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Concerted Mechanisms for the Thermal Dissociation of $X_2N{-}NX_2$ Molecules ($X = NH_2$, SH) into Conjugated NX_2 π-Radicals

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The decomposition of substituted hydrazine molecules N_2X_4, in which X is a π-donor substituent, leads to two conjugated NX_2 π-radicals.[1] If X is a single-faced ($X = NR_2$) or a double-faced π-donor with two nonequivalent lone pairs (X = SR), the cleavage of the N−N bond may be accompanied by a rotation of each π-donor substituent around the adjacent N−X bond. The purpose of this Communication is to show, both by qualitative MO analysis (extended Hückel method) and by ab initio calculations, that there is one mechanism for which the concerted rotation of π-donor substituents is strongly favored.

Let us consider first the $N_2(NH_2)_4$ molecule in its trans conformation. The structure with the NH_2 groups perpendicular to the N−N−N plane of each $N(NH_2)_2$ unit (**1**) is found more stable by 0.85 eV (EH calculations)[2,3] than that in which these groups are rotated by 90° to become coplanar with one of the N−N−N planes.[4] In the radicals formed upon dissociation, these groups are rotated by 90°, so that the terminal lone pairs are parallel to the central nitrogen p orbital (**2**). This conformation is more stable by 1.5 eV than that with the NH_2 groups perpendicular to the N−N−N planes.[4] Therefore, the N−N central bond breaking is accompanied by a rotation of the amino groups (Scheme 1). Starting from structure **1**, five concerted mechanisms have been studied (Chart 1). EH calculations have been performed within the following geometrical model:[5,6] the N−N bond is lengthened by steps of 0.2 Å, and, at the same time, each NH_2 group is rotated by 15°. At each point, the angle between the central N−N bond and the N−N−N plane of the $N(NH_2)_2$ units is optimized.

The total energy curves associated with the five reaction paths are reported in Figure 1. These curves reveal that one of the mechanisms (DISR1) is much more favored than the others. An electronic factor associated with the way the NH_2 groups are rotated is revealed by the simplified orbital correlation diagrams[7] given in Figure 2 for the easiest (DISR1) and the most unfavorable (DISR3) pathways. In these diagrams, only the lowest unoccupied MO (σ_{NN}^*) and the highest occupied MO of same symmetry are reported. In the first mechanism (DISR1), the σ_{NN}^* vacant orbital of **1** correlates with the highest π orbital of the products (the out-of-phase combination (π_3^-) of the antibonding π_3 orbitals of the allyl-like radicals[8]), and the occupied MO correlates with a lower energy orbital of the products. On the contrary, in the mechanism DISR3, σ_{NN}^* in **1** tends to correlate[9] with a low-lying occupied orbital of the radicals and the occupied orbital with the π_3^- one. Since these two orbitals are of the same symmetry, the crossing is actually avoided, but, in the first part of the reaction, two electrons are strongly destabilized.

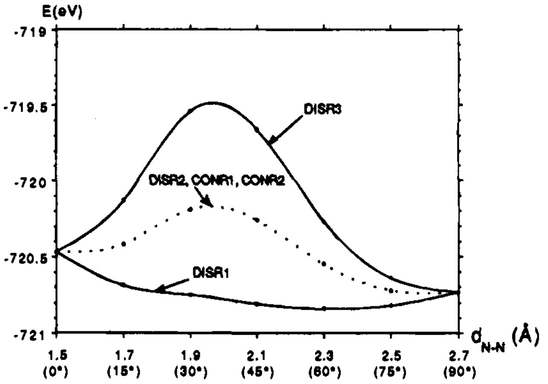


Figure 1. Total energy curves (EH calculations) for the five reaction paths (see text) studied for the dissociation of $N_2(NH_2)_4$ in its trans conformation **1** into two $N(NH_2)_2$ π-radicals.

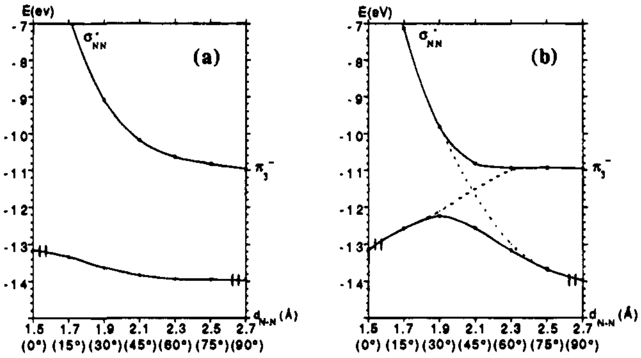
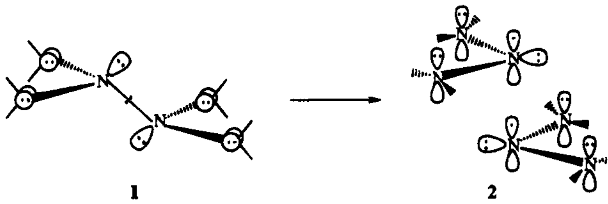


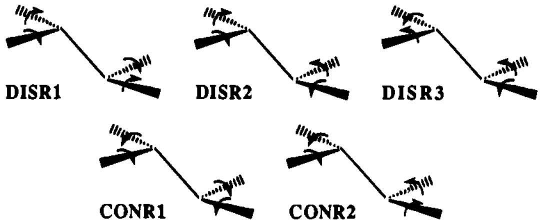
Figure 2. Simplified orbital correlation diagrams for the dissociation of $N_2(NH_2)_4$ (**1**) into two $N(NH_2)_2$ π-radicals, according to mechanisms DISR1 (a) and DISR3 (b).

Scheme 1



1 **2**

Chart 1



One can rationalize this striking difference by looking at the shape of the MOs in the reactant (Scheme 2). The σ_{NN}^* orbital, mainly concentrated on the central nitrogen atoms, is destabilized by an antibonding mixing with the terminal nitrogen lone pairs (**3**) and the occupied MO is an antibonding combination

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[1] (a) Schlosser, K.; Steenken, S. *J. Am. Chem. Soc.* **1983**, *105*, 1504. See also: (b) Miura, Y.; Makita, N.; Kinoshita, M. *Tetrahedron Lett.* **1975**, 127. (c) Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 6151. (d) Miura, Y.; Tanaka, A. *Chem. Commun.* **1990**, 441.

[2] Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; 3449; Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[3] The calculations were performed using the weighted H_{ij} formula: Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

[4] Full details on the dimer and radical structures will be given in a forthcoming paper.

[5] The following geometrical parameters were used: $N{-}NH_2 = 1.447$ Å; $N{-}H = 1.008$ Å; $H_2N{-}N{-}NH_2 = 109.7°$; $H{-}N{-}H = 111.9°$; $N{-}NH_2$ units are assumed to be planar.

[6] Atomic parameters (ξ, H_{ii}) are as follows: (1.30, −13.6 eV) for $1s_H$, (1.95, −26.0 eV) for $2s_N$, and (1.95, −13.4 eV) for $2p_N$.

[7] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[8] The monoconfigurational closed shell description of the system is inadequate for the products since π_3^+ and π_3^- (or σ_{NN}^*) MOs become degenerate and both are singly occupied. The orbital occupation given in Figure 2 is thus approximately valid only for the first part of the reaction. This is taken into account in our ab initio GVB(1,2) calculations.

[9] Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009.

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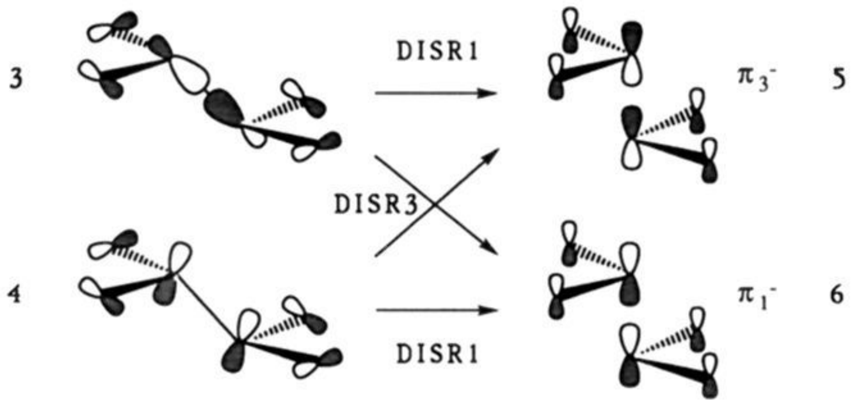
Scheme 2



of the terminal nitrogen lone pairs with the central nitrogen ones (**4**). Natural correlations in the DISR1 process connect σ_{NN}^* with π_3^- (**3** → **5**) and the occupied orbital **4** with the low-lying π_1^- orbital (**6**, the out-of-phase combination of the bonding π_1 orbitals of the allyl-like radicals), in agreement with the correlation diagram given in Figure 2a. For the DISR3 process, the reverse is true (**3** → **6** and **4** → **5**), which entails the avoided crossing pictured in Figure 2b. Similar calculations on the gauche conformation of **1** lead to the same conclusions.

Further EH optimizations show that while the NH_2 groups are actually rotated by 90° in the radicals **2**, they are rotated by 29° in the DISR1 way in the dimer **1**. Since the σ_{NN}^* orbital is very high in energy because of the short N−N distance, it is not likely that the reason why the dimer itself evolves along the DISR1 path comes only from the analysis given above for the dissociation mechanism. In fact, the rotation found in the dimer is such that the overlap between the in-phase combination of the terminal nitrogen lone pairs and the lone pair of the vicinal central nitrogen atom *vanishes* (**7** → **8** for one $N(NH_2)_2$ unit).

7

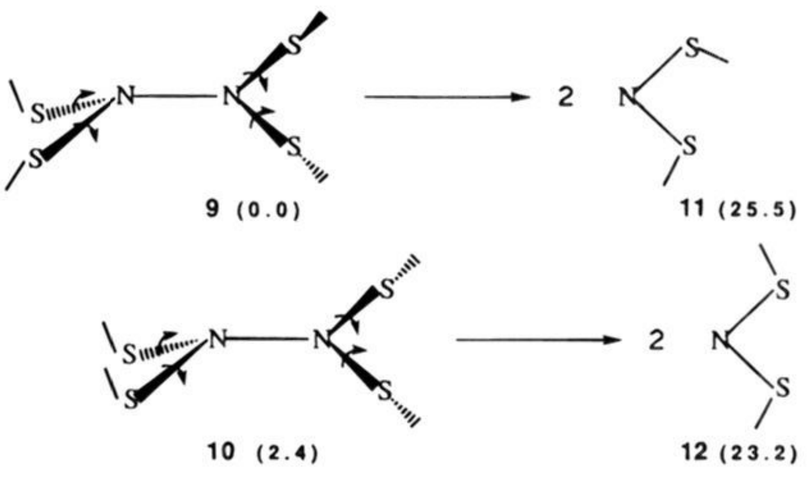
8

Since it is a four-electron repulsion, a stabilization results from this rotation, and the only way to stabilize both $N(NH_2)_2$ units is to perform a coupled rotation in the DISR1 way. The same argument can be used to explain the 90° rotation in the products: the central lone pair is now lying in the N−N−N plane, and its overlap with the terminal nitrogen lone pairs is equal to zero.

Our main qualitative conclusions are thus: (i) the DISR1 pathway is the only one which allows a natural correlation between the reactant and the products orbitals, without any energy barrier associated with an avoided orbital crossing; (ii) at the same time, this mechanism is that which minimizes the repulsion between the terminal and central nitrogen lone pairs.

We believe there is a relationship between these two factors. As a matter of fact, the occupied MO given in Figure 2 is antibonding between the central and the terminal nitrogen lone pairs (**4**), and its energy level reflects the strength of the repulsive interactions between these lone pairs. In the DISR1 mechanism, this orbital tends to correlate with the low-lying π_1^- occupied orbital (first factor), and simultaneously the overlap between the terminal and the central nitrogen lone pairs decreases (**7** → **8**, second factor). Both factors rationalize the decrease in energy of this orbital along with the DISR1 process (Figure 2a). The opposite is true for the most unfavorable pathway, DISR3, both factors resulting in a large destabilization of this orbital in the first part of this reaction path (Figure 2b). For the other mechanisms (DISR2, CONR1, and CONR2), these electronic factors are neither fully favorable (++++) nor fully unfavorable (− − − −): there are two favorable and two unfavorable interactions (various permutations of (++ − −)). As noticed by a referee, the fact that the energy curves associated with these three mechanisms are almost identical (Figure 1) shows that the electronic effects involved are approximately additive.

Ab initio calculations were performed at the GVB(1,2)/6-31G* level.[10] In the fully optimized geometry of $N_2(NH_2)_4$ (gauche conformation), the NH_2 groups are pyramidalized and already twisted around the adjacent N−N bond by about 35° in the DISR1 way,[4] as it was found by EH calculations. The central N−N bond has then been elongated, all other geometrical parameters being optimized. The dissociation energy is found to be endothermic by 25.7 kcal/mol,[11] and the overall rotation found for the NH_2 groups is that given by the DISR1 mechanism. An interesting extension is the way the related $N_2(SH)_4$ molecules dissociate into $N(SH)_2$ π-radicals. Ab initio calculations were performed on two isomers (**9** and **10**) which differ by the orientation of the S−H bonds. In each case, a full geometry optimization leads to a gauche structure for the N_2S_4 skeleton,[4] the p lone pairs on the sulfur atoms playing the role of the nitrogen lone pairs in $N_2(NH_2)_4$. As in the above example, the S−H groups are rotated in the dimer (by about 20°) in the DISR1 way.[4] The dissociation of **9** and **10** leads to *different* radicals, **11** and **12**, respectively, whose geometry is that expected from the DISR1 mechanism. What is also new in this example is that the electronic effects *overcome the steric factors*: dissociation of **9** leads to the radical products **11**, since the formation of the more stable W isomer (ΔE(**11**/**12**) = 2.3 kcal/mol) would have required a conrotatory mechanism. On the other hand, since **9** is found to be slightly more stable than **10** (by 2.4 kcal/mol), there is a crossing between the potential energy curves associated with the dissociation reactions **9** → **11** and **10** → **12**.



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(10) (a) Bobrowicz, F. B.; Goddard, W. A. In *Methods of electronic structure theory*; Schaefer, III, Ed.; Plenum Press: New York, 1977; pp 79−127. (b) Peterson, M.; Poirier, R. The MONSTERGAUSS package; Department of Chemistry, University of Toronto, Canada, 1989. 6-31G* basis set: (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(11) In previous ab initio calculations,[12] performed at a lower level than ours (SCF level in 6-31G basis set), the dissociation was found to be exothermic ($\Delta H = -4.8$ kcal/mol).[12b] Two reasons explain this discrepancy: (i) the SCF method is known to severely underestimate dissociation energies when the two fragments are calculated separately, due to the lack of correlation energy in the reactant, and (ii) the lack of polarization functions in the 6-31G basis set also leads to a poor description of the bond. Note finally that the experimental dissociation energies we have found for similar molecules are positive (endothermic reactions). For instance, it is equal to about 20 kcal/mol for $N_2F_4 \rightarrow 2NF_2$: Evans, P. J.; Tschulikow-Roux, E. *J. Phys. Chem.* **1978**, *82*, 182. Davies, P. B.; Kho, C. J.; Leong, W. K.; Lewis-Bevan, W. *Chem. Commun.* **1982**, 690.

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