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THE THREE ELECTRON π-BOND IN HYDRAZYL RADICAL. AN AB INITIO SCF-MO INVESTIGATION OF TORSIONAL AND INVERSIONAL STEREOMUTATION[1a]

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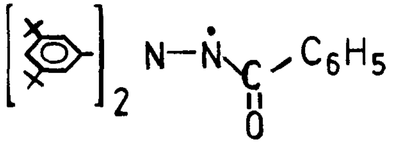
Summary: The mechanism for stereomutation in hydrazyl radical is analyzed in terms of simple perturbational molecular orbital theory and SCF-MO calculations. The ground state is planar due to three electron π-stabilization. The torsional barrier (29 kcal/mol) is approximately half that of the hydrazyl cation. Torsion and planar inversion have barriers comparable in magnitude, resulting in a mechanism intermediate between these two extremes.

In a pioneering series of experimental investigations, Balaban and co-workers[2] have obtained evidence for a stereolabile configurational unit in the ESR spectra of a number of N,N-diarylhydrazyl free radicals of the "push-pull" type (also referred to as capto-dative[3] or merostabilized[4]). They have shown that the two aryl rings are distinguishable (diastereotopic) since the ESR spectra exhibit non-equivalent hyperfine coupling constants (h.f.c.) for corresponding protons in the two aryl rings. In one case, 1, comparison of simulated and experimental ESR spectra at various temperatures provided a determination of the barrier to stereomutation: $\Delta G^* = 8$ kcal/mol (32 kJ/mol).[2] In order to provide a theoretical framework for evaluating the stereochemical effects on the ESR spectra of such systems[2,5] and to assess the ability of simple perturbational molecular orbital theory (PMO) to account for the experimental findings we have carried out unrestricted Hartree-Fock *ab initio* SCF-MO calculations on the hydrazyl radical in a variety of conformations. Previous theoretical investigations on "push-pull" free radicals have focused on carbon centered radicals which lack the lone pair present in hydrazyl.[6,7]

The hydrazyl system represents a useful model for evaluation of the dependence of torsional barriers on the electron population of the π-system. Simple PMO theory suggests that hydrazyl cation and anion which have two and four electrons in the π-system, respectively, should exhibit different types of torsional barriers.[8] Hydrazyl cation should have a planar ground state corresponding to an achiral structure in the maximally labelled derivative and a high 2-electron torsional barrier (T_A barrier).[9] By contrast, the lower 4-electron torsional barrier in hydrazyl anion interconverts two non-planar ground states which are chiral in maximally labelled derivatives (T_C).[9] The essential features of the PMO analysis have been supported by *ab initio* calculations.[10] The hydrazyl radical represents an intermediate case between the cation and anion, and it is therefore of interest to compare its behavior with the systems previously studied.



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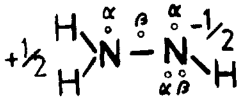

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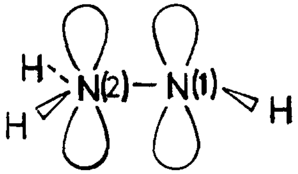

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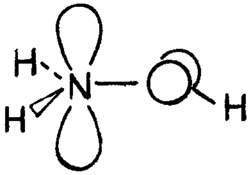

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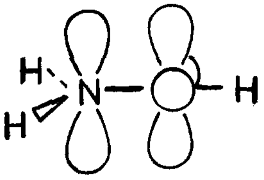

2c

TABLE 1: Geometries and Energies of Hydrazyl Radical.

Structure	Bond lengths, A			Bond angles, deg.		Relative energy	
	N(1)H	N(2)H	N-N	N(2)N(1)H	N(1)N(2)H	kcal/mol	kj/mol
2a	1.01	0.99	1.36	107.8	120.3	0	0
2b(opt)	0.99	0.99	1.31	131.5	120.8	29.7	124
2b(rigid)	1.01	0.99	1.33	107.8	120.0	39.4	165
2c	0.98	0.99	1.30	180.0	120.1	44.1	185

We can consider two limiting geometries with respect to torsion about the N-N bond, 2a and 2b. For simplicity in analysis as well as in calculation we have constrained the amino group to planarity.[13] Based upon symmetries of the maximally labelled derivatives we term 2a achiral and 2b chiral. The major electronic factor contributing to the energy difference between 2a and 2b derives from interaction of p-orbitals on the two nitrogen atoms leading to π and π^* orbitals which can occur only in geometry 2a. This interaction is expected to be stabilizing for the radical (3-electron population) as it is for hydrazyl cation (2-electron population), although to a lesser extent. By contrast, the interaction is destabilizing in hydrazyl anion (4-electron population). The stabilization for the radical should be about half that in the cation since the stabilization resulting from occupation of the π-level is partially offset by the single electron in the π^* level. Thus, we may conclude that hydrazyl radical should adopt conformation 2a as its ground state and exhibit a T_A torsional barrier (with transition state 2b) about half as large as that observed for hydrazyl cation. This qualitative prediction is equivalent to the suggestion[5] from the Linnett double quartet theory[14], as expressed in structure 3, that the N-N bond should have a bond order of 1.5.

In considering the stereomutation of maximally labelled hydrazyl radicals (or the D->H topomerization[8] of 1 or 2a) we must consider two mechanistic possibilities. Stereomutation can occur by torsion about the N-N bond (T_A) or by planar inversion (I_A) of the diligated nitrogen atom *via* transition state **2c**. It should be noted that the relationship between these two mechanisms is alternative (I_A OR T_A) and that the observed barrier will correspond to the lower energy process. Neither the PMO nor Linnett analyses offer grounds for choice between mechanisms. Calculations on hydrazyl cation indicated that stereomutation (or topomerization) should occur by an I_A process. The much higher T_A barrier could be estimated only by rigid rotation in which the HN(1)N(2) angle was held constant (T_A, 74 kcal/mol; I_A, 29 kcal/mol).[10] In the analogous situation of imine stereomutation both limiting mechanisms have been considered as well as mechanisms intermediate between the two.[8]

UHF *Ab initio* SCF-MO calculations[11] were carried out on hydrazyl radical, HN(1)-N(2)H_2, using a 4-31G[12] basis set with optimization of N-H and N-N bond lengths and HN(1)N(2) and N(1)N(2)H bond angles with various HNNH dihedral angles. The geometry at N(2) was constrained to planarity and the two N(1)N(2)H bond angles and N(2)H bond lengths were held equal. The I_A transition state (**2c**) was calculated by constraining the HN(1)N(2) angle to 180°. A rigid rotation transition state corresponding to **2b** was also calculated to facilitate comparison with calculations on hydrazyl cation. Here, all bond lengths (except N-N) and angles were set equal to those in the ground state. The geometries and energies of **2a**, **2b** (both optimized and rigid), and **2c** are given in Table 1.

The calculated results summarized in Table 1 clearly support the qualitative conclusions of the PMO analysis. The singly occupied molecular orbital (SOMO) of the ground state is an N-N π^* orbital, with nearly identical coefficients on the two nitrogen atoms, in accord with the nearly equivalent nitrogen h.f.c.'s (0.875 & 0.89mT) reported for **1**.[2] When torsion about the N-N bond takes place the π-bonding between the p-orbitals on the two nitrogens is lost. However, it is replaced by less effective overlap between the p-orbital on N(2) and the hybridized in-plane orbital on N(1) which corresponds to the lone pair orbital in the ground state. Thus, the π^* character of SOMO is retained in the torsional transition state but here there is considerable density in the 2s orbital on N(1) reflecting the hybridization of the atomic orbital. The SOMO orbital in the linear I_A transition state, **2c**, is also a π^* orbital but differs from that in the ground state in that the density on N(1) is now larger than that on N(2). The rigid rotation torsional barrier is approximately half that obtained for the cation (39 kcal/mol *vs* 74 kcal/mol), reflecting the relative strengths of 2-electron and 3-electron π-bonds. The I_A inversion barriers in the two systems differ as well, although less dramatically (cation 29 kcal/mol, radical 44 kcal/mol). The change in the mechanism for stereomutation in the radical as compared with the cation (i.e. from I_A to T_A) results mainly from the substantial drop in the torsional barrier.

There is a significant difference between the geometries and energies of the rigid rotation and optimized transition states (both corresponding to **2b**). The optimized structure is nearly 10 kcal/mol lower in energy and has a greatly increased N(2)N(1)H bond angle. Within the framework of the PMO analysis we can interpret the expansion of this angle as facilitating the π-overlap between the two nitrogens. Clearly, further expansion of this angle would lead to greater stabilization from π-overlap leading eventually to the I_A transition state, **2c**. The rigid rotation (T_A) and the planar inversion (I_A) transition states represent extremes in a series of possible transition states with different values for the HN(1)N(2) bond angle. The optimized T_A transition state is intermediate between these two extremes. It represents an intermediate mechanism largely torsional but with some inversional character. It seems likely that such intermediate mechanisms will occur when the rigid rotation and inversional transition states are of similar energy. We may suppose that structural changes which would lower the energy of 2c would increase the I_A character of the transition state. Thus, various mechanisms with different amounts of torsional and inversional character are possible for the compounds which have been investigated experimentally. Indeed, the presence of π-withdrawing groups on N(1) would be expected to lower the inversion barrier. This may account for the much lower barrier found experimentally for 1.

REFERENCES AND NOTES

1. (a) Supported by the Fund for Basic Research, administered by the Israel Academy of Sciences and Humanities (D.K.) and the National Institutes of Health M.B.R.S. Program (M.R.). (b) Visiting Professor of Chemistry at BGU on sabbatical leave from Wayne State University, Detroit, MI 48202.

2. Capriou, M. T.; Elian, M.; Grecu, N.; Negoita, N.; Balaban, A. T. J. Chem. Soc. Perkin 2, 1983, 591, and previous papers cited therein.

3. Viehe, H. G.;Merenyi, R.; Stella, L.; Janousek, Z. Angew. Chem. Int. Ed. Engl., 1979, 18, 917.

4. Baldock, R. W.; Hudson, P.; Katritzky, A. R. J. Chem. Soc. Perkin 1, 1974, 1422.

5. Biehl, R.; Mobius, K.; O'Connor, S. E.; Walter, R. I.; Zimmerman, H. J. Phys. Chem., 1979, 83, 3449.

6. Crans, D.; Clark, T.; Schleyer, P. v. R. Tetrahedron Lett., 1980, 21, 3681.

7. Leroy, G.; Peeters, D.; Wilante, C.; Khalil, M. Nouv. J. Chim., 1980, 4, 403.

8. Raban, M.; Kost, D. Tetrahedron, 1984, 40, 3345.

9. Achiral Torsional (T_A) barriers like those in amides, olefins, enolate anions, nitrite esters, etc. feature achiral ground states and lead to interconversion of diastereomers. Chiral Torsional (T_C) barriers experimentally observed in sulfenamides, hydrazines, hydroxlamines, etc. result in interconversion of stereoisomers which differ in configuration at a chiral configurational unit (chiral axis). Achiral Inversion (I_A) refers to the planar inversion or inplane shift mechanism which has been proposed for imine stereomutation. For a complete discussion of this classification scheme and its consequences see reference 8.

10. Kost, D.; Aviram, K.; Raban, M. Isr. J. Chem., 1984, 23, 124.

11. The GAUSSIAN 70 program system was used: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. QCPE, 1974, 10, 236.

12. Ditchfield, R.; Hehre, W. J.; Pople, J. A. J. Chem. Phys., 1971, 54, 724.

13. Planarity (or near planarity) at nitrogen should be the rule for the N,N-diaryl derivatives which have been investigated experimentally as the result of lone pair conjugation by aromatic rings.

14. Linnett, J. W. "The Electronic Structure of Molecules," Methuen, London 1964.

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