J. Am. Chem. Soc. **1998,** *120,* 9053−9058

Density-Functional Approach to Hardness Evaluation and Its Use in the Study of the Maximum Hardness Principle

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Received December 8, 1997. Revised Manuscript Received May 11, 1998

Abstract: An alternative method for computing chemical hardness, based on the Janak's extension of density-functional theory for fractional occupancies, is employed in the study of the maximum hardness principle for HCN, HSiN, N_2H_2, HCP, and O_3H^+ isomerizations. The hardness is found to be a good indicator of the more stable isomer in all cases. The hardnesses and the energy profiles, as a function of the reaction coordinate, are generally opposite in nature only for the isomerization reactions of O_3H^+ and HSiN, for which there is a negligible variation of the chemical potential. The electronic and nuclear-repulsion energy changes show good correlation with the relative stability of a species even when the constraint of constant chemical potential is not obeyed.

Introduction

The Pearson hard−soft-acid−base[1] principle and the Sanderson electronegativity equalization[2] principle have offered the possibility to predict site reactivities and possible reaction mechanisms. By using these principles and the concepts associated with them, such as hardness (η), softness (S), and electronegativity (χ), a great deal of experimental information has been theoretically interpreted. While the concepts of hardness and softness have proved useful in many ways, it was only when to them was given a rigorous foundation in the framework of density-functional theory (DFT)[3] by Parr and coworkers[4] that it became possible to assign numerical values to these properties.

More recently, Pearson proposed another tool to gain further insight into chemical behavior, namely, the maximum hardness principle (MHP): "It seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible".[5] A formal proof of MHP was provided under the constraint of constant temperature and chemical potential (μ) by Parr and Chattaraj.[6] Subsequently, Parr and Gazquez[7] have pointed out that hardness is at an extremum at any point where both electronic energy (E_{el}) and nuclear-repulsion energy (V_{nn}) reach respective extreme values, under the condition of a constant product of the number of electrons and the chemical potential. The MHP has been further examined within the Gyftopolous−Hatsopolous three-level model by Chattaraj et al.[8] It has been shown that as a molecule approaches equilibrium, at some fixed chemical potential and temperature, its hardness most often approaches a maximum value.

The MHP has been numerically studied by a number of investigators. Most of the ab initio SCF (self consistent field) calculations of the hardness profile have been concerned with molecular deformations and internal rotations.[9−13] The results show that the MHP is obeyed when μ remains essentially constant along a reaction path. In a very recent ab initio SCF study, Kar and Scheiner[14] have examined the potential-energy hypersurface (PES), hardness, chemical potential, and electronic and nuclear-repulsion energies for various isomerization reactions. They found that generally the most stable isomer is associated with the highest η value even though μ varies but that the hardness does not pass through a minimum near or at the transition state (TS). DFT also has been used to study numerically the validity of MHP for exchange, deformation, and isomerization reactions.[15,16] All these computations indicate that the MHP is potentially a powerful tool for studying molecular electronic structure and better understanding various reaction mechanisms.

Although the results that support the MHP have been accumulating, less attention has been given to the approximation used for hardness computations. The ab initio SCF and DFT computations of η have been, in general, performed using the simple orbital theory that allows one to compute the hardness as the energy difference between the highest occupied orbital

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S0002-7863(97)04149-8 CCC: $15.00

and the lowest unoccupied orbital:[5]

$$\eta_{\mathrm{HL}} = \frac{\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}}{2} \tag{1}$$

With this formula it is difficult to study the MHP for species with a HOMO−LUMO gap close to zero. Furthermore, the Kohn−Sham[17] (KS) orbitals are different from the canonical molecular orbitals, and DFT calculation of η in terms of the HOMO−LUMO gap is not straightforward. On the other hand, DFT must be considered as a most desirable bridge between the study of chemical reactions through the wave function theory and the concepts of chemical hardness, softness, and frontier orbital theory. This motivates use of a definition of η within DFT itself in further studies of the MHP.

Recently, Liu[18] has proposed a rigorous DFT procedure for the molecular orbital hardness determination and applied it to the computation of the HCN hardness matrix. Unfortunately, this procedure is time-consuming.

In the present study, a method for hardness computation, proposed previously[19] in the framework of Xα approximation,[20] is employed into the Kohn−Sham formalism using Janak's[21] theorem for fractional occupancies. With the aim of checking MHP's validity, we have chosen some isomerization reactions, for one of which the constraint of constant chemical potential is obeyed (O_3H^+) and for the other of which the chemical potential varies (HCN, HSiN, N_2H_2, HCP) along the reaction path.

Method

Incorporation of the concepts of hardness and softness into DFT has led to the mathematical identification of η as the second derivative of the total energy with respect to the number of electrons N:[22,23]

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

or, equivalently

$$\eta = \left[\frac{\partial \mu}{\partial N}\right]_{\nu(\mathbf{r})} \tag{3}$$

Where the chemical potential, μ, is the first derivative of the total energy relative to the electron number. Derivatives are taken at constant external potential $\upsilon(\mathbf{r})$. Softness is defined as the inverse of hardness:

$$S = \frac{1}{\eta} \tag{4}$$

While the chemical potential is constant everywhere within the molecule, the hardness, and then the softness, is a function of the position. Thus, in addition to the global definition of η and S, the local hardness[24] and local softness[25] have been introduced as follows:

$$\eta(\mathbf{r}) = \frac{1}{N}\int \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\,\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \tag{5}$$

$$\mathrm{s}(\mathbf{r}) = \left[\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right]_{\nu(\mathbf{r})} = \frac{1}{\eta}\left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_{\nu(\mathbf{r})} \tag{6}$$

where $F[\rho]$ is the Hohenberg and Kohn universal functional[26] and $\rho(\mathbf{r})$ is the electron density. These expressions are obtained through the integration of the hardness and softness kernels:

$$\eta(\mathbf{r},\mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{7}$$

$$\mathrm{s}(\mathbf{r},\mathbf{r}') = -\left[\frac{\partial\rho(\mathbf{r})}{\partial u(\mathbf{r}')}\right]_{\nu(\mathbf{r})} = -\frac{1}{\eta}\left[\frac{\partial\rho(\mathbf{r}')}{\partial u(\mathbf{r})}\right]_{\nu(\mathbf{r})} \tag{8}$$

where $u(\mathbf{r})$ is the modified potential,[3]

$$u(\mathbf{r}) = \nu(\mathbf{r}) - \mu = -\frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})} \tag{9}$$

The local hardness and local softness are reciprocals in the sense that

$$\int \mathrm{s}(\mathbf{r})\eta(\mathbf{r}) = 1 \tag{10}$$

Other definitions of local hardness have been proposed, but they will not concern us here.

To compute local variables for a particular site in a molecule, an approach based on the fractional occupation number concept can be employed. The original idea to exploit fractional occupation numbers in the framework of DFT is from Janak who generalized the earlier work of Slater, using the Xα approach. The validity of the Janak theorem in DFT for N- and υ-representable densities has been discussed by many authors.[27−34] Recently Kohn et al.[35] have pointed out that fractional occupancies can be always defined for subsystems of molecules such as atoms or functional groups.

In Janak's formulation of DFT, the KS one-electron orbital energies are defined as the first derivatives of the total energy with respect to the occupation numbers n_i:

$$\epsilon_i = \left(\frac{\partial E}{\partial n_i}\right) \qquad i = 1, ..., N \tag{11}$$

and can be interpreted as the orbital electronegativities.[36] This formula is obtained through the relation between the total electron density and the Kohn−Sham orbitals Ψ_i:

$$\rho(\mathbf{r}) = \sum_i n_i|\Psi_i(r)|^2 \qquad 0 \le n_i \le 1 \qquad \sum_i^k n_i = N \tag{12}$$

Now it is convenient to expand the total energy functional in a Taylor's series around the number of electrons N or, in analogy with

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the Slater's Xα, around the state, characterized by the corresponding set of occupation numbers n^0 $(n_1^0, n_2^0, ..., n_k^0)$ and by the corresponding KS eigenvalues $\epsilon^0 = (\epsilon_1^0 ..., \epsilon_k^0)$.

$$\Delta E = \left(\frac{\partial E}{\partial N}\right)\Delta N + \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)(\Delta N)^2 + ...$$

$$= \sum_i \frac{\partial E}{\partial n_i}\Delta n_i + \frac{1}{2}\sum_{ij}\frac{\partial^2 E}{\partial n_i \partial n_j}\Delta n_i \Delta n_j + ... \tag{13}$$

where $\Delta n_i = n_i - n_i^0$. The first derivatives with respect to the occupation numbers give the KS eigenvalues (eq 11) and the second derivatives

$$\frac{\partial^2 E}{\partial n_i \partial n_j} = \eta_{ij} \tag{14}$$

give the hardness tensor as defined by Liu and Parr.[36] For a nonsingular matrix (η_{ij}), the Mors lemma[37] states that accounting for the higher order terms of the Taylor's expansion does not change qualitatively the properties of the expanded function. Thus we truncate the energy function (eq 13) series at the second-order term.

By taking the derivative of eq 7 with respect to occupation numbers, at constant $\upsilon(\mathbf{r})$, we found that the hardness tensor elements are given by

$$\eta_{ij} = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\frac{\partial\rho(\mathbf{r})}{\partial n_i}\frac{\partial\rho(\mathbf{r}')}{\partial n_j} \tag{15}$$

As previously demonstrated,[38] the kinetic hardness term vanishes and the hardness depends only on the second derivative of the Coulomb $(J[\rho])$ and exchange-correlation $(E_{xc}[\rho])$ energies. Hence, η_{ij} can be represented as follows:

$$n_{ij} = \frac{\delta^2[J[\rho] + E_{xc}[\rho]]}{\delta\rho(r)\delta\rho(r')}\frac{\partial\rho(r)}{\partial n_i}\frac{\partial\rho(r')}{\partial n_j} = \int \frac{\Psi_i{}^*(r)\Psi_i(r)\Psi_i{}^*(r')\Psi_i(r')}{|r - r'|}\,\mathrm{d}r\,\mathrm{d}r' + \int \frac{\delta^2 E_{xc}(\rho)\Psi_i{}^*(r)\Psi_i(r)\Psi_i{}^*(r')\Psi_i(r')}{\delta\rho(r)\delta\rho(r')}\,\mathrm{d}r\,\mathrm{d}r' \tag{16}$$

The Janak theorem (eq 11) and the hardness tensor definition (eq 14) allow one to calculate η_{ij} as the first derivative of the Kohn–Sham orbital eigenvalues with respect to the orbital occupation numbers:[19]

$$\eta_{ij} = \frac{\partial \epsilon_i}{\partial n_i} \tag{17}$$

Numerically, the latter derivatives can be computed using the finite difference approximation

$$\eta_{ij} = \frac{\epsilon_i(n_j - \Delta n_j) - \epsilon_i(n_j)}{\Delta n_j} \tag{18}$$

This expression takes into account the response of the *i*th orbital to the change of the occupation number of the *j*th orbital.

Since the local hardness and local softness are reciprocal to each other (eq 10), the softness matrix is the inverse of the hardness one:

$$[s_{ij}] = [\eta_{ij}]^{-1} \tag{19}$$

Equation 19 holds for a nonsingular η_{ij} matrix.

The relation between the global and local hardness is given through the equation

$$\eta = \int \eta(r)f(r)\,\mathrm{d}r \tag{20}$$

where

$$f(r) = \left[\frac{\partial\mu}{\partial\nu(\mathbf{r})}\right]_N = \left[\frac{\partial\rho}{\partial N}\right]_\eta \tag{21}$$

is the Fukui function, as previously defined.[3,39] The total softness is obtained as an integral of the local softness:[3]

$$S = \int s(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{22}$$

Consequently, the total softness is an additive function of $s(r)$, and S can be approximated to

$$S = \sum_{ij} s_{ij} \tag{23}$$

Now the total hardness becomes

$$\eta = \frac{1}{S} = \frac{1}{\sum_{ij} s_{ij}} \tag{24}$$

Also the chemical potential can be computed from the orbital softness values through the use of the orbital Fukui index[18,19,39]

$$f_i = \frac{\partial n_i}{\partial N} = \frac{\Delta n_i}{\Delta N} = \left(\frac{\partial n_i}{\partial\mu}\right)\left(\frac{\partial\mu}{\partial N}\right) = \eta\sum_j s_{ij} \tag{25}$$

with $\sum_i f_i = 1$. From the energy functional expansion (eq 13) and the latter equation it follows that the chemical potential can be expressed as[18,19]

$$\mu = \frac{\partial E}{\partial N} = \sum_i \frac{\partial E}{\partial n_i}\left(\frac{\Delta n_i}{\Delta N}\right) = \sum_i \epsilon_i f_i \tag{26}$$

In the simple orbital-theory approach (see eq 1) the chemical potential is given by

$$\mu = \epsilon_H f_H + \epsilon_L f_L = \frac{1}{2}(\epsilon_H + \epsilon_L) \tag{27}$$

assuming a value of 0.5 for Fukui functions of HOMO and LUMO orbitals.

Equations 17–19 and 23–27 provide a simple but accurate scheme that allows one to take into account the influence of all valence orbitals in the total hardness and chemical potential computations.

Computational Details

We have used the method described above to study the hardness profile of different isomerization reactions: 1,2-hydrogen shift for HCN, HSiN, and HCP and cis → trans interconversion of N_2H_2 and O_3H^+.

The results presented here have been obtained using a modified version of deMon code.[40] All calculations were performed by employing the gradient-corrected functional of Perdew[41] for correlation and that of Perdew and Wang[42] for exchange energy.

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Table 1. Calculated Hardnesses from Valence-Shell Electrons (η) and from the HOMO−LUMO Energy Difference (η_{HL}), Total Energy (E), Electronic Energy (E_{el}), and Nuclear Energy (V_{nn}) in EV for Minima and Maxima of Different Isomerization Reactions

system	E	E_{el}	V_{nn}	η	η_{HL}	μ
t-N_2H_2	−2549.686 558	−3281.494 067	732.613 089	6.36	1.27	−13.5
c-N_2H_2	−2549.512 602	−3280.259 580	730.765 386	6.28	1.33	−10.0
TS	−2547.904 203	−3279.893 491	731.989 058	5.94	1.26	−16.5
HCN	−2152.911 322	−2697.972 892	545.061 570	6.96	3.92	−3.9
HNC	−2152.325 487	−2703.406 013	551.080 526	6.42	3.31	−6.3
TS	−2151.159 800	−2700.465 759	549.305 995	6.35	2.65	−12.3
HSiN	−7937.095 631	−8825.035 885	887.940 253	4.48	1.72	−2.4
HNSi	−7939.537 683	−8843.429 618	903.891 936	4.59	2.30	−4.8
TS	−7936.664 194	−8816.503 086	879.838 892	4.41	0.76	−4.9
t-O_3H^+	−5200.032 891	−6884.742 485	1684.709 594	6.54	0.88	−20.0
c-O_3H^+	−5199.897 362	−6888.208 252	1688.310 890	6.45	0.93	−20.4
TS	−5199.229 612	−6877.222 357	1677.992 745	5.81	0.00	−19.8
HCP	−8748.581 938	−9588.267 230	839.685 292	4.01	2.28	−4.9
HPC	−8745.797 268	−9573.463 056	827.665 788	3.89	1.99	−28.8

To locate the extreme points on the potential-energy hypersurface, the Broyden−Fletcher−Goldfarb−Shanno minimization algorithm[43] for the minima has been used. For the saddle-points search the Abashkin and Russo[44] algorithm has been employed. Along the reaction path, critical points have been classified as minima or transition states on the basis of vibrational analysis. The points along the reaction paths have been obtained by fixing the appropriate reaction coordinate and optimizing all the other geometrical parameters. The orbital and auxiliary basis sets used are of triple-ζ quality.[45]

The calculations of the hardness matrix elements and, consequently, of the absolute hardness values have been carried out by taking into account only the occupied valence orbitals and LUMO. In accordance with the Slater transition-state method,[20] the variations of the occupation numbers Δn_i were set to be 0.5 for the molecules and 0.25 for the ion.

Results and Discussion

In Table 1 we report the calculated hardness (η) values together with the chemical potential (μ) and the total (E), electronic (E_{el}), and nuclear (V_{nn}) energies of the minima and the maxima of the reactions studied. All results show that the respective most stable isomers have greater hardness values than do the transition states (TS). For comparison, we include also the hardness values obtained from the HOMO−LUMO energy difference (η_{HL}). These do not correctly predict the relative stability of the isomers for N_2H_2 and O_3H^+. Moreover, results for O_3H^+ show that this approximation gives zero hardness at the TS.

As already mentioned, the MHP can be rigorously applied only under the condition of constant chemical potential. The computed chemical potential along the reaction path is found to remain practically constant only for the isomerization reaction of O_3H^+ (μ varies from −20.36 to −19.83 eV). All the other reported chemical potential values (Table 1) account for a variation of μ along the reaction path. Although μ is not constant, the η values in Table 1 show that hardness is a reasonable measure of relative stability.

To check the hardness behavior along the whole reaction path, the variation of η as a function of the reaction coordinate for the above reactions has been examined. The energy and hardness profiles for the interconversion between trans and cis forms of O_3H^+ are drawn in Figure 1 as a function of the dihedral angle O−O−O−H (α). The trans isomer is more stable than the cis one by about 4 kcal/mol, and the transition state occurs at α = 90° and lies about 21 kcal/mol above the global minimum. For this energy path, η decreases on going from its maximum value of 6.54 eV, for the trans form, to 5.81 eV for the transition state. Then, it increases and reaches the value of 6.45 eV, which characterizes the cis isomer. As previously mentioned, the η_{HL} value does not account correctly for the relative isomer stability, although its behavior is similar in shape to that of η (see Figure 1).

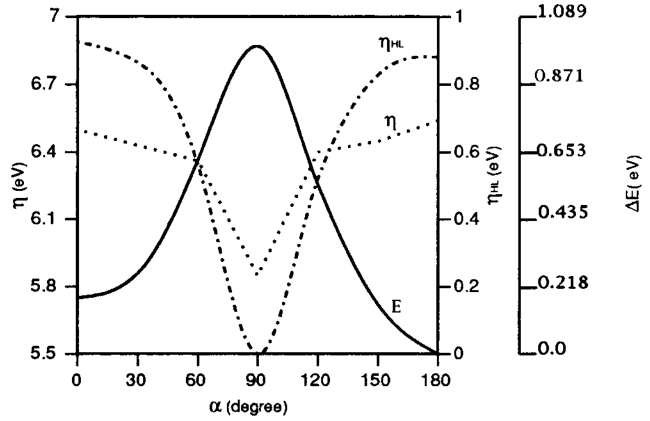

Figure 1. Hardness, computed from the valence-shell orbitals (η) and from the HOMO−LUMO energy difference (η_{HL}), and total energy difference (ΔE) profiles of O_3H^+ as a function of the α-dihedral angle.

A different behavior has been found for 1,2-hydrogen shifts in HCN and HSiN. We focused our attention on these isomerization reactions because the potential-energy surface of HCN contains two minima separated by an energy difference of 16.0 kcal/mol, while for HSiN the energy gap is 66.5 kcal/mol. Moreover, while the HSiN → HNSi interconversion is accompanied by a variation in the chemical potential of 2.52 eV, for HCN the variation in the numerical values of μ goes from −3.87 to −12.30 eV. The dependence of the total energy and the hardness upon the HCN-angle (θ) is illustrated in Figure 2a. Starting from the HNC minimum ($\theta = 0°$), η (6.42 eV) drops until reaching a minimum (6.28 eV) at $\theta = 35°$, whereas the energy maximum corresponds to a θ value of 68.4°. Going to the most stable isomer, HCN ($\theta = 180°$), η climbs to a maximum value of 6.96 eV.

In Figure 3a is drawn the hardness profile for the HSiN isomerization together with the potential-energy surface. The most stable isomer, HNSi ($\theta = 0°$), is found to be the hardest ($\eta = 4.59$ eV). Going to the TS ($\theta = 90°$), η decreases to 4.41 eV and reaches the minimum of 4.40 eV at $\theta = 120°$, but this

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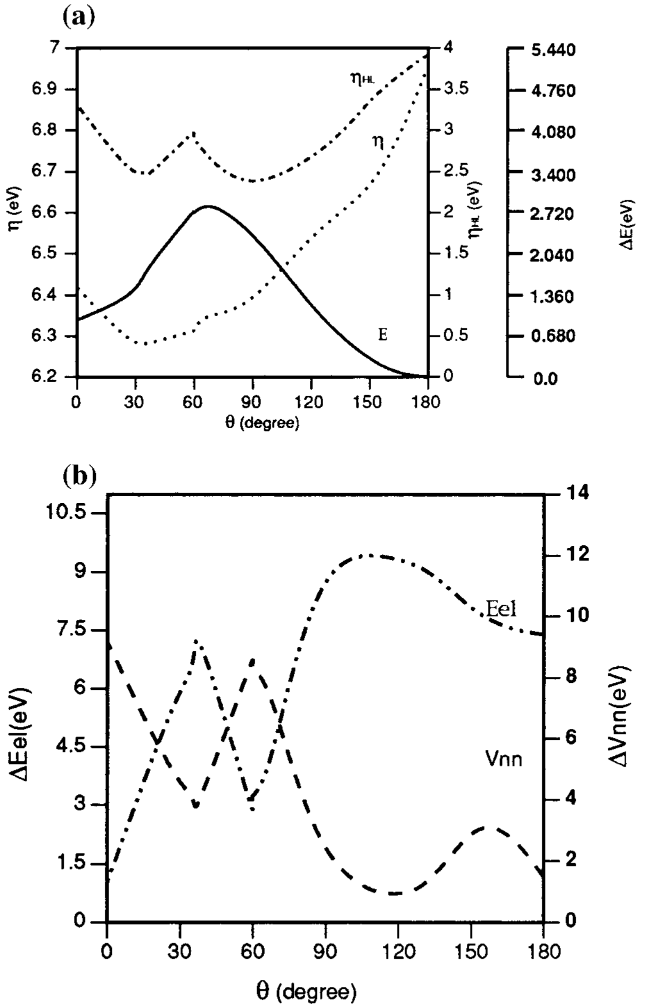

Figure 2. (a) Hardness, computed from the valence-shell orbitals (η) and from the HOMO−LUMO energy difference (η_{HL}), and total energy difference (ΔE) profiles of HCN as a function of the θ-valence angle. (b) Electronic energy (ΔE_{el}) and nuclear-repulsion energy (ΔV_{nn}) differences of HCN as a function of the θ-valence angle.

discrepancy can be due to numerical errors. Indeed, these hardness values differ only by 0.01 eV. In Figures 2a and 3a are also sketched the calculated hardness values as HOMO−LUMO energy differences along the reaction coordinate. While in the case of HSiN, η_{HL} passes through a minimum at the TS, and the η_{HL} profile of HCN is maximized at the energy minima and goes through two minima separated by a maximum ($\theta = 55°$) that does not correspond to a stationary point at all. Almost the same behavior for HCN isomerization was found by Kar and Scheiner.[14]

To check the Parr and Gazquez statement,[6] the electronic and nuclear energies as a function of the reaction coordinate are illustrated in Figure 2b for HCN and in Figure 3b for HSiN isomerizations. In the case of HCN there is not a coincidence in the extrema of η either with E_{el} or with V_{nn} profiles. The electronic energy for HSiN isomerization is found to have the same profile as the total energy and is a nearly perfect mirror of the nuclear energy.

Another reaction that does not obey the constraint of constant chemical potential is the cis−trans isomerization of hydrazine. The hardness and total energy profiles are given in Figure 4a as a function of the in-plane valence angle NNH (θ). In this case the valence angle varies from 112.7° (*cis*-N_2H_2) to 253.3° (*trans*-N_2H_2), passing through a value of 177.6° for the TS structure. Notwithstanding that η attains a minimum at the TS,

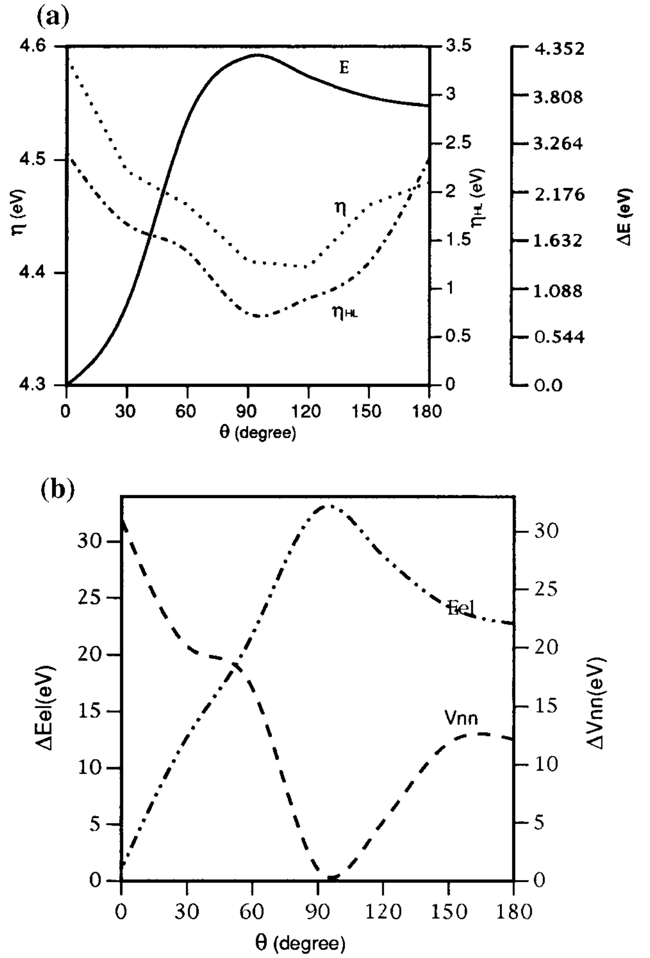

Figure 3. (a) Hardness, computed from the valence-shell orbitals (η) and from the HOMO−LUMO energy difference (η_{HL}), and total energy difference (ΔE) profiles of HSiN as a function of the θ-valence angle. (b) Electronic energy (E_{el}) and nuclear-repulsion energy (V_{nn}) differences of HSiN as a function of the θ-valence angle.

the hardest species ($\eta = 6.52$ eV) corresponds to the valence angle of 230°, but this point is not a minimum of the potential-energy hypersurface. Also, in this case a possible relationship between η and the electronic and nuclear energy profiles has been examined (see Figure 4b). It is apparent that the electronic energy has extrema at the same points that the nuclear energy does. Moreover, for this reaction, the extrema in η coincide with those in the electronic energy. The profile of η_{HL} (Figure 4a) goes through two minima at $\theta = 145°$ and 200°. Neither the electronic nor the total energy passes through an extremum at these points.

Finally, the HCP → HPC isomerization reaction has been studied. It is interesting to note that, until now, the phosphorus analogue of the hydrogen isocyanide, isophosphaethyne, has eluded experimental detection.

The potential-energy surface for this reaction has not yet been well established. However, Ma et al.[46] have carried out very extensive calculations concluding that all of the employed levels of theory give HCP as a minimum. The isophosphaethyne, HPC, is found to be a potential energy minimum using the Moller−Plesset procedures (RMP2, RMP4, UMP2, UMP3, and UMP4) but becomes a second-order saddle point when the more reliable quadratic configuration interaction and Brueckner doubles computations are employed. In agreement with the

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[46] Ma, N. L.; Wong, S. S.; Paddon-Row, M. N.; Li, W. K. *Chem. Phys. Lett.* **1993**, *213*, 189.

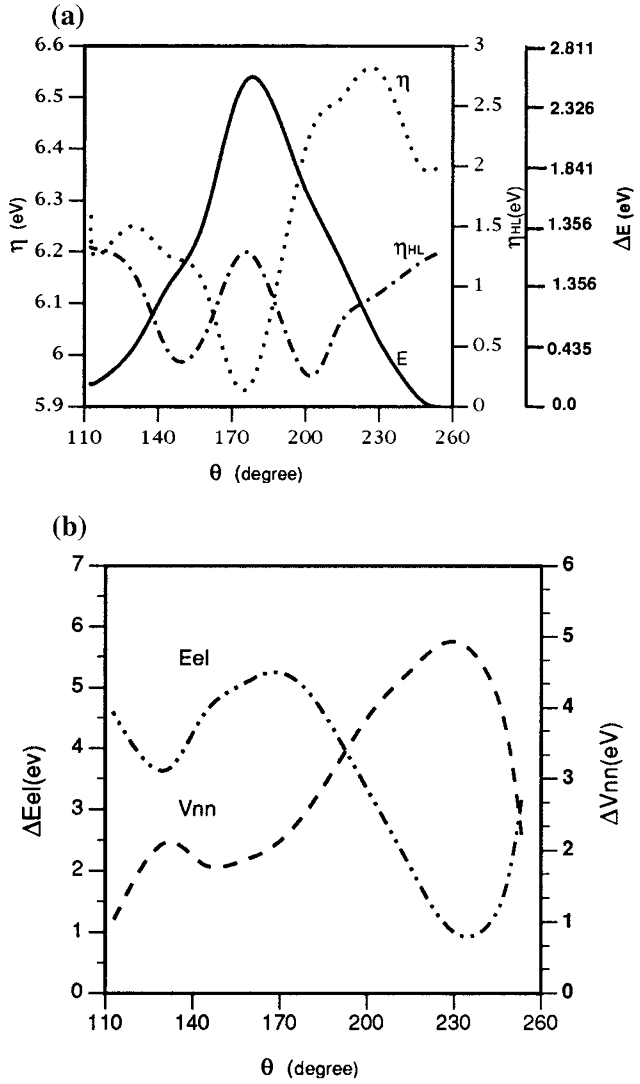

Figure 4. (a) Hardness, computed from the valence-shell orbitals (η) and from the HOMO−LUMO energy difference (η_{HL}), and total energy difference (ΔE) profiles of N_2H_2 as a function of the θ-valence angle. (b) Electronic energy (E_{el}) and nuclear-repulsion energy (V_{nn}) differences of N_2H_2 as a function of the θ-valence angle.

latter hypothesis and with previous CASSCF[47] studies, our calculations confirm the nature of the maximum of the HPC isomer (the vibrational analysis gives two negative eigenvalues of the Hessian matrix). In Figure 5a the energy profile is reported together with that of the hardness as a function of the HCP angle (θ). While the energy curve clearly shows that HPC is a maximum, it is difficult to explain the presence of three maxima in the η and η_{HL} profiles. A similar shape of the hardness profile (η_{HL}) has been previously found at the ab initio 6-31G** level of computation.[13] Since the potential μ varies significantly along the reaction path, no conclusion can be drawn on the possible existence of a transition state. We only observe that the maximum hardness value corresponds to the energetic minimum that is well characterized on the PES. Figure 5b illustrates the E_{el} and V_{nn} behaviors, which are nearly perfect mirrors of one another. It is worth noting that the extrema in η and η_{HL} coincide with those in the two components of the total energy.

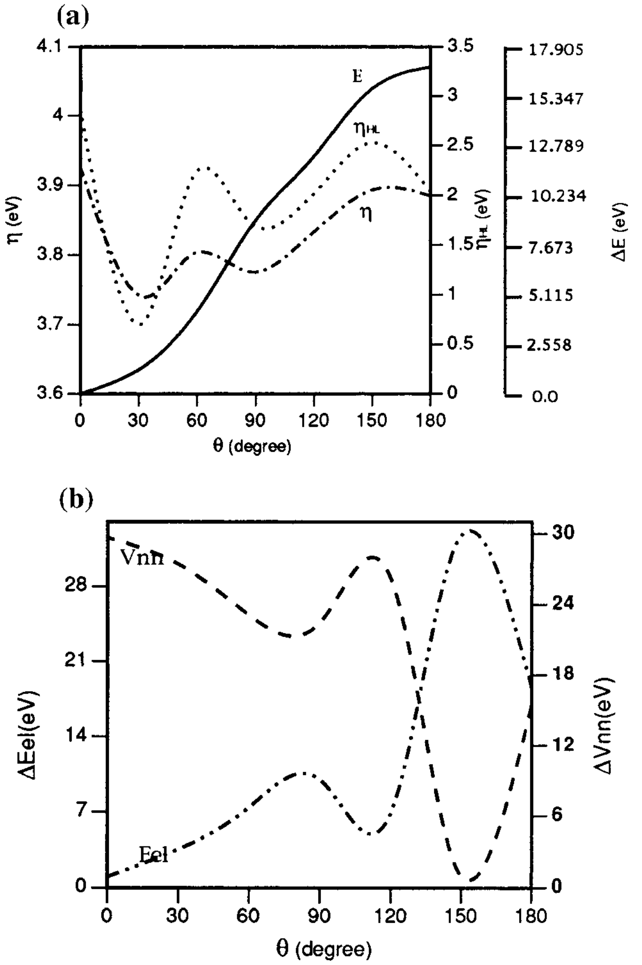

Figure 5. (a) Hardness, computed from the valence-shell orbitals (η) and from the HOMO−LUMO energy difference (η_{HL}), and total energy difference (ΔE) profiles of HCP as a function of the θ-valence angle. (b) Electronic energy (E_{el}) and nuclear-repulsion energy (V_{nn}) differences of HCP as a function of the θ-valence angle.

Conclusion

In this paper we have studied the relationship between hardness and energy profiles for a series of isomerization reactions with the aim of ascertaining the validity of MHP by employing a new procedure for the hardness computation. Results show that this method gives good correlation between the energy and hardness profiles and support the statement that greater hardness implies greater stability. Even though, for all the studied reactions, the hardness is increasing toward the maximum value in coincidence with the global minimum on the PES, the minimum in the hardness profiles does not coincide with the TS location when μ is far from constant. Indeed, we found that the MHP is respected only for O_3H^+ and HSiN isomerizations, for which the chemical potential does not vary significantly during the reactions. In addition, we note that a good correlation between electronic energies and hardness profiles exists, except in HCN.

Much work is necessary in order to understand and clarify the hardness behavior along the reaction path, and we think that our work could stimulate the study of chemical reactions in terms of the hardness concept in the framework of density-functional theory.

JA974149V

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[47] Goldstein, E.; Jin, S.; Carrillo, M. R.; Cave, R. J. *J. Comput. Chem.* **1993**, *14*, 186.