

# Structural and Molecular Orbital Analyses of the Hydrazyl Cation, Radical, and Anion: A Paradigm for Stereomutations in Stereolabile Configurational Units<sup>1,2</sup>

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An analysis and classification of the stereochemical changes in stereolabile configurational units are presented, and the associated NMR consequences are discussed. It is shown that the barriers to conformational changes observed in various molecules are closely related to the electron occupancy in their  $\pi$ -systems. Thus, two-electron  $\pi$ -systems such as imines, amides, and nitrosamines have achiral torsional ground states and undergo achiral torsion ( $T_A$ ) or achiral inversion ( $I_A$ ). By contrast, four-electron systems including substituted hydroxylamines, sulfenamides, hydrazines, and other molecules with adjacent lone pairs undergo topomerization between ground structures that are chiral in principle, when maximally labeled, by either a torsion ( $T_C$ ) or inversion ( $I_C$ ) mechanism. The structural and MO analyses are described by means of the hydrazyl model system,  $NH_2NH$ , in which changes in electron occupancy alone (from the cation through the radical to the anion) bring about changes in stereochemical classification. The discussion is supported by ab initio self-consistent field MO calculations on the hydrazyl system.

## Introduction

Since the development of dynamic NMR spectroscopy the literature has seen a wealth of reports<sup>4</sup> on investigations of stereomutations of stereolabile configurational units.<sup>5</sup> Most of these stereomutations have been described simply as rotation (torsion) or inversion, although these terms oversimplify the stereochemical nature of the processes.

Often such barriers derive in substantial part from either two- or four-electron interactions, which have different stereochemical consequences.<sup>6</sup> Within the realm of electron spin resonance (ESR) spectroscopy similar processes in free radicals can be related to three-electron interactions.

It has been our purpose to provide an overall scheme that distinguishes between different barrier types on the basis of their stereochemical behavior on one hand and the underlying electronic structure, as expressed by frontier molecular orbital (FMO) analysis, on the other. The FMO analysis is supported by the results of ab initio SCF MO calculations. The stereochemical classification of barrier types makes a bridge between the electronic origin of the stereolabile configurational units and the consequent nonequivalence of diastereotopic groups in NMR and ESR spectroscopy.

To arrive at a meaningful comparison of the different stereochemical classes, we wished to examine a molecular

framework in which the various barrier types could exist depending on electron population alone. We chose the hydrazyl system as a suitable model since the hydrazyl cation, radical, and anion, which differ only by electron population, represent paradigms for two-, three-, and four-electron  $\pi$ -systems.

## Stereochemical Characterization of Hydrazyl Stereomutation

In discussing stereomutations that involve neither bond breaking nor bond making, it is appropriate to distinguish between two elementary processes: torsion and inversion. Torsion refers to a process in which changes in dihedral angles are dominant, whereas in inversion the significant change is in bond angles.<sup>7</sup>

We can also distinguish stereomutations which interconvert the configurations of chiral units (e.g., nitrogen inversion in amines), from those in which configuration is changed at achiral configurational units (e.g., *E,Z* isomerism in amides). Thus we recognize four general categories of stereomutation: chiral inversion ( $I_C$ ), chiral torsion ( $T_C$ ), achiral inversion ( $I_A$ ), and achiral torsion ( $T_A$ ). All of these processes can be exemplified within the stereochemistry of the hydrazyl system. For the sake of simplicity we shall first discuss the torsional processes,  $T_C$  and  $T_A$ .

To restrict our initial discussion to the torsional processes, we begin with a hydrazyl model that is planar at the  $NH_2$  group. We can then consider two limiting geom-

(1) This article is dedicated to Professor Kurt Mislow on the occasion of his 65th birthday.

(2) For preliminary publications see: (a) Kost, D.; Aviram, K.; Raban, M. *Isr. J. Chem.* 1983, 23, 124. (b) Raban, M.; Aviram, K.; Kost, D. *Tetrahedron Lett.* 1985, 26, 359.

(3) (a) Ben Gurion University. (b) Wayne State University.

(4) For reviews see: (a) Oki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry*; Verlag Chemie: Weinheim, 1985. (b) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982. (c) Jackman, L. M.; Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1975. (d) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 411. (e) Kalinowski, H. O.; Kessler, H. *Top. Stereochem.* 1973, 7, 295. (f) Lambert, J. B.; Featherman, S. I. *Chem. Rev.* 1975, 75, 611. (g) Shvo, Y. *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: London, 1975; Chapter 21. (h) Lambert, J. B. *Top. Stereochem.* 1971, 6, 19. (i) Lehn, J.-M. *Top. Curr. Chem.* 1970, 15, 311.

(5) Raban, M.; Kost, D. *Tetrahedron* 1984, 40, 3345.

(6) Of course steric effects are also involved in barriers to stereomutation, in addition to electronic effects. In this study we focus on the latter, as they form the basis for a general classification that is introduced.

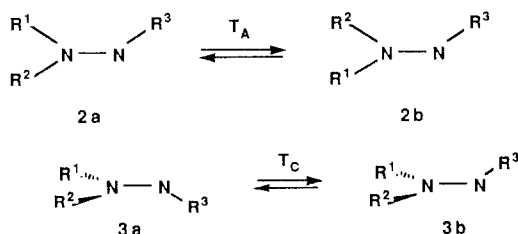
(7) (a) There are more complex stereomutations of both types that are excluded from our analysis. It is clear, for example, that the Berry mechanism for pseudorotation, which interconverts various substitution patterns at pentavalent atoms which adopt the trigonal bipyramidal geometry, involves changes in bond angles and is clearly related to inversion. Similarly the interchanges involving ring geometries, such as chair-chair interconversion in cyclohexanes (ring reversal) and pseudorotation of five-membered rings, involve dihedral angle changes and are torsional in character. The stereomutations in propeller type triarylmethanes exemplified by the one-ring flip mechanism also can be considered torsional.<sup>7b</sup> While it is clear that the one-ring flip can be described as torsional stereomutation, it is not always possible to define a configurational unit that is generated by slow one-ring flip. This situation, which has been termed "residual stereoisomerism" is clearly not covered by our categorization. We stress that this analysis is applicable only to the primitive processes. Although it will be applicable in most situations, there are many complex systems for which such an approach is not valid. (b) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* 1973, 95, 8172; 1974, 96, 3198. Mislow, K. *Acc. Chem. Res.* 1976, 9, 26.

etries, the planar geometry **1a** and the nonplanar geometry **1b**. Both hydrazyl geometries belong to point group  $C_s$ .



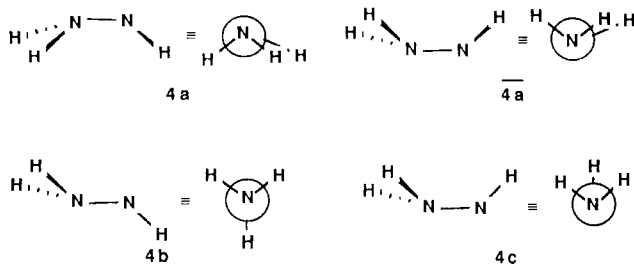
However, we describe **1a** as achiral and **1b** as chiral since these terms are appropriate for maximally labeled derivatives  $R^1R^2NNR^3$ , which correspond to point groups  $C_s$  and  $C_1$  for **1a** and **1b**, respectively. It will be made clear that maximal labeling is not necessary or even desirable in the design of experiments to measure or distinguish between the two processes, although it does provide a convenient nomenclature.

Geometries **1a** and **1b** represent typical ground and transition states for torsional barriers. If **1a** represents the ground state and **1b** represents the transition state, the barrier will be associated with an achiral torsional process ( $T_A$ ). Torsion about the N-N bond in the maximally labeled derivative will result in the interconversion of two achiral diastereomers, **2a** and **2b**. If, by contrast, the ground state is the chiral structure **1b** and the transition state is the achiral **1a**, we can describe the process as chiral torsion ( $T_C$ ). When the system is maximally labeled, torsion about the N-N bond interconverts two enantiomers (**3a** and **3b**), a process that can be described as degenerate racemization.



The interconversion **2a**  $\rightleftharpoons$  **2b** can also be accomplished by increasing the  $NNR^3$  bond angle until a transition state is reached when the angle is approximately  $180^\circ$ .<sup>8</sup> This process, which has been termed planar inversion, or in-plane shift, clearly is an inversional process, since it involves a continuous bond angle change rather than a dihedral angle change.<sup>9</sup> Since two achiral ground-state structures are interconverted by this inversion, we refer to it as achiral inversion,  $I_A$ .

To best exemplify chiral inversion ( $I_C$ ) in the hydrazyl system, we relax the constraint of our initial planar hydrazyl model to allow pyramidalization of the  $NH_2$  group. The pyramidal counterpart of **1a** is represented by structure **4a** and its enantiomer **4a**. On the other hand,



pyramidalization of **1b** can lead to two diastereomeric limiting structures, **4b** and **4c**, which have occasionally

been referred to as the Y and W forms, respectively, on the basis of the vague resemblance of their Newman projection formulas to these letters. Within the framework of our scheme we refer to the interconversions of **4a**  $\rightleftharpoons$  **4a** as well as **4b**  $\rightleftharpoons$  **4c** as chiral inversions ( $I_C$ ).

Let us now examine the manifestations of these four processes in NMR and ESR spectroscopy. When such processes are slow on the NMR or ESR time scales, we consider the slow process in a suitably substituted molecule to be associated with a stereolabile configurational unit (or proconfigurational unit).<sup>10</sup> If structure **1a** represents the ground state, the molecule will undergo an  $I_A$  or a  $T_A$  process. In the case of maximal labeling either process will lead to interconversion of diastereomers, which differ in configuration at an achiral configurational unit. Clearly maximal labeling is not necessary for observation or measurement of such a barrier by DNMR spectroscopy. If we consider an unlabeled system,  $R^1 = R^2 = R^3 = R$ , we note that two ligands, R, at the trisubstituted nitrogen are diastereotopic in geometry **1a** and should differ in NMR chemical shifts when torsion is slow on the NMR time scale but become homotopic on time average when torsion becomes rapid. Thus, the rate constant (and free energy of activation) for topomerization will correspond to those for torsion about the N-N bond. Similarly, in ESR spectroscopy we may expect the two diastereotopic R groups to exhibit different hyperfine coupling constants.<sup>11</sup>

If, on the other hand, the chiral structure **1b** (or **4b** or **4c**) represents the ground state, we deal with a  $T_C$  (and/or  $I_C$ ) process. In the maximally labeled derivative stereomutation will result in degenerate racemization, i.e., interconversion of enantiomers (**3a**  $\rightleftharpoons$  **3b**). Although labeling (i.e.,  $R^1 \neq R^2$ ) is necessary to create chirality, it is neither necessary nor sufficient in order to observe the process by magnetic resonance spectroscopy. Rather, it is necessary to incorporate either a chiral or a prochiral probe group. Consider first a prochiral group of the form  $-CX_2Y$  attached to the amino nitrogen as in **5**. The DNMR behavior of species **5** can illustrate the difference between the two barrier types. For a  $T_A$  barrier (i.e., in geometry **1a**) the two benzyl groups as a whole will be diastereotopic, while the two methylene protons within each group are enantiotopic. Upon rapid torsion about the N-N bond, the two benzyl groups will become homotopic on time average, and topomerization will be accompanied by coalescence of two singlets (one for each of the diastereotopic benzyl groups) to one singlet. For the  $T_C$  process we consider geometry **1b** (or **4b** or **4c**). Here the two benzyl groups as a whole will be enantiotopic while the two protons within each benzyl group will be diastereotopic. Torsion about the N-N bond will render the two protons within each group enantiotopic on time average, and topomerization will be accompanied by coalescence of an AB quartet to a singlet.

Observation of the dynamic process by NMR or ESR can likewise be accomplished by incorporation of a chiral

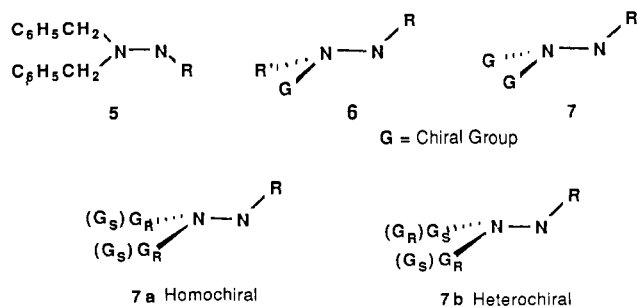
(10) (a) We prefer the term proconfigurational unit to encompass the structural features that have been referred to as prochiral and prochiral.<sup>10b</sup> As Mislow has pointed out,<sup>10c</sup> the terms chiral center and prochiral center do not actually describe symmetry characteristics but rather denote the generation of stereoisomers or topomers. Thus the terms "stereogenic unit"<sup>10c,d</sup> and "configurational unit" are synonymous and focus attention on the existence of stereoisomers which differ in configuration. (b) Hansen, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731. (c) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319. (d) McCasland, G. E. *A New General System for the Naming of Stereoisomers*; Chemical Abstracts: Columbus, OH, 1953.

(11) For a dynamic ESR spectroscopic study of substituted captodative hydrazyl radicals see: Caproiu, M. T.; Elian, M.; Grecu, N.; Negoita, N.; Balaban, A. T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 591. For the special structural features of captodative hydrazyl radicals see: Kost, D.; Raban, M.; Aviram, K. *J. Chem. Soc., Chem. Commun.* **1986**, 346.

(8) Only when  $R^1 = R^2$  will the transition state be linear. When  $R^1 \neq R^2$ , symmetry considerations require a nonlinear transition state.

(9) In a strict sense, the dihedral angle is not invariant and undergoes a discontinuous change at the transition state.

probe group, as in 6. However, in this case all four processes,  $I_A$ ,  $T_A$ ,  $I_C$ , and  $T_C$ , involve interconversion of diastereomers. In the slow-exchange situation the molecule



exists in two diastereomeric forms, regardless of whether the ground-state conformation corresponds to the achiral (1a) or chiral (1b) model structures. Thus, every NMR-active group in the molecule is diastereotopic by external comparison with respect to its counterpart in the diastereomeric molecular conformation and hence is expected to give rise to two signals in the slow-exchange limit. Rapid interconversion of diastereomers by any one of the four processes will render these diastereotopic groups homotopic on time average and isochronous, and as a result coalescence of the two (uncoupled) signals due to each group into one signal will be observed. Obviously, incorporation of a chiral group in the molecule in this manner is of little use for the determination of the barrier type and can serve only to make the conformational change observable and render the barrier height measurable.

Similar arguments hold for ESR spectroscopy of the radical, except that here we deal with nonequivalence of hyperfine coupling constants for diastereotopic nuclei.

This stereochemical analysis would not be complete without mentioning the consequences of introducing two chiral groups attached to the amino nitrogen, as in 7. The results are quite different for the chiral and achiral labile configurational units. In the achiral case (characterized by a ground state of type 1a) substitution by chiral G ligands does not differ significantly from any other R ligand substitution. Thus at the ground state the two chiral G groups, whether homo- or heterochiral, are diastereotopic, and at the slow-exchange conditions each NMR-active group in G gives rise to two signals. Rapid stereomutation by either a  $T_A$  or an  $I_A$  mechanism renders the two G groups chemical shift equivalent on time average: in the case of homochiral substitution (7a) the G groups become homotopic, while in the heterochiral case (7b) rapid interconversion renders the G groups enantiotopic. However, the NMR consequences (in achiral solvents) are identical in both cases: rapid interconversion brings about coalescence of signals due to each group in a similar manner.<sup>12</sup>

If the substituted hydrazyl system 7 constitutes a labile chiral configurational unit due to either a  $T_C$  or an  $I_C$  stereomutation, 7a and 7b will behave differently. At the slow-exchange limit 7a belongs to  $C_1$  symmetry point group. Hence the G groups are diastereotopic, and each NMR-active set of nuclei will give rise to two equally intense signals. Upon rapid degenerate racemization by either  $T_C$  or  $I_C$ , the G groups are rendered homotopic on time average, resulting in coalescence of the two signals due to each active group.

(12) The NMR consequences of chiral substitution of amide ligands has been discussed, and in the case of three chiral ligands has been suggested as a method for distinguishing meso from *dl* secondary amines: Raban, M.; Yamamoto, G. *J. Org. Chem.* 1975, 40, 3093.

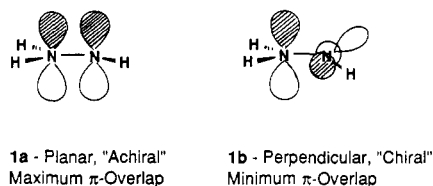


Figure 1. FMO  $\pi$ -interactions in the hydrazyl system.

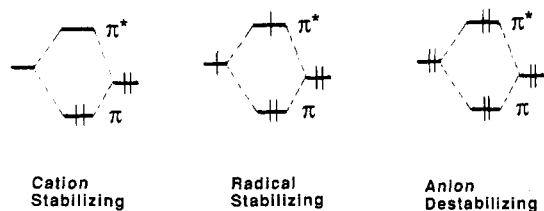


Figure 2. Electron occupancies and  $\pi$ -interactions in the hydrazyl cation, radical, and anion in geometry 1a.

Structure 7b provides an example of a *pseudoasymmetric* stereolabile configurational unit. It has  $C_s$  symmetry and hence is achiral at the slow-exchange region. The G groups are enantiotopic and isochronous. Stereomutation interconverts two meso diastereomers, the *r* and *s* isomers, which are generated by the stereolabile pseudoasymmetric unit: in the case of an  $I_C$  unit (in which exchange is dominated by slow nitrogen inversion), we deal with a pseudoasymmetric center at nitrogen; in case of a predominantly torsional process of a  $T_C$  unit, the isomers are due to the presence of a *pseudoasymmetric axis*. The G groups, which are enantiotopic within each diastereomer, are diastereotopic by external comparison of the diastereomers. Rapid stereomutation averages the signals due to the diastereomers, by rendering the G groups enantiotopic.

The *d,l* and meso isomers, 7a and 7b, can be distinguished in principle on the basis of their different NMR behavior: in both compounds stereomutation is associated with coalescence of signals due to the diastereotopic G groups; however, in 7b the exchange is between two diastereomers, i.e., between *unequally intense* signals, whereas in 7a diastereotopic groups *within* the same molecule, which are bound to be equally intense, coalesce. This idea has been utilized in sulfenamide chemistry as a method for distinguishing meso from *d,l* secondary amines.<sup>13</sup>

### Frontier Molecular Orbital Analysis

The hydrazyl model system serves to demonstrate the various stereomutation mechanisms. In this section we discuss the close correspondence between the exchange process of the stereolabile unit and its electronic structure. For the FMO analysis we view the molecule as being composed of two fragments, the amino ( $NH_2$ ) and imino ( $NH$ ) fragments. These are then conceptually connected at various conformations, and the FMO interactions between them are considered. The major frontier MOs on each fragment are the p-lone-pair orbitals. The second lone-pair orbital on the  $NH$  group is a hybrid orbital with substantial *s* character and is not effective in forming  $\pi$ -interactions. Since the major fragment interactions are of the  $\pi$ -type, we may, to a first approximation, neglect the effect of this orbital.

Let us first consider the torsional process, using structures 1a and 1b as our model system. When the two fragments are combined to form 1a, the fragment MOs are perfectly aligned for  $\pi$ -interaction (Figure 1). However,

(13) Kost, D.; Raban, M. *J. Am. Chem. Soc.* 1972, 94, 2533. Raban, M.; Lauderback, S. K.; Kost, D. *J. Am. Chem. Soc.* 1975, 97, 5178.

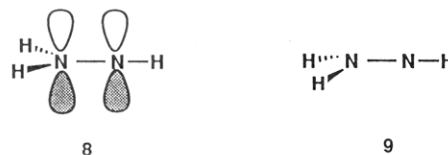
this  $\pi$ -interaction is effectively eliminated when the fragments are combined along perpendicular planes to form **1b**. Clearly the major FMO interaction, whether stabilizing or destabilizing, operates only in **1a**. Which one of the two conformations, **1a** or **1b**, is the ground state for the torsional process (and hence determines the nature of the process as either  $T_A$  or  $T_C$ ) depends now only on whether the interaction in **1a** is stabilizing or destabilizing. The answer to this question depends, in turn, on the electron occupancy in the  $\pi$ -system: in the hydrazyl cation model the  $\pi$ -orbital is doubly occupied while the  $\pi^*$ -orbital is unoccupied (Figure 2). Thus the overall  $\pi$ -interaction is a two-electron bonding interaction, and the hydrazyl cation molecule is stabilized in conformation **1a** relative to **1b**. It follows that **1a** is the torsional ground-state conformation for the hydrazyl cation and **1b** the transition state, i.e., the molecule is a  $T_A$  configurational unit. This is the situation in many other molecules, in which a two-electron  $\pi$ -interaction takes place in the ground state: imines, nitrosamines, amides, and analogous systems. In some cases the stabilizing interaction is between a lone-pair orbital and a conjugated  $\pi^*$ -acceptor orbital, rather than an atomic p-orbital. This is the case in amides, in which the nitrogen p lone pair of electrons is conjugated with the carbonyl  $\pi^*$ -orbital, resulting in a stable planar ground-state conformation.

In contrast to the cation, formation of **1a** from the anion fragments produces a four-electron  $\pi$ -system, in which both  $\pi$  and  $\pi^*$  orbitals are doubly occupied. The net  $\pi$ -interaction is destabilizing, and hence **1a** represents the torsional transition state of the hydrazyl anion. There are many molecular systems featuring adjacent lone pairs of electrons, which belong to the  $T_C$  class in analogy to the hydrazyl anion: hydroxylamines, hydrazines, sulfenamides, sulfenates, disulfides, and others. They all have in common the four-electron, destabilizing interaction at the torsional transition state, which is often referred to as "lone-pair repulsion". Thus, the number of electrons in the dihedral-angle-dependent  $\pi$ -interaction determines the type of torsional process and hence the type of configurational unit to which a compound belongs.

Between the well-defined  $T_A$  and  $T_C$  processes generated by two- and four-electron occupancies of structure **1a** in the hydrazyl cation and anion, respectively, lies the case of the hydrazyl radical with three electrons in its  $\pi$ -system. Figure 2 suggests that the radical should behave qualitatively like the hydrazyl cation: in the cation the dominant feature is the two-electron  $\pi$ -bonding interaction, while in the radical the same interaction is only partly offset by a single electron occupying the  $\pi^*$ -orbital. Thus the radical belongs to the  $T_A$  classification, with **1a** being the torsional ground state separated from the transition state by a relatively small energy barrier. This conclusion is fully supported by the calculations discussed in the next section and is in accord with the well-known fact that radicals are stabilized by adjacent electron-donor groups.

Let us now release the initial geometrical constraint that imposed planarity of the  $NH_2$  group and examine the effect of electron occupancy on the inversional process. In the hydrazyl cation the  $\pi$ -stabilization is sufficiently strong to favor rehybridization of nitrogen in the  $NH_2$  group to  $sp^2$ , such that a pure atomic p-orbital is available for the interaction. Conformation **1a** is thus the ground structure for the cation even when the  $NH_2$  group is not held planar. Pyramidalization of the  $NH_2$  nitrogen will take place only during the torsional process and at its transition state, when  $\pi$ -interaction is insignificant, and thus the torsional process, if imposed, is  $1a \rightleftharpoons [4b \text{ or } 4c]$ , a  $T_A$  process that

involves both torsion and inversion. This is the actual mechanism for many of the analogous two-electron systems, such as amides. In fact  $\pi$ -bonding in geometry **1a** of the hydrazyl cation is so intense that it prevents stereomutation of the cation by this  $T_A$  mechanism. The lowest energy path available for stereomutation of the hydrazyl cation does not involve breaking of the  $\pi$ -bond: during attempted torsion about the N-N bond, the NH fragment rehybridizes to maintain the stabilizing interaction, by opening up the N-N-H angle and promoting the hybrid lone-pair orbital eventually to a pure p-orbital. Thus the process is described as planar inversion,  $I_A$ , rather than torsion, and its transition structure (**8**) has a collinear



N-N-H arrangement. This situation is similar to that in imines. Imines adopt planar structures with a formal double bond and can undergo stereomutation by either a  $T_A$  or an  $I_A$  mechanism or a combination of the two (in which torsion about the C=N bond is accompanied by increase of the C=N-H or C=N-R bond angle).<sup>14</sup>

Relaxation of the geometrical constraint in the hydrazyl anion leads to a pyramidal  $NH_2$  group in both the ground (**4b** or **4c**) and transition (**4a**) states. Since the  $\pi$ -interaction in **1a** as well as in **4a** is now repulsive, it is reduced by reducing the p-character of the interacting fragment orbitals, by way of rehybridization (i.e., pyramidalization) of the  $NH_2$  nitrogen.

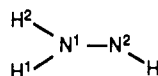
While electron occupancy in the anion determines the ground-state conformation and hence unambiguously places it in the chiral configurational unit class, it does not a priori permit further classification into one of the two chiral subgroups ( $I_C$  or  $T_C$ ). Thus, depending on specific structural features, each analogous compound may belong to either one: in the hydrazyl anion itself the lower energy path leads through the inversion transition structure, though only by a marginal difference from torsion, and hence the process is defined as  $I_C$  (see Table I for computational results). However, the question of whether substituted hydroxylamines, for instance, belong to  $I_C$  or  $T_C$  does not have a straightforward answer, for the two barriers are of comparable magnitudes and are indistinguishable by NMR methods. Often a change in substitution at the hydroxylamine can alter the mechanism for topomerization. This question had been the focus of a literature controversy for several years and was extensively examined in a recent review.<sup>5</sup>

By contrast, in the analogous four-electron system of acyclic substituted sulfenamides, torsion about the sulfur-nitrogen bond is associated with substantially higher activation barriers than nitrogen inversion, and hence sulfenamides generally belong to the  $T_C$  category.

The behavior of the radical upon relaxation of the planarity constraint is of interest, as there is little experimental evidence on this system, which is intermediate between the cation and the anion. While  $\pi$ -bonding in the cation is sufficient to favor a planar  $NH_2$  group, the anion is pyramidal in both the ground and transition structures. Is the three-electron interaction in hydrazyl radical suf-

(14) For a review on imine stereomutation see: McCarty, C. G. *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Wiley: London: Chapter 9. A similar collinear transition structure was calculated for the  $CH_2OH^+$  stereomutation: Kost, D.; Aviram, K. *J. Am. Chem. Soc.* 1986, 108, 2006.

Table I. Calculated Energies and Geometries for the Hydrazyl Anion, Radical, and Cation



structure (type) <sup>a</sup>	total energy, au	rel energy, kcal/mol	point group	NIMAG <sup>b</sup>	bond lengths, <sup>c</sup> Å				bond angles, <sup>c</sup> deg			dihedral, <sup>d</sup> deg	
					NN	N <sup>2</sup> H	N <sup>1</sup> H <sup>1</sup>	N <sup>1</sup> H <sup>2</sup>	N <sup>1</sup> N <sup>2</sup> H	N <sup>2</sup> N <sup>1</sup> H <sup>1</sup>	N <sup>2</sup> N <sup>1</sup> H <sup>2</sup>	D1	D2
Anion													
4b (GS)	-110.312986	0	C <sub>s</sub>	0	1.540	1.031	1.009	1.009	100.1	107.8	107.8	122.7	-122.7
4c (GS)	-110.307299	3.57	C <sub>s</sub>	0	1.513	1.048	1.012	1.012	103.3	113.0	113.0	61.2	-61.2
4a (T <sub>C</sub> )	-110.300109	8.08	C <sub>1</sub>	1	1.578	1.036	1.014	1.010	100.8	111.5	105.0	11.5	125.2
4c (I <sub>C</sub> ) <sup>e</sup>	-110.300961	7.54	C <sub>s</sub>	1	1.489	1.044	0.996	0.996	102.7	121.7	121.7	89.1	-89.1
1a (T <sub>C</sub> I <sub>C</sub> )	-110.285533	17.22	C <sub>s</sub>	2	1.567	1.035	0.994	0.990	99.0	126.0	115.8	0 <sup>f</sup>	180 <sup>f</sup>
Radical													
1a (GS)	-110.405296	0	C <sub>s</sub>	0	1.356	1.011	0.990	0.987	108.3	123.9	116.4	0 <sup>f</sup>	180 <sup>f</sup>
4b (T <sub>A</sub> )	-110.358089	29.61	C <sub>s</sub>	1	1.312	0.994	0.994	0.994	130.2	119.5	119.5	101.3	-101.3
9 <sup>g</sup>	-110.334252	44.57	C <sub>s</sub>	1	1.301	0.975	0.991	0.991	180	120.0	120.0	93.4	-93.4
Cation													
1a (GS)	-110.131866	0	C <sub>s</sub>	0	1.213	1.016	1.009	1.007	116.4	124.8	117.8	0 <sup>f</sup>	180 <sup>f</sup>
8 (I <sub>A</sub> )	-110.084945	29.43	C <sub>2v</sub>	1	1.192	1.000	1.010	1.010	180	121.3	121.3		

<sup>a</sup>Type of stationary point: GS for ground state, the appropriate process descriptor for transition state. <sup>b</sup>Number of imaginary vibrations. <sup>c</sup>Atoms labeled as shown. Where applicable H<sup>1</sup> is syn to H. <sup>d</sup>D1 is the dihedral angle defined by the sequence H1-N1-N2-H, and D2 is the corresponding angle for H2. <sup>e</sup>The NH<sub>2</sub> group is essentially planar. <sup>f</sup>Required by symmetry. <sup>g</sup>9 approximates the I<sub>A</sub> transition state but is not a true stationary point. See text for details.

ficiently stabilizing to promote the sp<sup>3</sup> lone pair into a pure p-orbital, as in the cation? Or is it too weak, resulting in a pyramidal NH<sub>2</sub> group at the torsional ground state, as in the anion? Our calculations, presented in the following section, indicate that the hydrazyl radical behaves like the cation, i.e., the overall ground state is planar and corresponds to structure 1a. However, the two species differ in their transition structures for stereomutation: while π-bonding in the cation is so important that it imposes planar inversion (I<sub>A</sub>) without breaking of the π-bond, rather than rotation, the low-energy path for the radical involves rotation through a "Y"-type (4b) transition structure, with pyramidalization of the NH<sub>2</sub> group (Table I).

### Molecular Orbital Calculations

To support the stereochemical analysis and to demonstrate the various transformations and barriers, we have carried out nonempirical SCF MO calculations on the hydrazyl system. Since the aim of this part was initially limited to the support and better understanding of the previous discussion, no attempt was made to arrive at accurate energies of activation. Rather, trends in barriers as a function of structure and electron occupancy were sought. Hence the basis set employed throughout the calculations was the split valence shell 4-31G basis<sup>15</sup> as implemented in the GAUSSIAN-82<sup>16</sup> program package. The hydrazyl cation and anion were calculated by using the restricted Hartree-Fock (RHF) method, while the radical was calculated with the unrestricted Hartree-Fock (UHF) method suitable for open-shell systems.

The geometries of all of the structures were fully optimized with respect to minimum energy by using Schlegel's gradient method,<sup>17</sup> within the symmetry constraints required for the definition of certain stationary points on the energy surface. Optimizations were followed by vi-

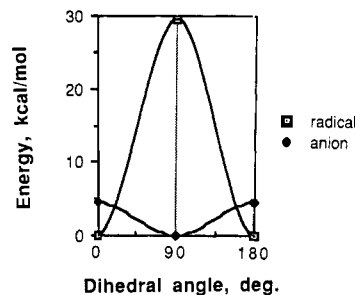


Figure 3. Torsional energy profiles for the hydrazyl radical and anion.

brational-frequency calculations to ascertain the nature of the stationary point as a ground or transition structure, by observing the number of imaginary vibrations (characterized by negative frequencies) in each calculated structure. We resisted the temptation to calculate intermediate structures along a reaction coordinate (rotation or inversion) other than stationary points (i.e., ground or transition structures), as only the latter are adequately well defined.<sup>18</sup>

The results of these calculations are summarized in Table I. The rotational profiles for the hydrazyl anion and radical are shown in Figure 3. The cation could not be included as it does not undergo a torsional process: optimization of a torsional transition structure led to linear structure 8, with an activation barrier for planar inversion (I<sub>A</sub>) of 29.4 kcal/mol, essentially equal to the torsional barrier for the radical. Obviously, the rotational barrier for the cation would have been higher had there not been a lower barrier available for stereomutation, via linear structure 8. Thus our qualitative statement that the radical is intermediate between the anion and cation in terms of the torsional process is verified, as well as the expectation that the radical and cation behave similarly: the ground structure for both is represented by 1a.

(15) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* 1971, 54, 724.

(16) Binckley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN-82; Carnegie Mellon University: Pittsburgh, PA, 1982.

(17) Schlegel, H. B. *J. Chem. Phys.* 1982, 77, 3676.

(18) In a preliminary publication<sup>2a</sup> we reported energy profiles calculated at various intermediate points. To arrive at such profiles, some geometrical constraints had to be imposed, at the cost of reduced accuracy.

Structure 8 is the only true transition state (with a single negative frequency) found for the cation. Of course, the planar inversion mechanism is not accessible to many of the real two-electron systems, such as amides, "push-pull" olefins, and others, which undergo torsion with substantially high activation barriers. One molecular system that does resemble the hydrazyl cation is the imine, and our results suggest that it should undergo stereomutation by an  $I_A$  mechanism.

The calculations confirm the differences between cation and radical, on one hand, and the anion on the other, resulting from their different electron occupancies: the cation and radical belong to the  $I_A$  and  $T_A$  classes, while the torsional profile for the anion is inverted, placing it in the  $T_C$  class (Figure 3). Since the four-electron interaction is a secondary effect, relative to two-electron interaction, resulting from the *difference* between stabilizing and destabilizing interactions, it should be substantially weaker than two-electron interaction. This is also borne out by the calculations: both torsional and inversional barriers for the hydrazyl anion (8.1 and 7.5 kcal/mol, respectively) are much lower than those for the cation (29.4 kcal/mol for planar inversion, and presumably much higher for rotation, which is not a stationary point on the potential energy surface).

The only true transition structure for stereomutation of the hydrazyl radical is **4b**, the torsional transition state, located by a transition-state optimization and featuring a single imaginary frequency. The calculated  $T_A$  barrier is 29.6 kcal/mol. Thus the calculations demonstrate the different stereomutation mechanisms,  $I_A$  and  $T_A$ , respectively, for the hydrazyl cation and radical. These result directly from the different electron occupancies: In the cation, rotation would involve breaking of the two-electron  $N=N$   $\pi$ -bond, which has been estimated recently at 60<sup>19</sup> or 82.5<sup>20</sup> kcal/mol. Rather than losing all of this bonding interaction, the system promotes the hybrid lone pair on the NH fragment to pure p, in an  $I_A$  process, at the reduced energetic cost of only 29.4 kcal/mol. In the radical, on the other hand, rotation involves breaking of a *three*-electron  $\pi$ -bond, which is not nearly as strong as the two-electron bond, a process less costly in terms of activation energy than the lone-pair promotion associated with the  $I_A$  process. Hence the low-energy mechanism for the radical is rotation about the NN bond.

For the sake of comparison with the cation it was of interest to determine also an  $I_A$  barrier for the radical, by imposing collinearity of the NNH sequence, assuming that this would lead to the  $C_{2v}$  symmetric structure 8. However, the  $NH_2$  group in the collinear radical optimized into the slightly pyramidal geometry 9, with the dihedral angle between the geminal NH bonds, as seen in a Newman projection along the NN axis, being 186.9° rather than the 180° required for 8. The reduced symmetry of 9 requires that the NNH array be *not* collinear in a true stationary point, and thus such a point describing planar inversion of the radical cannot be located. We have nevertheless retained the results for 9 in Table I, as it is almost planar and can serve as a close approximation of the  $I_A$  transition structure of the radical. The approximate  $I_A$  barrier obtained for the radical in this way is 44.6 kcal/mol.

For the hydrazyl anion both the rotation and inversion transition states can be calculated. Unlike in the cases of the cation and radical, where there is only one true tran-

sition structure for each, in the anion *both* transition states are characterized each by a single negative frequency, and both are true transition states along the reaction coordinate describing the topomerization. This is due to a fundamental difference in the processes: in the cation and radical stereomutation is brought about *either* by rotation *or* by planar inversion, or by a given mixture of the two, i.e., by torsion accompanied by an increase in the NNH angle, through a single unique transition structure. This type of mechanism has been described as the "OR" arrangement.<sup>5</sup> By contrast, a complete topomerization of the anion requires *both* inversion *and* rotation, which occur in a consecutive manner, and is referred to as the "AND" type mechanism.<sup>5</sup> For this reason both transition structures in the anion are stationary points that can be located accurately, while in the cation and radical only one stationary point can be found for the transition state.

It is always of interest in a case of an AND type stereomutation, where two consecutive barriers are involved, to examine the possible joint, simultaneous mechanism. The transition structure for such a mechanism would involve the molecular deformations typical of *both* of the changes associated with each of the barriers and hence might be expected to be significantly higher in energy than each of the individual transition structures. Indeed this is the case in the hydrazyl anion: structure **1a** involves both flattening of the  $NH_2$  pyramid as well as a torsional angle corresponding to maximum four-electron  $\pi$ -interaction and thus represents a double transition state, for both nitrogen inversion and rotation about the NN bond. Accordingly, the structure is found to have two negative vibrational frequencies (Table I), each associated with the geometrical changes describing one of the processes, rotation or inversion. In addition we find that the activation energy required for this simultaneous interconversion, 17.2 kcal/mol, is substantially higher than the individual barriers, in agreement with expectation.<sup>21</sup>

## Conclusion

A convenient classification is developed for the various stereomutations that stereolabile configurational units (i.e., geometrical arrangements, generally centered around nitrogen, which have relatively low barriers for isomerization) undergo. Four such classes are defined,  $T_C$ ,  $I_C$ ,  $T_A$ , and  $I_A$ , according to the ground-state conformation (chiral or achiral) and the nature of the major process (torsion or inversion). Examination of the molecular orbitals of the  $NH_2NH$  model system reveals that the stereochemical classes are closely related to the electron occupancy of the central ( $N=N$ )  $\pi$ -orbitals. Thus in the chiral classes ( $T_C$  and  $I_C$ ) both  $\pi$ - and  $\pi^*$ -orbitals are doubly occupied, whereas in the achiral systems only the  $\pi$ -orbital is occupied. A two-electron  $\pi$ -system generates a planar (achiral) ground state. The three-electron radical system qualitatively parallels that of the cation, since in both systems the  $\pi$ -interaction is stabilizing overall. All four stereochemical transformations are demonstrated with the hydrazyl model, and their relative magnitudes are calculated at the 4-31G level of theory.

(21) Another example of the AND situation involves the topomerization of trialkylamines.<sup>22</sup> In some cases both barriers can be measured separately. In others only a combined barrier is measured. Thus in *N,N*-dialkyl-*tert*-butylamines the torsional barrier actually decreased at the inversional transition state, in contrast to the present discussion. This apparent violation of the rule is due to special steric effects in this system and disappeared in less crowded amines.

(22) Bushweller, C. H.; Anderson, W. G.; Stevenson, P. E.; Burkey, B. L.; O'Neil, J. W. *J. Am. Chem. Soc.* 1974, 96, 3892.

(19) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* 1987, 109, 5217.

(20) Kost, D.; Bond, D.; Schleyer, P. v. R., unpublished results.