbf{r})$  are similar among all nontotally symmetric modes.

It is worth noting that the existence of BLA modes that do not comply with the MHP and MPP is not a particular feature of pyridine. We have found that molecules such as benzene, naphthalene, anthracene, or phenanthrene possess BLA modes that violate the generalized MHP and MPP. The discovery of these new counterexamples of the generalized MHP and MPP implies that the conditions at which these two widespread principles hold must be reestablished. This revision may affect the conclusions reached in some chemical studies where these commonly accepted principles are routinely used.<sup>5–25,34</sup>

In summary, we have shown that not only in chemical reactions but also even in the favorable case of nontotally symmetric vibrations where  $\mu$  and  $\nu(\mathbf{r})$  keep approximately constant, the generalized MHP and MPP may not be obeyed. We have checked that this conclusion remains valid irrespective of the expression used to compute the hardness (either eq 1 or  $\eta = (I - A)/2$ ). Finally, we have also found that different methods and basis sets lead qualitatively to the same result.

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**Supporting Information Available:** A Table containing the B3LYP/6-31++G\*\* values of the HOMO and LUMO energies, chemical potential, chemical hardness, and polarizability for all molecular distortions of pyridine along its nontotally symmetric normal modes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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