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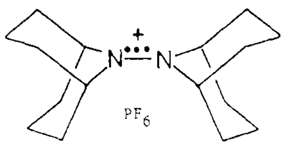
Communications to the Editor

Twisted and Bent Hydrazine Radical Cations

Sir:

The recent X-ray structure determination of bis(9-azabicyclo[3.3.1]nonane) radical cation hexafluorophosphate (**1**) showed that this hydrazine radical cation has an olefin-like structure.[1] The four α carbons are coplanar with the nitrogens, formally leaving pure p-hybridized orbitals to bear the three π electrons, and the N–N bond length is surprisingly short at 1.269 (7) Å. Electrochemical[2] and ESR[3] studies are also consistent with an olefin-like geometry for other tetraalkylhydrazine radical cations, although modest amounts of bending at nitrogen are facile, and, if the alkyl groups destabilize a planar structure, as for **2**, the equilibrium geometry is nonplanar at N.[3a] In this work, the destabilization resulting when a tetraalkylhydrazine radical cation is forced to be twisted at the N–N bond or strongly pyramidal at nitrogen is estimated by measuring changes in $E^{\circ\prime}$, the standard potential of the hydrazine–hydrazine radical-cation couple (room temperature, in acetonitrile containing 0.1 M sodium perchlorate as supporting electrolyte, vs SCE for the work reported here). This allows determination of the difference in the hydrazine–hydrazine radical-cation free-energy gap for strained and unstrained examples.



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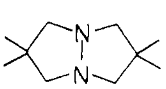

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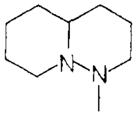
Compounds **3–6** are a good series for study of the effect of introducing twisting strain into a hydrazine radical cation. All have one methyl and three alkyls of similar size substituted on the hydrazine unit; so in the absence of twisting effects they would be expected to show quite similar IP_1 and $E^{\circ\prime}$ values. These data are summarized in Table I. The lone-pair peak separation of 1.0_4 eV, measured by photoelectron spectroscopy (PES), observed for **3** is as expected for the trans-fused, axial methyl conformation **3e(ea)**, known to be the major conformation in solution from low-temperature NMR studies.[4] A distinct peak for IP_2 of the **3e(ee)** conformation was not observed, but the onset of σ ionizations obscures the region in which it should appear. At least two conformations are occupied for **4**,[5] the major one showing $\mathrm{IP}_2 - \mathrm{IP}_1$ of 1.0_1 eV, and a minor one with a 1.4-eV splitting. Which conformations are involved is not clear from our data, although the major one seems likely to be the chair–chair **4e** conformation.[6] A significantly larger $\mathrm{IP}_2 - \mathrm{IP}_1$ difference was found for **5** than for **6**.



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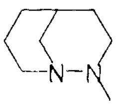

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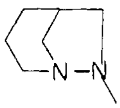

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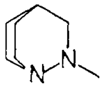

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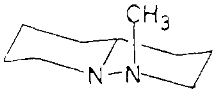
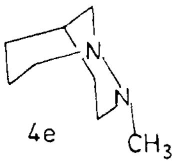


3e(ea)



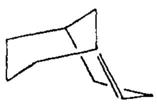
4e

Table I. Photoelectron Spectroscopic and Electrochemical Data

compd	PES data	$E^{\circ\prime}$ [a]	$\Delta E^{\circ\prime}$, kcal/mol [b]
$Et_2NNMeEt$	8.02, 8.52	+0.25	+0.2
3	7.70, 8.74	+0.22	+0.6
4	7.69, 8.70, 9.12	+0.25	+1.3
5	8.18, 8.83	+0.68	+9.5
6	8.02, 8.53[c]	irrev[b]	
8	7.63	+0.76	+13.8
10	8.12[d]	+0.36[d]	+2.4

[a] In CH_3CN containing 0.1 *M* $NaClO_4$ as supporting electrolyte, vs. SCE, at 23 ± 1 °C. [b] See text. [c] From ref 7. [d] From ref 3c.

Hydrazine $E^{\circ\prime}$ values show a weak dependence on IP_1, and we shall discuss the strain effects in terms of $\Delta E^{\circ\prime}$ (kcal/mol) = 23.06 ($E^{\circ\prime}$ (obsd, V) − $E^{\circ\prime}$ (correln, V)), where $E^{\circ\prime}$ (correln, V) = $-0.96_1 + 0.15\,\mathrm{IP}_1$, as discussed previously.[2c] $\Delta E^{\circ\prime}$ is defined as 0 for tetramethylhydrazine, is negative when $E^{\circ\prime}$ is smaller than the correlation line predicts (as when the alkyl groups are tied back, for example in 1,1′-bispyrrolidine; so alkyl–alkyl interaction in the cation radical is smaller than in tetramethylhydrazine radical cation), and positive when $E^{\circ\prime}$ is larger (as when steric interactions in the cation radical are larger than those between the methyls of tetramethylhydrazine radical cation). $\Delta E^{\circ\prime}$ is larger for **3** than for triethylmethylhydrazine, as expected because of the strain introduced upon flattening at the nitrogens of the six-membered rings.[2b,c] $\Delta E^{\circ\prime}$ for **3** should be a good model for that expected for **4** in the absence of twisting or bending effects in $\mathbf{4}^{+\cdot}$. The $\Delta E^{\circ\prime}$ of **4** is <1 kcal/mol higher than that of **3**. This might be considered surprising considering the olefin-like geometry of hydrazine radical cations and the 12-kcal/mol strain found by Lesko and Turner[8] for the bridgehead olefin **7** compared with an acyclic model. The strain in **7** is not twisting strain, however, but bending strain, and the small $\Delta E^{\circ\prime}$ for **4** corroborates the less quantitative conclusion from the ESR work[3] that hydrazine radical cations are easily bent at nitrogen.



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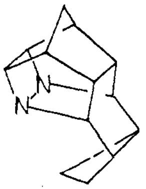
$5^{+\cdot}$ must be twisted as well as bent, and $\Delta E^\circ{}'$ for **5** is sharply increased compared with that of **4**. The amount of twist attained cannot be determined without a knowledge of the amount of bend, but it is clear that twisting substantially destabilizes $5^{+\cdot}$.[9] For $6^{+\cdot}$, even more twisting is required (if N_2 is flat, the angle between the two orbitals on nitrogen bearing the three "nonbonding" electrons would be 90°), and the species is far less long-lived than other hydrazine radical cations. No reduction wave could be observed for $6^{+\cdot}$ in a cyclic voltammogram, even at rapid scan rate and low temperature (50 V/s at −50 °C). The hydrazine cation is so twisted that it behaves like an amine cation radical, and rapidly decomposes, presumably by deprotonation. The oxidation peak potential is +0.84 V vs SCE at 200 mV/s and 0.91 at 50 V/s, at room temperature. If the electron-transfer rate remains rapid relative to the scan rate, $E_p{}^{ox}$ would be less positive than $E^\circ{}'$, and $\Delta E^\circ{}'$ would be >15 kcal/mol for **6**.

The caged hydrazine **8**[10] was prepared by catalytic hydrogenation of **9**, obtained by the method of Berning and Hünig.[11]



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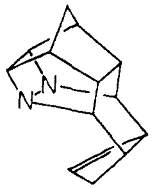

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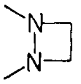

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Its radical cation is not very long-lived, but $E^\circ{}'$, could be determined at room temperature by cyclic voltammetry, and is the largest yet observed for a hydrazine with saturated alkyl substituents. The $\Delta E^\circ{}'$ for **8**, at +13.8 kcal/mol, shows that $8^{+\cdot}$ is very destabilized compared with the less restricted diazetidine **10**. This destabilization is clearly a result of the nitrogens of $8^{+\cdot}$ not being able to flatten very much because of its caged structure. The nitrogen ESR splitting of $8^{+\cdot}$ is 26.8 G (−90 °C, butyronitrile, $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6{}^-$ oxidation; $a(2\ \text{H}) = 8.4$ G), far larger than for $\mathbf{10}^{3c}$ ($a(2\ \text{N}) = 15.0$ G) and indeed 8 G larger than for any other hydrazine radical cation yet studied.[3] Although bending a nitrogen a modest amount is not very destabilizing at all (as in **4**), requiring a great amount of bending seriously destabilizes a hydrazine radical cation (as in **8**). Great twisting of the radical cation is not only at least as costly in energy but makes the cation lifetime extremely short.

Acknowledgment. We thank the National Science Foundation for support of this work, both through research grants and the Major Instrument program.

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(5) (a) **4** was prepared from the corresponding bicyclic hydrazide[5b] by $LiAlH_4$ reduction followed by reductive methylation using $NaBH_3CN$, formaldehyde. The empirical formula was established by high resolution mass spectroscopy; spectral properties were consistent with assigned structure. (b) Mikhlina, E. E.; Komarova, N. A.; Rubstov, M. V. *Khim. Geterotsikl. Soedln., Akad, Nauk Latv. SSR* **1966**, 259; **1969**, 851.

(6) This assumes that the chair–chair form is the stablest, as it is in other bridgehead unsubstituted bicyclo[3.3.1]nonane derivatives which are not endo substituted at C_3 or C_7. Unfortunately, low-temperature ^{13}C NMR studies by W. C. Hollinsed have failed to define the conformations of **4**. Although conformational broadening of several of the lines is observed near −90 °C, and the temperature dependence of the chemical shifts before significant broadening is observed requires at least two conformations to be significantly populated, only a single eight-line pattern was observed at −130 °C, and we lack models to adequately assign the lines.

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(9) There is a modest negative increment in $\Delta E^\circ{}'$ for **5** because of the flattening occurring in a five-membered ring, in contrast to that in the six-membered rings of **3** and **4**; see ref 2c. With its five-membered ring, **5** might be slightly strained relative to **3**, **4**, and **6**; this could slightly decrease $\Delta E^\circ{}'$.

(10) **8** had mp 132–133 °C. The empirical formula was established by high resolution mass spectroscopy; spectral properties were consistent with assigned structure.

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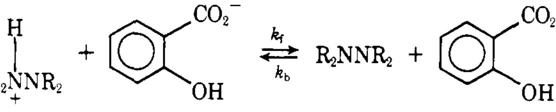
Anomalous Brønsted Behavior of the Proton-Transfer Equilibrium and Rate Constants for Tetraalkylhydrazines and Salicylic Acid

Sir:

Reaction 1 has been studied with several tetraalkylhydrazines in dimethyl sulfoxide containing 0.10 M tetraethylammonium perchlorate as supporting electrolyte. Values for $K = k_f/k_b$ were measured by potentiometric titration using a glass electrode (Ag/0.01 M $AgNO_3$ in Me_2SO as reference electrode) and those for k_f by a chronoamperometric technique developed by Evans and Kinlen[1] for this purpose. Data for the 13 hydrazines studied which have methyl and/or substituted methylene substituents are summarized in Table I. The order listed is that of decreasing log K (increasing basicity). The basicity of these hydrazines is seen to be rather sensitive to the nature of the alkyl substituents, K varying by five decades in this series. Lengthening the alkyl chains decreases basicity for the acyclic compounds (**1–6**) compared with that of tetramethylhydrazine (**7**). Tetraisobutylhydrazine was too feeble a base for measurement of log K by our method. The cyclic compounds **8–13** are more basic than **7**. The lone pair–lone pair dihedral angle, θ, of the unprotonated form may be of some importance in determining basicity. We note that **13**, which has $\theta \sim 0°$,[2] is ≥2.2 pK units more basic than the other compounds. Other factors are also clearly contributors.



(1)

The rate constants for proton transfer are also sensitive to structural changes in the alkyl substituents, k_f varying by 3.5 decades and k_b by 7.3 decades in the compounds studied. Two features of these rate data are remarkable. The first is that very slow rates of proton transfer are observed for these systems, despite the fact that proton transfer is occurring between oxygen and nitrogen, so that one might have anticipated these to be "normal" proton-transfer systems.[3] The rate constants quoted in Table I correspond to $\Delta G^{\ddagger}$ values varying between 7.5 and 17.4 kcal/mol. Slow proton transfers in dimethyl sulfoxide have been previously observed.[4] The second unusual feature of these systems is illustrated by the Brønsted plot of log k_f vs. log K shown in Figure 1. Considerable scatter from a straight line is observed; these compounds have not been chosen to minimize steric differences between them, but to provide a variety of equilibrium N–N rotation conformations. Nevertheless, it is clear that the plot has a negative slope (the least-squares line through **1–12** shown has $\alpha = -1.16$, correlation coefficient 0.92, average deviation 0.31 log units), requiring that the Brønsted plot for the reverse reaction, log k_b vs. log K^{-1}, has the slope $\beta = +2.16$ (same average deviation as for the foreward reaction, correlation coefficient 0.98). A

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