

# Keto $\rightleftharpoons$ Enol, Imine $\rightleftharpoons$ Enamine, and Nitro $\rightleftharpoons$ *aci*-Nitro Tautomerism and Their Interrelationship in Substituted Nitroethylenes. Keto, Imine, Nitro, and Vinyl Substituent Effects and the Importance of H-bonding

Koop Lammertsma<sup>\*,†,‡</sup> and Prasad V. Bharatam<sup>†,§</sup>

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294,  
Department of Chemistry, Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083,  
1081 HV Amsterdam, The Netherlands, and Department of Chemistry, Guru Nanak Dev University,  
Amritsar 143 005, India

lammert@chem.vu.nl

Received February 29, 2000

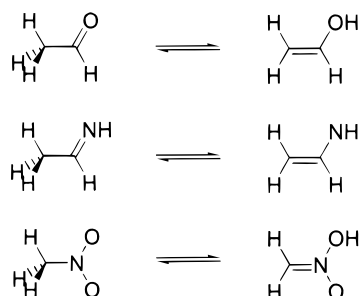
Tautomeric isomers and conformers of 2-nitrovinyl alcohol (**1**), 2-nitrovinylamine (**2**), and 1-nitropropene (**3**) are reported at the MP2 and B3LYP levels of theory, using the 6-31G\* basis set, with energy evaluation at B3LYP/6-311+G\*\* and G2MP2. The nitroalkenes are the global minima on their respective potential energy surfaces. The barriers for the concerted 1,5-H transfer to the corresponding nitronic acids amount to only 5.0 kcal/mol for **1**, 13.2 kcal/mol for **2**, and a sizable 37.8 kcal/mol for **3**. Whereas the *aci*-nitro tautomer of 2-nitrovinyl alcohol is easily accessible,  $\beta$ -iminonitronic acid has little kinetic stability. H-bonding is a strong stabilizing factor in these nitroalkenes, estimated at 7.0 and 3.7 kcal/mol for the OH and NH<sub>2</sub> derivatives, respectively, while its stabilization in their nitronic acids amounts to as much as 13 kcal/mol. The H-bonds are evident from the very short O $\cdots$ H and N $\cdots$ H distances and are characterized by bond critical points. The NO<sub>2</sub> substituent effect of about 11.4 kcal/mol at G2MP2 on both the classical keto  $\rightleftharpoons$  enol and imine  $\rightleftharpoons$  enamine tautomeric processes stabilizes the nitroethylene derivatives. The keto, imine, and vinyl substituent effects at G2MP2 on the nitro  $\rightleftharpoons$  *aci*-nitro tautomeric process are also determined as are their  $\pi$ -resonance components. The substituents have a large influence on the ionization energies of the nitroethylene derivatives.

## Introduction

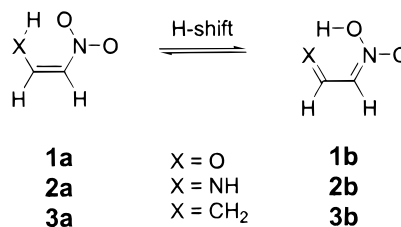
In the many studies devoted to tautomerism in conjugated systems, the nitro group has received less attention than for example the keto and imine groups (Scheme 1). In the present study we explore the combined effect of the keto  $\rightleftharpoons$  enol,<sup>1</sup> imine  $\rightleftharpoons$  enamine,<sup>2b</sup> and nitro  $\rightleftharpoons$  *aci*-nitro<sup>2</sup> tautomeric processes in conjugated systems. Particular emphasis is placed on the 1,5-H shift in *cis*-2-nitroethenol **1**, *cis*-2-nitrovinylamine **2**, and *cis*-1-nitropropene **3** to investigate the accessibility of nitronic acids (Scheme 2).

Nitronic acids<sup>3</sup> are compounds containing a  $\text{N}(=\text{O})\text{OH}$  or *aci*-nitro group. They are the thermodynamically

## Scheme 1



## Scheme 2



<sup>†</sup> University of Alabama at Birmingham.

<sup>‡</sup> Vrije Universiteit.

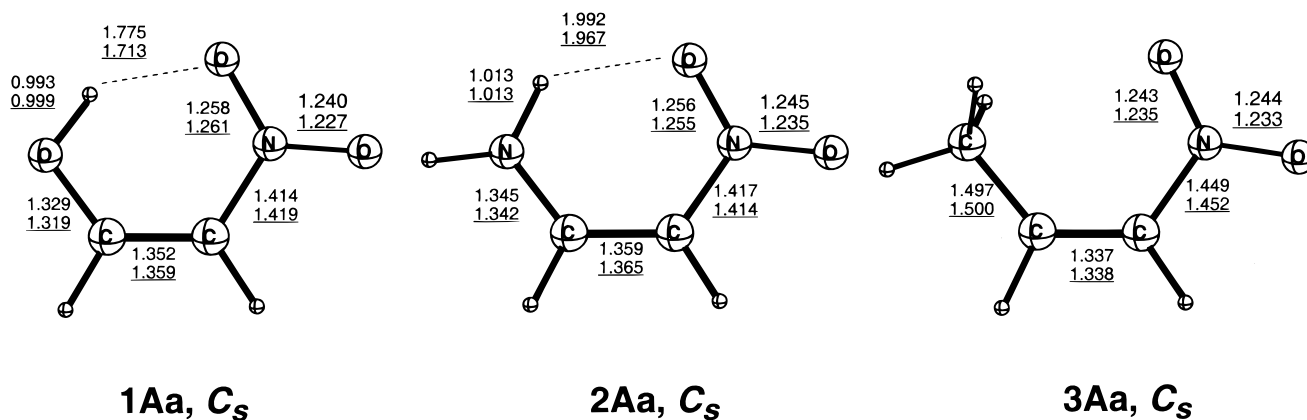
<sup>§</sup> Guru Nanak Dev University.

(1) (a) *The Chemistry of Enols*; Rappaport, Z., Ed.; Wiley: Chichester, 1990. (b) Capon, B.; Guo, B.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135 and references therein. (c) Smith, B. J.; Nguyen, M. T.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 6452. (d) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1992**, *114*, 36. (e) Nagaoka, M.; Suenobu, K.; Yamabe, T. *J. Am. Chem. Soc.* **1997**, *119*, 8023. (f) Fraser, R. R.; Banville, J. *J. Chem. Soc., Chem. Commun.* **1979**, 47.

(2) (a) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1993**, *115*, 2348 and references therein. (b) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642. (c) Harris, N. J.; Lammertsma, K. *J. Am. Chem. Soc.* **1996**, *118*, 8045.

(3) (a) Nielson, A. T. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Interscience: New York, 1969; Part 1, p 349. (b) Noland, W. E. *Chem. Rev.* **1955**, *55*, 137. (c) *The Chemistry of Amine, Nitroso, and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982. Morrison, H. A., p 165; Chow, Y. L.; Batt, L., p 417. (d) *International Agency of Carcinogenic Risk of Chemicals to Man*; WHO: Lyon, 1982; Vol. 29, p 331.

unfavorable tautomers of nitroalkanes,<sup>2–4</sup> as illustrated by the 14 kcal/mol energy difference (G2 theory) between the nitromethane tautomers. Still, nitronic acids play an important role as reactive intermediates in many redox, photochemical, and pyrolysis processes,<sup>2–6</sup> and in syntheses such as the Nef and Victor Meyer reactions.<sup>7</sup> Nitronic acids become more stable on aromatic substitution of the  $\alpha$ -carbon as in diphenylmethanenitronic acid,<sup>8</sup>



**Figure 1.** Selected geometric parameters for **1Aa**, **2Aa**, and **3Aa** at MP2/6-31G\* and B3LYP/6-31G\* (underlined). Distances are in angstroms and angles in degrees.

and by inter-<sup>8</sup> or intramolecular<sup>9</sup> hydrogen bonding.<sup>9</sup> As a radical cation the *aci*-nitro tautomer is even preferred over that of nitromethane.<sup>10</sup> Due to the high energy barrier for 1,3-hydrogen transfer, nitronic acids are typically formed via acid–base equilibria.<sup>2,8,11</sup> Both the protonation<sup>12</sup> and deprotonation<sup>13</sup> of nitromethane have been the subject of theoretical studies.

Appropriately substituted aromatic nitro derivatives may also yield nitronic acids as suggested by the incipient formation of anthranil derivatives during pyrolysis of, e.g., *o*-nitrotoluene.<sup>14</sup> In such conjugated systems the 1,5-hydrogen transfer formally represents a 6 e<sup>-</sup> thermally allowed sigmatropic rearrangement. Politzer et al.<sup>15</sup> reported the nitro ⇌ *aci*-nitro tautomerism in *o*-nitrophenol indeed to be a low energy process at HF/3-21G, but also found such a process not to be feasible for *o*-nitroaniline. In an earlier related study, the nitro ⇌

*aci*-nitro tautomerism for *cis*-1-nitropropene was reported to be a high energy process.<sup>16</sup>

In the present study, using different levels of ab initio theory, we explore various tautomeric processes with emphasis on the 1,5-H-shifts in parent olefinic systems that render nitronic acids. To provide accurate energies for this process we report in detail on a spectrum of structural conformers and isomers. The extent of H-bonding associated with the 1,5-H-shifts will be detailed as will be the substituent effect on the classic tautomeric processes.

## Computational Methods

Ab initio molecular orbital<sup>17</sup> and density functional (DFT)<sup>18</sup> calculations were performed with the GAUSSIAN94<sup>19</sup> suite of programs using IBM RS6000 workstations. Geometries of 2-nitrovinyl alcohol (**1A**), 2-nitrovinylamine (**2A**), and 1-nitropropene (**3A**); their nitronic acid tautomers (**1–3B**); the related keto (**1C**) and enamine (**2C**) tautomers and 3-nitropropene (**3C**); the corresponding anions (**1–3D**); and the transition structures for the 1,5-H shift (**1–3E**) were optimized at the HF, MP2(full),<sup>20</sup> and B3LYP<sup>21</sup> levels of theory using the 6-31G\* basis set. All the isomers and conformers of these systems that are used in this study are identified in Scheme 3. Selected structures are displayed with their important geometrical parameters in Figures 1–5. For all species the Hessian index, which is the number of negative eigenvalues of the force constant matrix, was determined at the SCF level. HF/6-31G\* zero point vibrational energies (ZPE) are scaled by a factor of 0.8929.<sup>22</sup> Single-point calculations were performed at B3LYP/

(4) (a) McKee, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5784. (b) McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 369. (c) Qian, K.; Shukla, A.; Futrell, J. *J. Am. Chem. Soc.* **1991**, *113*, 7121. (d) Ritchie, J. P. *J. Org. Chem.* **1989**, *54*, 3553. (e) Ritchie, J. P. *Tetrahedron Lett.* **1988**, *44*, 7465. (f) Tao, Y. *Top. Mol. Organ. Eng.* **1996**, *14*, 421. (g) Khrapkovski, G. M.; Shamov, A. G.; Shamov, G. A.; Shlyapochnikov, V. A. *Mendeleev Commun.* **1997**, 169.

(5) *The Chemistry of Amine, Nitroso, and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982; Schwarz, H.; Levens, K., p 85. (b) *Ibid.* Fry, A. J., p 319. (c) Sartori, G.; Bigli, F.; Maggi, R.; Tomasini, F. *Tetrahedron Lett.* **1994**, *35*, 2393. (d) Hey-Motherwell, R. S.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1994**, 2223.

(6) (a) Kheir, A. A.; Haw, F. *J. Am. Chem. Soc.* **1994**, *116*, 817. (b) Allouche, A. *J. Phys. Chem.* **1996**, *100*, 1820.

(7) (a) Edward, J. T.; Tremaine, P. H. *Can. J. Chem.* **1971**, *49*, 3483. (b) Edward, J. T.; Tremaine, P. H. *Can. J. Chem.* **1971**, *49*, 3489.

(8) Bock, H.; Dienelt, R.; Schodel, H.; Havlas, Z.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1758.

(9) Kang, F.-A.; Yin, C.-L.; She, S.-W. *J. Org. Chem.* **1996**, *61*, 5523.

(10) Beijersbergen, J. H. M.; Zande, W. J. v. d.; Kistemaker, P. G.; Los, J.; Drevello, T.; Nibbering, M. M. *J. Phys. Chem.* **1992**, *96*, 9288.

(11) (a) Erden, I.; Keffe, J. R.; Xu, F.-P.; Zheng, J.-B. *J. Am. Chem. Soc.* **1993**, *115*, 9834. (b) Kresge, A. J. *Chemtracts: Org. Chem.* **1994**, *7*, 187. (c) Cao, W.; Erden, I.; Keffe, J. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1091.

(12) (a) Bernasconi, C. F.; Zitomer, J. L.; Schuck, D. F. *J. Org. Chem.* **1992**, *57*, 1132. (b) Bernasconi, C. F.; Wenzel, P. J.; Keffe, J. R.; Gronert, S. *J. Am. Chem. Soc.* **1997**, *119*, 4008.

(13) (a) Beksic, D.; Bertran, J.; Lluch, J. M.; Hynes, J. T. *J. Phys. Chem. A* **1998**, *102*, 3977. (b) Politzer, P.; Seminario, J. M.; Zacarias, A. G. *Mol. Phys.* **1996**, *89*, 1511.

(14) (a) He, Y. Z.; Cui, J. P.; Mallard, W. G.; Tsang, W. *J. Am. Chem. Soc.* **1988**, *110*, 3754. (b) Chattopadhyay, S. K.; Craig, B. B. *J. Phys. Chem.* **1987**, *91*, 323. (c) Menapace, J. A.; Marlin, J. E. *J. Phys. Chem.* **1990**, *94*, 1066.

(15) Politzer, P.; Seminario, M. J.; Bolduc, P. R. *Chem. Phys. Lett.* **1989**, *158*, 463.

(16) Cox, J. R.; Hillier, I. H. *Chem. Phys.* **1988**, *124*, 39.

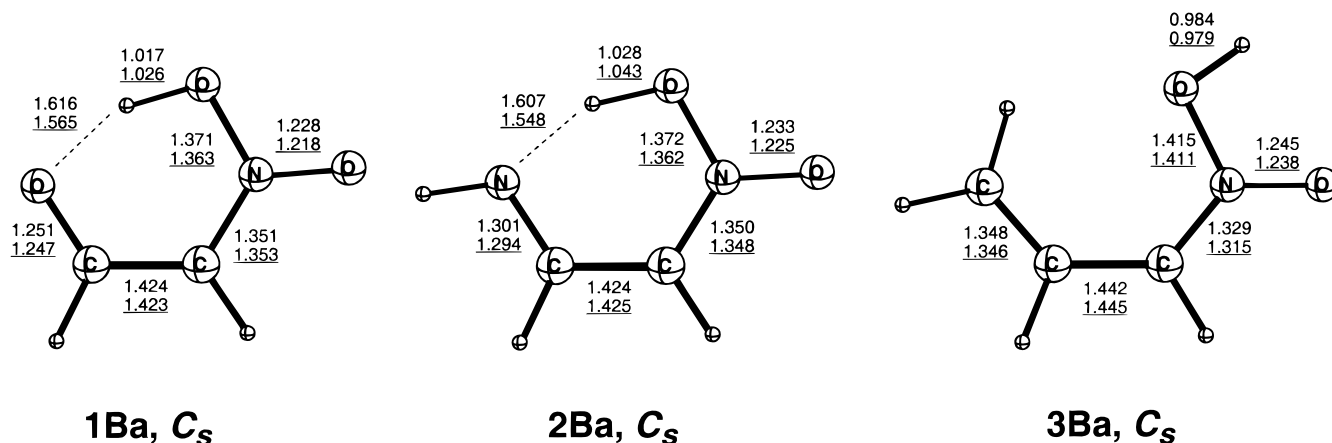
(17) For an introduction of the methods employed, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(18) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(19) Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, J. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

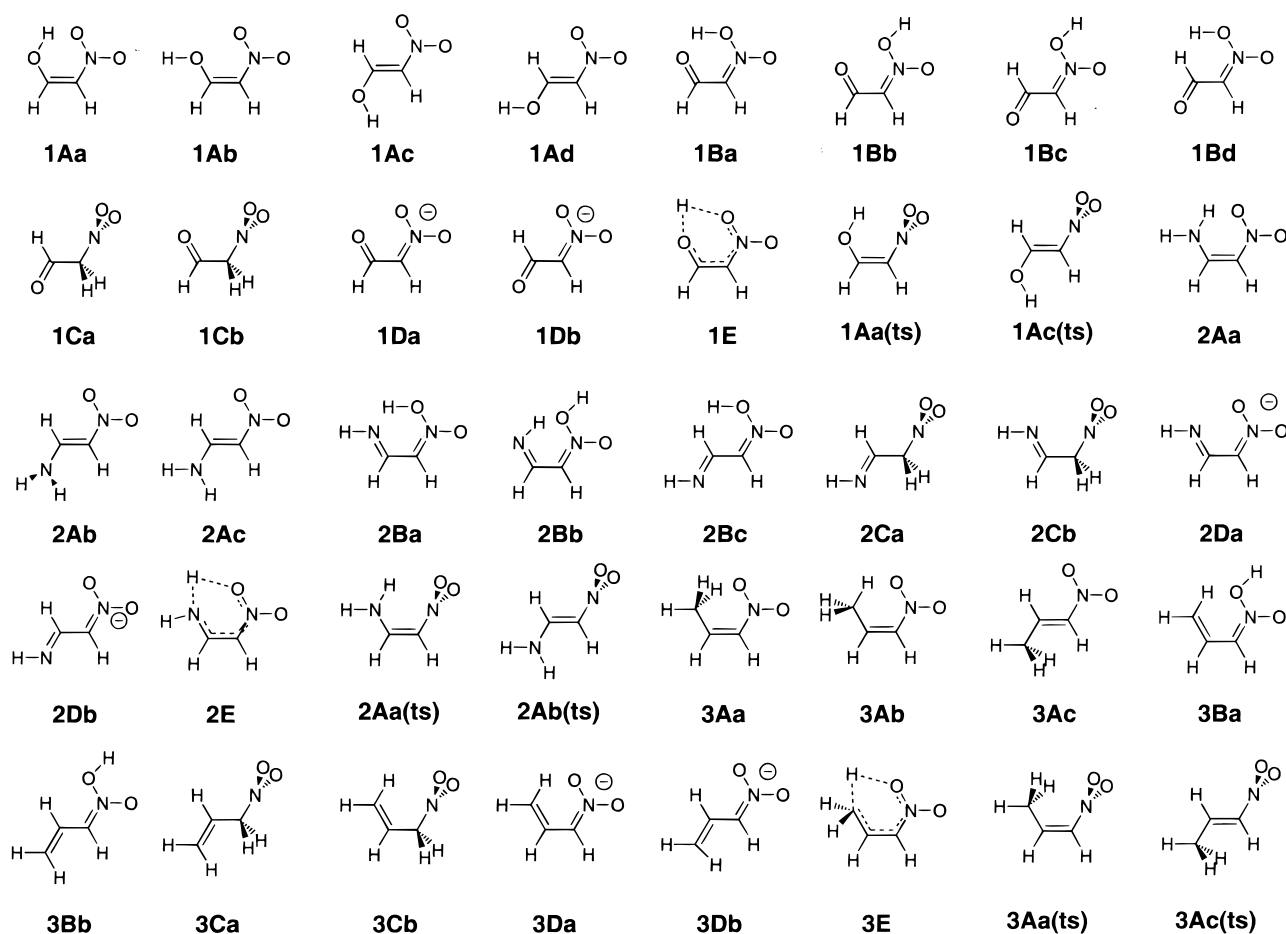
(20) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1. (c) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(21) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.



**Figure 2.** Selected geometric parameters for **1Ba**, **2Ba**, and **3Ba** at MP2/6-31G\* and B3LYP/6-31G\* (underlined). Distances are in angstroms and angles in degrees.

### Scheme 3



6-311+G\*\* and MP4(SDTQ)/6-31G\* using the B3LYP and MP2(full)/6-31G\* geometries, respectively, to obtain better estimates of relative energies. G2MP2 theory was used to obtain more accurate absolute energies on selected structures. Tables 1s–3s summarize the absolute energies (Supporting Information). Relative energies for all isomers and anions are summarized in Tables 1–3. Bonding properties were investigated at MP2(full)/6-31G\* with Bader's topological one-electron density analysis.<sup>23</sup> Bond critical points for **1–3A,B** are detailed in Table 4s (Supporting Information). Relief maps for  $\rho$  are shown in Figure 6 for **1A,B**. Throughout the discussion B3LYP/

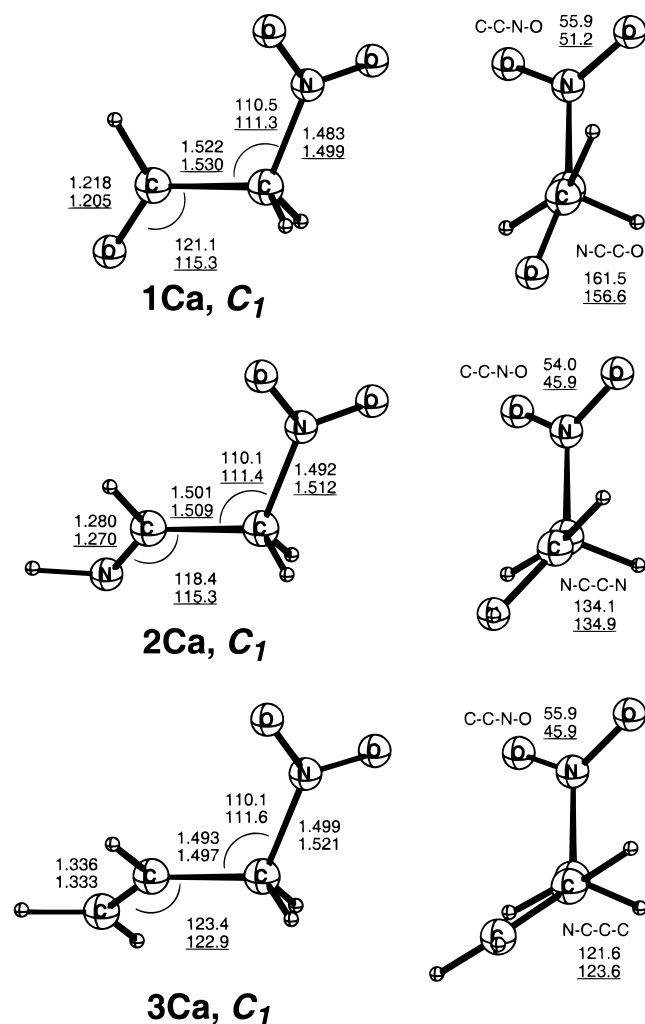
6-31G\* geometric parameters and B3LYP/6-311+G\*\* energies will be used unless indicated otherwise.

## Results and Discussion

The discussion is organized in three sections: (a) structures and energetics of stable molecules and anions, (b) 1,5-H shifts in substituted nitroethylenes, and (c) aspects of conventional keto–enol, imine–enamine, nitro-*aci*-nitro tautomerisms. Similarities and differences be-

(22) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 269.

(23) (a) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. Bader, R. F. W. In *Atoms in Molecules: A Quantum Theory*; University of Oxford Press: Oxford, 1990.



**Figure 3.** Selected geometric parameters for **1Ca**, **2Ca**, and **3Ca** at MP2/6-31G\* and B3LYP/6-31G\* (underlined) shown in two different orientations. Distances are in angstroms and angles in degrees.

tween the parent systems **1**, **2**, and **3** are the focal points in these sections.

**A. Isomers, Tautomers, and Conformers.** We start with the substituted nitroethylenes, followed by their related nitronic acids, 'aliphatic' nitro derivatives, and anions.

**1. Substituted Nitroethylenes.** A prerequisite for inducing 1,5-H-shifts is having access to *Z*-substituted derivatives. These structures **1Aa**, **2Aa**, and **3Aa** are indeed minima, which comes as no surprise in light of the maximum delocalization that results between the unsaturated groups<sup>16</sup> and the stabilizing hydrogen bonding between the olefinic OH and NH<sub>2</sub> substituents and the nitro group.<sup>24,25</sup> The strength of the H-bond can be estimated from the NO<sub>2</sub>-rotation barrier and from the differences in stabilities of both the *Z*-*E* isomers (double bond isomerism)<sup>26</sup> and the *syn*-*anti* conformers (substituent conformation).<sup>26</sup>

**cis-2-Nitrovinyl Alcohol (1A).** We start with the *syn*-conformer **1Aa** (C<sub>s</sub>), the global minimum for **1**, in which the alcohol group is directed toward the nitro group. The 15.3 kcal/mol needed for rotation around its C-NO<sub>2</sub> bond is much more than the 5.6 kcal/mol needed for the unsubstituted nitroethylene.<sup>27</sup> Attributing this enhanced barrier of 9.7 kcal/mol entirely to H-bonding seems appealing, but ignores the conjugative effect of the OH group that is evident from the difference in the NO<sub>2</sub> rotation barriers for **1Ac** (8.9 kcal/mol) and nitroethylene (5.6 kcal/mol). Incorporating this effect gives a H-bond strength of 6.4 kcal/mol.

Alternatively, C-OH bond rotation (**1Aa** → **1Ab**), which does not effect the π-delocalization between the nitro and olefinic groups, suggests a 11.9 kcal/mol H-bond strength, but ignores both the OH *syn*-*anti* effect and the O⋯O lone-pair repulsion. The *syn*-*anti* energy difference, Δ*E*(**1Ac**-**1Ad**), is a mere 0.3 kcal/mol (B3LYP) for the *E*-isomer (compared to 1 (ca. 2) kcal/mol at G1<sup>1d</sup> (exp.<sup>1</sup>) for unsubstituted vinyl alcohol). The O⋯O lone-pair repulsion in the *Z*-isomer is estimated at 4.1 kcal/mol, i.e., Δ*E*(**1Ab**-**1Ad**). Including these contributions gives a H-bond strength of 7.5 kcal/mol, which is also obtained from the energy difference of the *cis* (**1Aa**) and *trans* (**1Ac**) isomers. Averaging the values obtained by these methods gives a H-bond strength of 7.0 kcal/mol at B3LYP. At MP2 and MP4 the averaged H-bonding estimates are 6.9 and 6.5 kcal/mol, respectively.

The strong intramolecular hydrogen bond in **1Aa** is also reflected in the short O⋯H distance of 1.713 (1.775) Å at B3LYP (MP2) between the nitro and alcohol groups and the presence of a bond critical point (ρ(r) = 2.63 e.Å<sup>-3</sup>) along the O⋯H path. The relief map of ρ(r) (Figure 6a) visualizes this hydrogen bond path.

**cis-2-Nitrovinylamine (2A).** The longer O⋯H distance of 1.967 (1.992) Å at B3LYP (MP2) and the less prominent O⋯H bond critical point (Table 4s) already suggest a weaker hydrogen bond in planar **2Aa**, the global minimum for **2**, than in *cis*-2-nitrovinyl alcohol.

Indeed, only a bond strength of 4.3 kcal/mol is estimated, based on the *cis* (**2Aa**) and *trans* (**2Ab**) energy difference. An even smaller value of 3.0 kcal/mol results from their difference in C-O<sub>2</sub> bond rotation barriers—that of **2Aa** is 14.7 kcal/mol—giving an averaged H-bond strength of 3.7 kcal/mol with MP2 and MP4 values of 3.6 and 3.1 kcal/mol, respectively. These energies show that the strength of the H-bond between the NH<sub>2</sub> and NO<sub>2</sub> groups is about half of the OH⋯ONO interaction, which is also reflected in the bond critical point (ρ(r) = 0.184 e.Å<sup>-3</sup>) of its bond path. This H-bonding causes the NH<sub>2</sub> group to be planar, albeit that the N-pyramidalization angle of **2Ab** is only 2.3°. In contrast, vinylamine has a N-inversion barrier of 1.4 kcal/mol at G1 (exp. 1.1 kcal/mol).<sup>2b,28</sup> We note that the geometric parameters of **2Ab** compare well with those reported for a X-ray crystal structure determination of *trans*-*N,N*-dimethyl-2-nitroethenamine.<sup>29</sup>

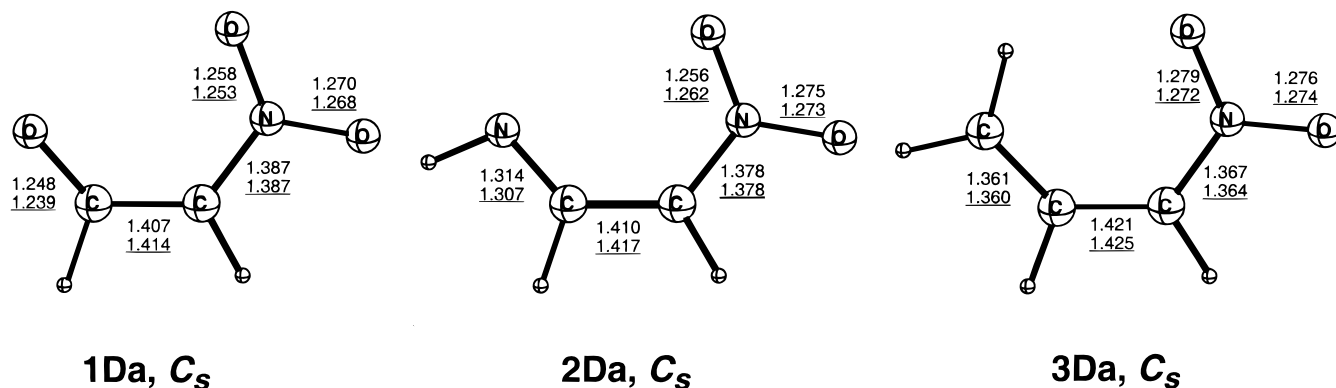
(26) (a) Luth, K.; Scheiner, S. *J. Phys. Chem.* **1994**, *98*, 3582. (b) Rovira, M. C.; Scheiner, S. *J. Phys. Chem.* **1995**, *99*, 9854. (c) Scheiner, S. *Hydrogen Bonding: A Theoretical Perspective*; Oxford University Press: New York, 1997.

(27) (a) The C-N rotation barrier was calculated from the B3LYP/6-31G\* energy differences between nitroethylene (-283.08790 au) and its rotational transition structure (-283.07729 au). (b) Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *173*, 585.

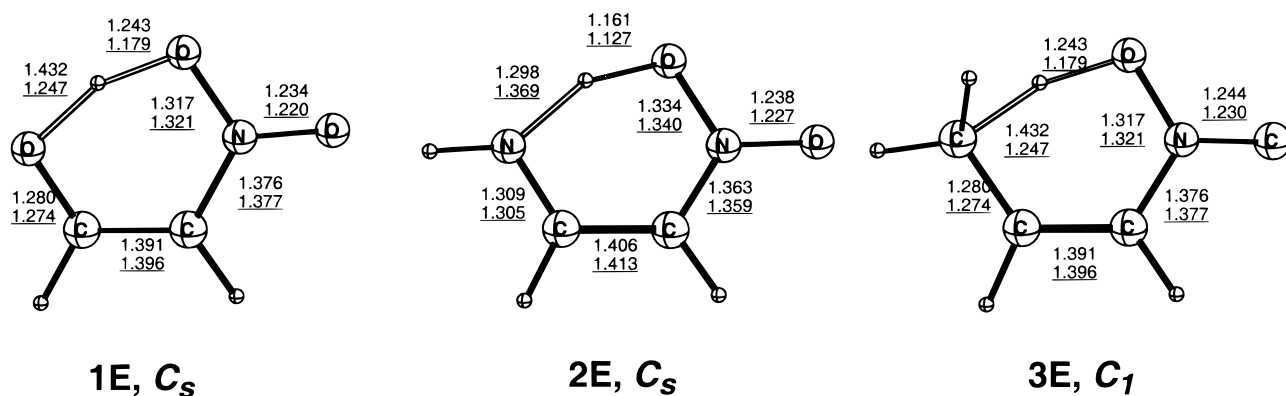
(28) (a) Prasad, B. V.; Uppal, P.; Bassi, P. S. *Chem. Phys. Lett.* **1977**, *276*, 31. (b) Prasad, B. V.; Uppal, P.; Grover, G.; Kaur, D. *THEOCHEM* **1999**, *458*, 227.

(24) (a) Varnali, T.; Aviyente, V.; Ruiz-Lopez, M. F. *Struct. Chem.* **1994**, *5*, 357. (b) Karelson, M.; Katritzky, A. R. *Int. J. Quantum Chem.* **1996**, *60*, 41. (c) Varnali, T.; Hargittai, I. *THEOCHEM* **1996**, *383*, 315.

(25) (a) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098. (b) Parrondo, R. M.; Karafiloglou, P.; Pappalardo, R. R.; Marcos, E. S. *J. Phys. Chem.* **1995**, *99*, 6461.



**Figure 4.** Selected geometric parameters for **1Da**, **2Da**, and **3Da** at MP2/6-31G\* and B3LYP/6-31G\* (underlined). Distances are in angstroms and angles in degrees.



**Figure 5.** Selected geometric parameters for **1E**, **2E**, and **3E** at MP2/6-31G\* and B3LYP/6-31G\* (underlined). Distances are in angstroms and angles in degrees.

**Table 1. Relative Energies (in kcal/mol) of Nitrovinyl Alcohol, **1**, and Its Conformers, Tautomers, and Anions**

structure	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	B3LYP/6-31G*	B3LYP/6-311+ G**	G2MP2
<b>1Aa</b>	0.0	0.0	0.0	0.0	0.0	0.0
<b>1Ab</b>	11.6	12.3	11.9	13.7	11.9	
<b>1Ac</b>	5.6	7.4	7.1	8.6	7.5	
<b>1Ad</b>	6.5	8.5	8.1	9.5	7.8	
<b>1Ba</b>	8.9	4.7	5.4	3.5	4.1	5.1
<b>1Bb</b>	13.7	12.7	12.3	12.9	12.9	
<b>1Bc</b>	10.1	10.0	9.3	10.3	9.6	
<b>1Bd</b>	22.5	18.9	18.3	18.2	16.9	
<b>1Ca</b>	-4.0	-3.4	-4.6	2.1	3.9	0.4
<b>1Cb</b>	-2.2	-2.6	-3.6	3.7	5.3	
<b>1Da</b>	347.1	346.0	348.0	347.1	336.2	332.5
<b>1Db</b>	340.2	340.4	342.3	341.5	330.2	326.7
<b>1E</b>	14.0	7.3	9.0	4.8	5.0	4.0
<b>1Aa (ts)</b>	15.4	14.3	13.7	18.9	15.3	
<b>1Ac (ts)<sup>a</sup></b>	10.7	8.0	7.8	10.3	8.9	

<sup>a</sup> Relative to **1Ac**.

**1-Nitropropene (3A).** The CH<sub>3</sub>-staggered form (**3Aa**) is the preferred conformation for the *Z*-isomer with a CH<sub>3</sub>-rotation barrier of 0.9 kcal/mol, implying an absence of H-bonding. The smaller C–NO<sub>2</sub> rotation barrier (3.7 kcal/mol) than in nitroethylene (5.6 kcal/mol) even signals a slight repulsion between the NO<sub>2</sub> and CH<sub>3</sub> groups. A van der Waals interaction between these groups is suggested by the electron density analysis (see Table 4s), which is not surprising given the 2.278 Å O⋯H distance. In fact, the *E*-isomer (**3Ac**) is more stable by 2.7 kcal/mol.

**2. Conjugated Nitronic Acids.** Again, the tautomers are discussed by substituent (O, N, C) with focus on H-bonding and relative stabilities. Only the most relevant isomers and conformers are used from the many that are possible due to the syn/anti arrangement of the nitronic acid group.

**$\beta$ -Ketonitronic Acid (1B).** Structure **1Ba**, having an *anti*-ONOH group and an *s-cis* conformation for the conjugated unsaturated functionalities, is the preferred nitronic acid. It is only 4.1 kcal/mol less stable than nitro isomer **1Aa**. The 1.565 Å short O⋯H distance in **1Ba** and the critical point data ( $\rho(\mathbf{r}) = 2.033 \text{ e } \text{\AA}^{-3}$ ,  $H(\mathbf{r}) = -3.126 \text{ Hartree } \text{\AA}^{-3}$ ) of its bond path, visualized in Figure

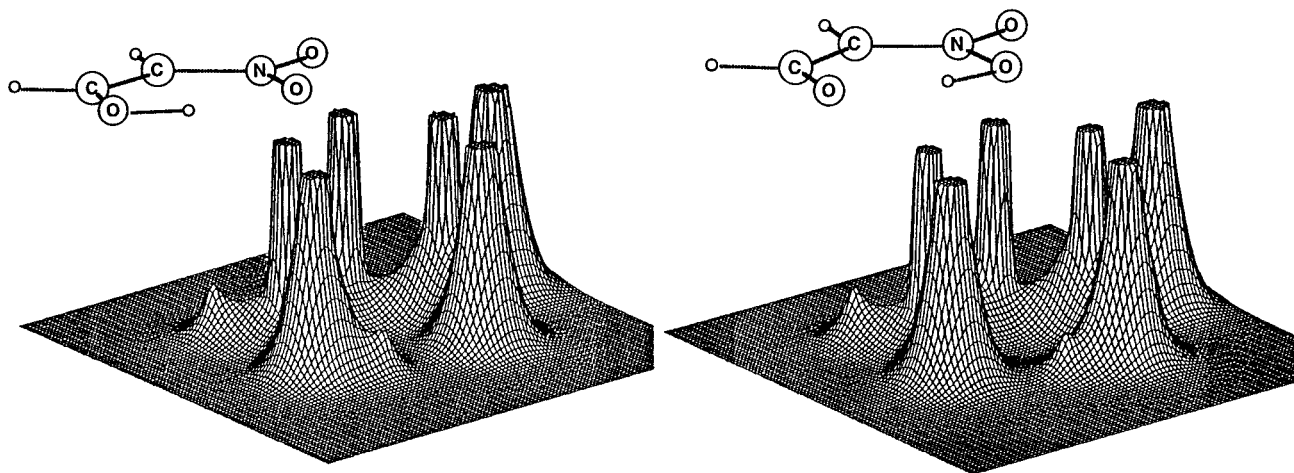


Figure 6. Relief maps of  $\rho(\mathbf{r})$  at MP2(full)/6-31G\* for (a) **1Aa** and (b) **1Ba**.

Table 2. Relative Energies (in kcal/mol) of Nitrovinylamine, **2**, and Its Conformers, Tautomers, and Anions

structure	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	B3LYP/6-31G*	B3LYP/6-311+G**	G2MP2
<b>2Aa</b>	0.0	0.0	0.0	0.0	0.0	0.0
<b>2Ab</b>	2.7	4.2	3.7	4.5	4.3	
<b>2Ac</b>	2.7	4.4	4.1	4.5	4.3	
<b>2Ba</b>	19.9	14.0	14.5	13.4	13.0	12.7
<b>2Bb</b>	19.7	18.5	16.6	19.2	19.0	
<b>2Bc</b>	32.9	29.3	27.4	28.8	27.3	
<b>2Ca</b>	4.7	4.5	2.5	10.3	12.4	7.3
<b>2Cb</b>	7.4	6.2	4.4	12.8	14.5	
<b>2Da</b>	370.5	367.6	368.8	368.4	357.2	350.5
<b>2Db</b>	360.8	359.2	360.3	360.0	348.5	342.3
<b>2E</b>	25.1	15.3	16.7	13.6	13.2	11.2
<b>2Aa (ts)</b>	14.3	12.6	11.6	16.4	14.7	
<b>2Ab (ts)<sup>a</sup></b>	12.6	9.7	9.1	12.9	11.7	

<sup>a</sup> Relative to **2Ab**.

Table 3. Relative Energies (in kcal/mol) of 1-Nitropropene, **3**, and Its Conformers, Tautomers, and Anions

structure	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	B3LYP/6-31G*	B3LYP/6-311 + G**	G2MP2
<b>3Ac</b>	0.0	0.0	0.0	0.0	0.0	0.0
<b>3Aa</b>	3.1	2.2	2.2	2.5	2.7	2.3
<b>3Ab</b>	3.4	2.9	2.9	2.6	2.6	
<b>3Ba</b>	21.5	21.4	20.9	17.3	12.8	13.9
<b>3Bb</b>	18.1	18.8	18.3	14.7	9.9	
<b>3Ca</b>	3.4	3.1	3.0	5.2	3.8	2.9
<b>3Cb</b>	5.7	4.7	4.7	7.3	5.8	
<b>3Da</b>	371.0	367.5	370.5	365.1	349.6	346.4
<b>3Db</b>	367.9	366.0	368.8	362.8	347.5	345.1
<b>3E</b>	61.1	44.4	47.7	39.8	37.8	39.6
<b>3Ac (ts)</b>	8.1	6.1	5.9	7.7	6.6	
<b>3Aa (ts)<sup>a</sup></b>	5.0	3.5	3.5	5.1	3.7	

<sup>a</sup> Relative to **3Aa**.

6b, imply strong H-bonding. Its strength can be estimated by rotation of the nitronic acid's OH group as well as by *s-cis* → *s-trans* rotation of the C=O and C=N groups around the C–C bond.

Changing to a *syn*-ONOH conformation raises the energy by 8.8 kcal/mol (8.0 and 6.9 kcal/mol at MP2 and MP4, respectively). Instead, nitromethane prefers the *syn*-ONOH form by 7.1 (6.8) kcal/mol at B3LYP (G1),<sup>2a</sup> which suggests an upper value of 15.9 kcal/mol for H-bonding in **1Ba**. Correcting for the 3.3 kcal/mol O⋯O lone-pair repulsion, based on the energetic preference of the *s-cis* over the *s-trans* conformation, gives a final H-bond strength of 12.6 kcal/mol. A nearly identical estimate of 12.8 kcal/mol results from the energy difference between **1Ba** and **1Bd**, both with *anti*-ONOH

groups. The corresponding MP2 and MP4 values are 14.2 and 12.9 kcal/mol. Evidently, H-bonding in the nitronic acid is much stronger than in *cis*-nitrovinyl alcohol **1Aa**.

**β-Iminonitronic Acid (2B)**. The imine derivative also prefers an *s-cis* conformation (**2Ba**), in analogy with  $\beta$ -ketonitronic acid **1Ba**, but it has a much larger energy difference (13.0 kcal/mol) with its nitro tautomer (**2Aa**). Still, the short O⋯H distance of 1.548 Å suggests significant H-bonding, which is also evident from the bond critical point data, i.e.,  $\rho(\mathbf{r}) = 2.077 \text{ e } \text{Å}^{-3}$ ,  $H(\mathbf{r}) = -3.374 \text{ Hartree } \text{Å}^{-3}$ . Its strength is estimated at 13.1 kcal/mol, based on the 6.0 kcal/mol energy difference between **2Ba** and **2Bb** and the 7.1 kcal/mol preference for the *syn*-ONOH conformation. The H-bond strength, calculated as the energy difference between the *s-cis* and

*s-trans* conformations ( $\Delta E = \mathbf{2Ba} - \mathbf{2Bc}$ ), is similar and amounts to 14.3 kcal/mol, giving an average value of 13.7 kcal/mol. The corresponding MP2 and MP4 values are 13.4 and 11.1 kcal/mol, respectively.

**3-Propylenenitronic Acid (3B).** The energy difference between *cis*-1-nitropropene **3Aa** and nitronic acid **3Ba** is 10.1 kcal/mol. The structure has a *syn*-ONOH arrangement because of steric congestion due to the neighboring methylene group. Consequently, structure **3Ba** displays no H-bonding and, in fact, the *s-trans* form **3Bb** is even 2.9 kcal/mol more stable. In passing, we note that 1,3-butadiene and  $X=C-C=X$ , ( $X = \text{NH, PH}$ ) prefer twisted *s-cis* forms with planarization barriers of ca. 2 kcal/mol.<sup>30</sup>

**3. Nonconjugative Nitro Derivatives.** Of the remaining tautomers nitroacetaldehyde (**1C**), nitroacetalimine (**2C**), and 3-nitropropene (**3C**), we highlight only features specific to these compounds because acetaldehyde, acetalimine, nitromethane, and propene have already been discussed extensively in the literature. These compounds can only have *anticlinal* and *synperiplanar* conformations (Figure 3) due to the gearing effect around the C–C and C–N single bonds. Of these the *anticlinal* form is preferred by 1.4, 2.1, and 2.0 kcal/mol for **1C**, **2C**, and **3C**, respectively. Its NCCX ( $X = \text{O, N, C}$ ) torsion angle becomes more pronounced on going from **1Ca** (156.6°) to **2Ca** (134.9°) to **3Ca** (123.6°), while the twists of the NO<sub>2</sub> group are similar ( $\angle \text{CCNO} = 46 - 51^\circ$ ), resulting in a nearly fully eclipsed conformation for the propene derivative. Of the *synperiplanar* arrangements the nitrogen of the NO<sub>2</sub> group of only **3Cb** deviates (14°) from the carbon plane, while all three structures have similar NO<sub>2</sub> rotations, i.e., 89° for **1Cb**, 90° for **2Cb**, and 73° for **3Cb**. None of the geometrical parameters of these structures displays any sign of delocalization between the two functional groups.

These nonconjugated nitro derivatives (*anticlinal* forms) are less stable than the conjugated global minima, but the energy differences are only 3.9 (0.4) kcal/mol for nitroacetaldehyde (**1Ca**) and 3.8 (2.9) kcal/mol for 3-nitropropene (**3Ca**) at B3LYP (G2MP2). Apparently, these systems are stabilized by a significant substituent effect. A larger difference of 12.4 (7.3) kcal/mol is obtained for nitroacetalimine (**2Ca**), which is also more sensitive to the theoretical method employed.

**4. Conjugated Anions.** Deprotonation of any of the tautomeric structures gives anions in which the charge is delocalized. This delocalization is reflected in the geometries of anions **1D**, **2D**, and **3D** (Figure 4). These favor a *s-trans* (**Db**) over a *s-cis* (**Da**) conformation by 6.0 (5.8), 8.7 (8.2), and 2.1 (1.3) kcal/mol at B3LYP (G2MP2), respectively. This *s-trans* preference of **1Db** and **2Db** results from the lone pair repulsion of the carbonyl and imine groups, respectively, with the NO<sub>2</sub> group. Because significant charge is located on the nitro group of these anions (Table 5s), they may even be viewed as nitronates.

The G2MP2 ionization energies for the global minima of *cis*-2-nitrovinyl alcohol, *cis*-2-nitrovinylamine, and *cis*-1-nitropropene to give the conjugated anions are 326.7, 342.3, and 345.1 kcal/mol, respectively. They are much lower than the 366.2, 378.6, 356.9, and 388.7

kcal/mol for acetaldehyde, acetalimine, nitromethane, and propene, respectively (similar G1 and G2 energies have been reported).<sup>2b</sup> Nitro substitution in these systems, because of its electron-withdrawing nature, clearly increases the acidity, thereby facilitating acid–base directed tautomerism.

**B. Sigmatropic 1,5-Hydrogen Transfer.** This pericyclic process concerns tautomerism between the above-discussed conjugated nitro derivatives and nitronic acids. G2MP2 energies used in this section (in parentheses) are without ZPE corrections to eliminate bias in discussing low activation energies.

*cis*-2-Nitrovinyl alcohol (**1Aa**) and  $\beta$ -ketonitronic acid (**1Ba**) differ in energy by only 4.1 (5.7) kcal/mol. Both have strong H-bonds, estimated at 7.0 and 12.7 kcal/mol, respectively, illustrating their close relationship. It is then not surprising that H-transfer is an extremely facile process with a **1Aa**  $\rightarrow$  **1Ba** barrier of 5.0 (7.1) kcal/mol and only 0.9 (1.4) kcal/mol for the reverse process. Expectantly, transition structure **1E** (Figure 5) shows similarities with both minima.

The energy difference of 13.0 (12.7) kcal/mol between *cis*-2-nitrovinylamine (**2Aa**) and  $\beta$ -iminonitronic acid (**2Ba**) is much larger, but also in this case both structures have distinct hydrogen bonds estimated at ca. 3.7 and 13.7 kcal/mol, respectively. H-transfer from the nitronic acid to the more stable nitro tautomer is, however an extremely facile process, requiring only 0.2 (1.2) kcal/mol, emphasizing the low kinetic stability of the nitronic acid. The geometrical parameters of transition structure **2E** (Figure 5) relate to those of the nitronic acid.

*cis*-1-Nitropropene (**3Aa**) and 3-propylenenitronic acid (**3Ba**) have also a rather large energy difference of 10.1 (11.6) kcal/mol. However, neither structure displays signs of H-bonding implying that the concerted H-transfer is energetically a much more demanding process than in the other two systems. The required methyl-group rotation in **3Aa** to enable H-transfer and the subsequently needed N–OH bond rotation to give nitronic acid **3Ba** also suggest a high barrier. Indeed, this barrier is estimated at a large 35.1 (40.2) kcal/mol. Transition structure **3E** (Figure 5) shows an out-of-plane motion for the transferring hydrogen. Following its intrinsic reaction coordinate in both directions confirmed **3E** as the transition structure for H-transfer.

Comparison between the sigmatropic 1,5 hydrogen shifts of **1**, **2** and **3** shows the tautomerism to be a facile process for **1**, does not lead to a kinetically stable nitronic acid tautomer in the case of **2**, and is a high energy process for **3**.

**C. Conventional Tautomerism.** Acid–base-induced 1,3 hydrogen shifts underlie the common keto  $\rightleftharpoons$  enol, imine  $\rightleftharpoons$  enamine and nitro  $\rightleftharpoons$  *aci*-nitro tautomeric processes in organic chemistry. The data of the present study enable an evaluation of the nitro, keto, imine, and vinyl substituent effects on these tautomerisms. Without substituents the equilibria favor the keto, imine, and nitro isomers as has been established in several theoretical studies.<sup>2</sup> Table 4 summarizes the B3LYP and G2MP2 energy differences for these parent acetaldehyde  $\rightleftharpoons$  vinyl alcohol, acetalimine  $\rightleftharpoons$  vinylamine, and nitromethane  $\rightleftharpoons$  *aci*-nitromethane tautomeric pairs. They compare well with reported G1/G2 energy differences for these systems.<sup>2a,b</sup> These earlier studies showed that the  $\Delta E$  values decrease with improved levels of theory. The illustration of this trend is not repeated here. Table 4

(30) (a) Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* **1991**, *113*, 7929. (b) Bharatam, P. V.; Kumar, R. S.; Mahajan, M. P. *Perkin Trans. 2*, submitted for publication.

**Table 4.** B3LYP/6-311+G\*\* (G2MP2) Energy Differences between Tautomers and the Influence of the NO<sub>2</sub>, CHO, CHNH, and Vinyl Substituent Effects<sup>a</sup>

	-H	-NO <sub>2</sub>	-C(H)=O	-C(H)=NH	-C(H)=CH <sub>2</sub>
$\Delta E$					
keto $\rightleftharpoons$ enol	10.4 (11.1)	-3.9 (-0.4)			
imine $\rightleftharpoons$ enamine	2.3 (4.0)	-12.4 (-7.3)			
nitro $\rightleftharpoons$ <i>aci</i> -nitro	14.1 (14.6)		0.2 (4.7)	0.6 (5.4)	9.0 (11.0)
substituent effect					
keto $\rightleftharpoons$ enol		14.3 (11.5)			
imine $\rightleftharpoons$ enamine		14.7 (11.3)			
nitro $\rightleftharpoons$ <i>aci</i> -nitro			13.9 (9.9)	13.5 (9.2)	5.1 (3.6)

<sup>a</sup> Energies are in kcal/mol.

also lists the energy differences for the nitro derivatives of the tautomeric pairs. For brevity, the HF, MP2, and MP4 data are not tabulated as the trends in decreasing  $\Delta E$  values are similar to those for the nonsubstituted pairs. The G2MP2 energies show that the NO<sub>2</sub> substituent effect is 11.5 kcal/mol for the keto/enol tautomeric pair and essentially the same (11.3 kcal/mol) for the imine/enamine pair. While very similar values are obtained at lower levels of theory, the respective NO<sub>2</sub> substituent effects of 14.3 and 14.7 kcal/mol obtained at B3LYP are slightly larger. The energetic preference of 1- over 3-nitropropene amounts to only 2.9 kcal/mol at G2MP2, and 3.8 kcal/mol at B3LYP. We consider the G2MP2 values to be the more accurate ones and assume that B3LYP slightly overestimates the NO<sub>2</sub>-stabilization.<sup>31</sup>

The significant NO<sub>2</sub> substituent effect in favor of the enol and imine forms has two contributors, i.e., intramolecular H-bonding and  $\pi$ -resonance delocalization. The resonance effect in the enol and imine can be obtained by subtracting the H-bond strengths (using average values from section A) from the NO<sub>2</sub> substituent effect. We perform this analysis at B3LYP and MP4 (given in parentheses) as not all data needed for G2MP2 analysis are available.

Subtracting the H-bond strength of 7.0 (6.5) kcal/mol from the 14.3 (12.6) kcal/mol NO<sub>2</sub> substituent effect gives a NO<sub>2</sub>  $\pi$ -resonance effect of 7.3 (6.1) kcal/mol for enol **1Aa**. The magnitude of this resonance effect compares well with the slightly larger 8.9 (7.8) kcal/mol for the NO<sub>2</sub> rotation barrier of **1Ac**. Likewise, subtracting the 3.7 (3.1) kcal/mol H-bond strengths from the 14.7 (11.0) kcal/mol NO<sub>2</sub> substituent effect for the imine/enamine tautomeric pair gives a  $\pi$ -resonance effect of 11.7 (7.9) kcal/mol for enamine **2Aa**. Again a good comparison is obtained with the rotation barrier of 11.0 (9.1) kcal/mol for **2Ab**. Apparently, because H-bonding is stronger in the enol and the  $\pi$ -resonance is more prominent in the imine, the NO<sub>2</sub> substituent effect is coincidentally the same for the enol and imine forms. We realize that neither  $\sigma$ -substituent effects nor steric factors were included in this analysis. The difference between the NO<sub>2</sub> substituent effect of 3.8 (3.0) kcal/mol for propene and the 6.6 (5.9) kcal/mol rotation barrier for **3Ac** may be illustrative of their contributions.

The influence of the keto, imine, and vinyl groups on the nitro  $\rightleftharpoons$  *aci*-nitro tautomerism can be determined in a manner similar as discussed above for the nitro substituent effect. Table 4 summarizes these substituent effects at B3LYP and G2MP2. Expectantly, the preference for the nitro derivatives reduces substantially by

stabilizing the nitronic acid through H-bonding and conjugation. We find similarly large keto and imine substituent effects of 13.9 (9.9) and 13.5 (9.2) kcal/mol, respectively: G2MP2 values are in parentheses. The magnitude of these effects largely results from the strong H-bonding of 12.6 and 12.9 kcal/mol in **1Ba** and **2Ba**, respectively. Consequently, the deduced resonance stabilization for the conjugated systems is small, 1.4 and 0.5 kcal/mol for the keto and imine groups, respectively, smaller than the 3.0 (3.6) kcal/mol vinyl substituent effect.

Finally, we briefly comment on the influence of substituents on the reactivity of nitroalkenes, which are used as dienes in Michael additions for the synthesis of delicate heterocycles.<sup>32</sup> Earlier studies mainly focused on the influence of the  $\alpha$ -substituent,<sup>32c</sup> but changing the  $\beta$ -substituent is also expected to modify the reactivity profile of the nitroalkene (or nitronate anion). The NPA<sup>33</sup> group charge distribution for the olefinic units of **1A-3A** (Table 5s, Additional Material) shows that on  $\beta$ -substitution (CH<sub>3</sub>  $\rightarrow$  NH<sub>2</sub>  $\rightarrow$  OH) the positive (group) charge reduces modestly at the  $\alpha$ -center with a concurrent strong increase at the  $\beta$ -center. Thus, the Michael (diene) acceptor ability of nitroethylenes is expected to increase with more electronegative  $\beta$ -substituents.

## Conclusions

Strong interrelationships are demonstrated for the prototypic keto  $\rightleftharpoons$  enol, imine  $\rightleftharpoons$  enamine, and nitro  $\rightleftharpoons$  *aci*-nitro tautomeric processes in  $\beta$ -substituted 1-nitroalkenes. Hydrogen bonding and substituent effects profoundly impact the tautomeric equilibria. The following specific conclusions are made:

(1) The  $\beta$ -OH,  $\beta$ -NH<sub>2</sub>, and  $\beta$ -CH<sub>3</sub> cis-substituted nitroethylenes are global minima.

(2) The NO<sub>2</sub>-substituent effect on the enol and enamine forms of the keto  $\rightleftharpoons$  enol and imine  $\rightleftharpoons$  enamine tautomers is about 11.4 kcal/mol for both. The NO<sub>2</sub> group reduces the keto  $\rightleftharpoons$  enol energy difference from 11.1 to -0.4 kcal/mol, favoring the enol form. Likewise it reverses the 4.0 kcal/mol energy difference for the imine  $\rightleftharpoons$  enamine pair to favor the enamine form by 7.3 kcal/mol. The conjugated 1-nitropropene is 2.9 kcal/mol more stable than the 3-nitro isomer.

(3) The HC=O, HC=NH, and HC=CH<sub>2</sub> substituent effects stabilize the nitronic acid tautomer of the nitro  $\rightleftharpoons$  *aci*-nitro pair by 9.9, 9.2, and 3.6 kcal/mol, respectively.

(32) (a) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137. (b) Denmark, S. E.; Hurd, A. R. *J. Org. Chem.* **1998**, *63*, 3045. (c) Barrett, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95.

(33) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(31) Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1997**, *101*, 7426.



(4) Intramolecular H-bonding is a major contributor to these substituent effects. The strength of the H-bond is 7.0 and 3.7 kcal/mol for the OH and NH<sub>2</sub> substituted nitroethylenes, respectively, and about 13 kcal/mol for the related nitronic acids of both. The H-bonds are characterized by critical points on correspondingly short O...H and N...H bond paths.

(5) The 5.0 kcal/mol barrier for intramolecular H transfer in 2-nitrovinyl alcohol makes the tautomeric process very facile. Tautomerism does not lead to a kinetically stable nitronic acid in the case of 2-nitrovinylamine, because its barrier of 13.2 kcal/mol for 1,5-H transfer is similar to the energy difference between the tautomers. Tautomerism by intramolecular H-transfer is a much more demanding process in 1-nitropropene with a barrier of 37.8 kcal/mol.

(6) The NH<sub>2</sub> group shows a slightly stronger conjugative stabilization than the OH group.

(7) 2-Nitrovinyl alcohol, 2-nitrovinylamine, and 1-nitropropene have low ionization energies of 326.7, 342.3, and 345.1 kcal/mol, respectively.

(8) Throughout, the B3LYP/6-311+G\*\* relative energies are slightly larger than the G2MP2 energies.

**Acknowledgment.** This work was supported by grant F49620-96-1-0450 from the Air Force Office of Scientific Research and contract F08635-90-K-0204 with the Energetic Materials Branch, Armament Directorate, Wright Laboratory at Eglin Air Force Base, to KL. The authors thank Prof. T. P. Hamilton for enlightening discussions and helpful comments.

**Supporting Information Available:** Tables 1s–3s, absolute energies of all the structures; Table 4s, bond critical point data of **1Aa**, **2Aa**, **1Ba**, and **2Ba**; Table 5s, NPA group charges. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO000283D