Sesquihomoadamantene (3).[33] To a vigorously stirred suspension of 22 g of Na (0.96 g atom) in 300 mL of refluxing xylene was added dropwise 140 g of adamantanone (0.93 mol) in 500 mL of xylene. After 3 h, the reaction was cooled to room temperature and quenched with 50 mL of MeOH and then 200 mL of H_2O. The mixture was acidified with 500 mL of 2 N H_2SO_4 and the precipitate which formed was filtered. The filter cake was washed with H_2O, MeOH, and pentane and then dried to give 124.4 g of 2,2′-dihydroxy-2,2′-biadamantane (88%). Recrystallization from 1:1 hexane–CCl_4 gave an analytical sample (mp 267–269 °C (lit.[33a] mp 267–269 °C; lit.[33c] mp 266–268 °C): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 2.50 (4 H, d, J = 11 Hz), 2.20 (4 H, m), 2.12 (4 H, br s), 1.9–1.4 (20H, m); IR 3620 cm^{-1}; MS, m/e 302(M^+), 150 (100%). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.35; H, 10.0.

To 42 g of H_2SO_4 stirred and chilled in an ice bath was added 15.6 g of 2,2′-dihydroxy-2,2′-biadamantane (51.6 mmol) over a 5-min period. After being stirred for 7 min more, the solution was poured onto 250 g of ice and the precipitate was taken up in Et_2O. The aqueous layer was removed and the Et_2O layer was extracted with H_2O and then saturated aqueous $NaHCO_3$. The Et_2O was dried with $MgSO_4$, filtered, and evaporated to give a quantitative yield of 14.6 g of spiro[adamantane-2,4′-(5′-homoadamantanone)]. Recrystallization from EtOH and then hexane removed the 5% impurity of adamantylidene–adamantane oxide to give 12.5 g of pure ketone (85% mp 178–179 °C, (lit.[33a] mp 176–178 °C, lit.[33] mp 177–178.5 °C)): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.72 (1 H, m), 2.54 (3 H, m), 2.2–1.5 (28 H, m); IR 1680 cm^{-1}; MS, m/e 284 (M^+). Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.93. Found: C, 84.6; H, 9.95.

To a stirred slurry of 1.82 g of $LiAlH_4$ (47.9 mmol) in 45 mL of Et_2O was added dropwise over an hour 12.5 g of spira[adamantane-2,4′-(5′-homoadamantanone)] (43.9 mmol) in 180 mL of Et_2O. After refluxing 3 h, the reaction was cooled to room temperature and quenched by addition of EtOAc, H_2O, and 100 mL of 2 M HCl. The Et_2O layer was separated and extracted with H_2O and then saturated aqueous $NaHCO_3$. The Et_2O layer was dried with $MgSO_4$, filtered, and evaporate to give 11.7 g of spiro[adamantane-2,4′-(5′-homoadamantanol)] (92%). Recrystallization from 1:2 hexane–CCl_4 gave 10.9 g of alcohol (87%, mp 188–192 °C (lit.[33b] mp 189–192 °C, lit.[33c] mp 191–193 °C)): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 4.12 (1 H, d, J = 5 Hz), 2.6–1.4 (29 H, m); IR 3410 cm^{-1}; MS, m/e 286 (M^+). Anal. Calcd for $C_{20}H_{30}O$: C, 83.85; H, 10.56. Found: C, 83.55; H, 10.5.

To 14 g of P_2O_5 and 40 mL of H_3PO_4 was added 10.9 g of spiro[adamantane-2,4′-(5′-homoadamantanol)] and then the reaction was heated to 140 °C for 2 h. The mixture was cooled and poured onto ice, and the precipitate was taken up in hexane. The aqueous layer was removed, and the hexane layer was extracted with H_2O, saturated aqueous $Na_2S_2O_3$, and brine. After drying with $MgSO_4$, the solution was filtered and evaporated to give 10.0 g of a 3:1 mixture of adamantylidene–adamantane (**1**) and sesquihomoadamantene (**3**). The mixture was dissolved in minimal CCl_4 and 8.9 g of Br_2 in 75 mL of CCl_4 was added dropwise. The resulting precipitate was filtered off, and the filtrate was extracted with saturated aqueous $Na_2S_2O_3$ and then dried with $MgSO_4$. Filtration and evaporation gave crude **3**, which was eluted through Florisil with hexane and evaporated to give 2.51 g (25%). Recrystallization from acetone, followed by sublimation at 0.1 Torr and 130–150 °C, gave 1.60 g of pure **3** (16%, mp 201–203 °C (lit.[33b] mp 199–201 °C, lit.[33c] mp 202–204 °C)): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.12 (4 H, m), 1.98 (4 H, m) 1.9–1.6 (20 H, m); IR 1435, 1355, 1070, 1019, 944, 930, 768, and 658 cm^{-1}; MS, m/e 268 (M^+). Anal. Calcd for $C_{20}H_{28}$: C, 89.48; H, 10.52. Found: C, 89.15; H, 10.5.

Acknowledgment. We thank Prof. P. v. R. Schleyer for his interest and the staff of the Regionales Rechenzentrum Erlangen for their cooperation. We thank Professor R. West (Wisconsin) and his group for use of their low-temperature optical spectroscopic equipment. We thank Dr. Nathan Yumibe for his assistance with the electrochemical flow cell. We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work.

Supplementary Material Available: Optical absorption spectra for $\mathbf{1}^{\cdot+}$–$\mathbf{5}^{\cdot+}$ (6 pages). Ordering information is given on any current masthead page.

---

[33] (a) Wynberg, H.; Boelma, E.; Wieringa, J. H.; Strating, J. *Tetrahedron Lett.* **1970**, 3613. (b) Boelema, E.; Wynberg, H.; Strating, J. *Tetrahedron Lett.* **1971**, 4029. (c) Gill, G. B.; Hands, D. *Tetrahedron Lett.* **1971**, 181.

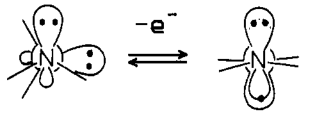
One-Electron Oxidation Equilibria for Acylated Hydrazines

Stephen F. Nelsen,*[†] Silas C. Blackstock,[†] Peter A. Petillo,[†] Ilana Agmon,[‡] and Menahem Kaftory[‡]

Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and Department of Chemistry, Israel Institute of Technology, Technion City, Haifa 32000, Israel. *Received March 11, 1987*

Abstract: Vertical ionization potentials (measured by photoelectron spectroscopy) and formal oxidation potentials (measured by cyclic voltammetry) are reported for trimethylformylhydrazine (**3**), trimethylacetylhydrazine (**4**), 1,2-dimethyl-3-ketopyrazolidine (**5**), 1,1′-bi(2-ketopyrrolidine) (**6**), 2,6-diketo-1,5-diazabicyclo[3.3.0]octane (**7**), 2,5-diketo-1,6-diazabicyclo[4.4.0]decane (**8**), and its 7,10-dimethylene-bridged analogue **9**. X-ray crystal structures are reported for **6** and **7**, ESR spectral data are given for the cation radicals of **7**–**9**, and the NN rotational barrier is reported for **6** (11.4 kcal/mol at −48 °C). The oxidation properties of these acylated hydrazines are compared with those of their tetraalkyl analogues with C═O replaced by CH_2. Large cation relaxation energies (energy differences between vertical and adiabatic cation radicals) are observed even when the nitrogens are planar in the neutral compound. It is concluded that amide resonance is mostly absent in the cation radicals.

Electron removal from tetraalkylhydrazines (R_4N_2) to give their cation radicals (shown for an acyclic example in eq 1) causes a large geometry change, which dominates the thermodynamics of electron transfer.[1] Neutral R_4N_2 have a substantial preference for pyramidal nitrogen atoms (average bond angle at nitrogen, α(av), ca. 107–111°) and a weak preference for lone pair,lone pair dihedral angle θ near 90°, while the cation radical $R_4N_2{}^+$ has much less preference for pyramidal nitrogen atoms (p-rich lone-pair hybridization) and a strong preference for coplanar lone pairs (θ = 180 or 0°). Removal of an electron from R_4N_2 may be thought of as generating roughly half a π bond between the



(1)

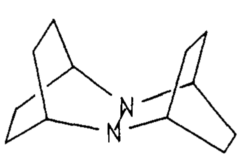
[†] University of Wisconsin.

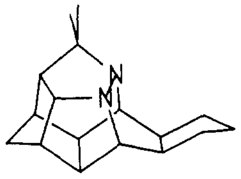
[‡] Israel Institute of Technology.

[1] (a) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Nelsen, S. F. *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, pp 1–86.

0002-7863/87/1509-5724$01.50/0

nitrogen atoms. Two of the remaining lone-pair electrons of $R_4N_2^+$ are in the bonding orbital dominated by π(NN) and the third is in the antibonding π^*(NN) orbital. The large geometry change between the oxidation states makes the thermodynamics for electron loss extremely sensitive to alkyl group structure. Very large differences in the thermodynamic ease of oxidation can occur even when only five- and six-membered rings are present, if the rings include both nitrogens (in N,N′ cyclic compounds). For example, the formal oxidation potential ($E°'$) for **1** is −0.53 V vs. SCE,[2] and that for **2**, +0.59 V,[1b] corresponding to a difference in ease of adiabatic electron loss in solution, $\delta\Delta G°_e$, of 25.8 kcal/mol.


1

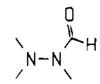
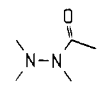
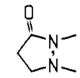
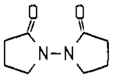
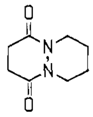
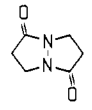
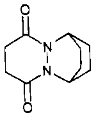

2

We return[3] here to examining the effect of substituents that have a strong electronic interaction with amino nitrogen lone pairs on electron loss. The electronic interaction between a nitrogen lone pair and an sp^2-hybridized carbon is anisotropic, reaching a maximum when the nitrogen lone pair is coplanar with the α p orbital of an unsaturated substituent. Polar effects make interaction with a directly attached carbonyl group especially large. Replacing a weakly electronically interacting alkyl group by an acyl group converts a dialkylamino to an amide nitrogen, making electron removal much more difficult. Because the nitrogen atoms of simple amides are planar, a principal component of the geometry changes that dominate the thermodynamics of electron removal from R_4N_2 might be expected to be removed from acylated hydrazines. It has been shown by X-ray crystallography, however, the *N,N′*-diacylhydrazines with restricted NNC bond angles and nearly coplanar nitrogen lone-pair axes can have substantial pyramidalization at nitrogen.[4] In this work, electron loss from three monoacylated and four N,N′-diacylated hydrazines is studied, including examples in which lone pair,lone pair interaction in the neutral form is forced to occur by the presence of N,N′ rings.

Results

PES, CV, and ESR Studies. The structures of the three monoacyl and four *N,N′*-diacyl alkylated hydrazines we consider in this work appear in Table I, along with their vertical ionization potentials (vIP), measured by photoelectron spectroscopy (PES), and $E°'$ values, measured by cyclic voltammetry (CV). The photoelectron spectra of acylated hydrazines are more complex than those of alkylated ones because a carbonyl group introduces two relatively high-lying orbitals, π(CO) and the oxygen p lone-pair orbital perpendicular to the π system, n_O, as well as low-lying σ-rich orbitals. The antibonding N lone pair, π(CO) combination orbital (π_2, mostly centered on the acylated N lone pair) and n_O occur at comparable ionization potentials (IP) in alkylated amides,[5] and the dialkylated nitrogen lone pair (n_N) is expected in the same region for **3**. Vibrational structure is expected for n_O of **3** because n_O of dimethylformamide shows a CO stretch at 1600 cm^{-1}.[5] The observed low-IP region for **3** is complex and appears to contain a Gaussian band centered at 9.08 eV, overlapping with a band showing three vibrational maxima (9.42, 9.62, and 9.82 eV, ν = 1600 cm^{-1}); we assign the vIP of n_O as 9.62 eV (it is the most intense of the three resolved peaks), but we are unable to tell whether π_2, π_N, or both are responsible for the first observed band at 9.08 eV. Semiempirical calculations do not handle acylated hydrazines particularly well (see the comparison of calculated structures with X-ray structures below), but MNDO calculations do obtain a very small energy difference between π_2 and n_N, with n_O more stabilized,[6] which is consistent with the observed spectrum. A distinct vibrational progression was not observed in the photoelectron spectra of any of the other compounds, which is not very surprising, because that for n_O of dimethylacetamide has a smaller ν(CO) of 1400 cm^{-1} and is rather indistinct even in this smaller molecule.[5] We deconvoluted the low-IP region of **4** into the two bands reported in Table I using overlapping Gaussians, but the first band probably contains the both the non-Gaussian blurred n_O band and π_2 or n_N (n_O is destabilized 0.34 eV in dimethylacetamide compared to dimethylformamide, and π_2 0.16 eV[5]), which makes the numbers quoted rather uncertain. Closure of the five-membered ring in going from **4** to **5** restricts NN rotation, and lone pair,lone pair interaction should cause the lowest IP to be that corresponding to the antibonding lone-pair combination (π_2,n_N). The observed spectrum shows two overlapping peaks, separated by only 0.23 eV, which does not seem attributable to a single conformation.[7] The

Table I. PES Data and Formal Redox Potentials for Some Acylated Tetrasubstituted Hydrazines[a]

compound	no.	vIP, V	$E°'$, V	$E_p^{ox} - E_p^r$, V
	**3**	9.08, 9.62	1.14[b]	0.20
	**4**	8.98, 9.70	1.17	0.20
	**5**	8.36, 8.59	0.51[c]	0.11
	**6**	9.02, 9.92	1.69[d]	0.20
	**7**	8.64	1.27[b]	0.063
	**8**	8.61	1.42[b]	0.067
	**9**	7.87	1.32[b]	0.065

[a] Conditions: room temperature in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, vs. a saturated calomel electrode, at a platinum working electrode. [b] From ref 3. [c] At gold; at Pt, the wave was very distended: $E°'$ ca. 0.57, $E_p^{ox} - E_p^r$ = 0.34 V. [d] Solvent contained 0.4% trifluoroacetic acid and 0.1% trifluoroacetic anhydride by volume.

---

(2) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366.

(3) Nelsen, S. F.; Blackstock, S. C.; Rumack, D. T. *J. Am. Chem. Soc.* **1983**, *105*, 3115.

(4) (a) Kaftory, M.; Agmon, I. *J. Am. Chem. Soc.* **1984**, *106*, 7785. (b) Agmon, I.; Kaftory, M.; Nelsen, S. F.; Blackstock, S. C. *Ibid.* **1986**, *108*, 4477.

(5) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5592.

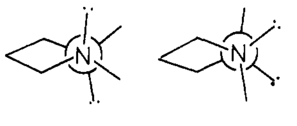
(6) MNDO gets C_s **3** stablest with the Me_2N lone pair syn to the CO group, which is anti to the NN bond, ΔH_f −8.80 kcal/mol, with π_2 at −10.09 eV, n_N 0.11 eV stabilized, and n_O 1.00 eV stabilized. The difference in ΔH_f for this neutral structure from that of the vertical cation gives vIP(π_2) = 9.59 eV(RHF) and 9.32 eV(UHF), the latter 0.24 eV higher than the observed vIP. The anti CO,NN C_s isomer with its Me_2N lone pair anti to the CO group is calculated to be only 1.1 kcal/mol less stable, and that with the CO group syn to the NN bond, 1.7 kcal/mol less stable. Both give n_N,π_2,n_O orbital orderings and small n_N,π_2 separations, 0.21 and 0.07 eV, respectively. Which of the C_s structures would actually be the stablest is not clear from these calculations, and the inaccuracy of the method for acylated hydrazines did not encourage further calculations.

Table II. PES Data and Formal Redox Potentials for Tetraalkylhydrazine Analogues of the Table I Compounds

no.	vIP, V	$E^{\circ\prime}$, V
3H	8.26, 8.81[a]	0.33[a]
4H	8.18, 8.71[b]	0.32[b]
5Htee	7.78, 10.08[c]	0.11[a]
5Htaa	8.32, 9.13[c]	
6H	7.91, 8.47[a]	0.02[a]
7Htw	7.93, 9.38[a]	0.08[a]
7Hecl	7.56, 9.73[a]	
8H	7.61, 9.92[a]	0.28[a]
9H	7.06, 9.35[d]	−0.04[d]

[a] Reference 10. [b] Reference 11. [c] Reference 8. [d] Reference 12.

analogue of **5** with its CO group replaced by CH_2, **5H**, has a photoelectron spectrum exhibiting bands for two conformations with opposite twist angles for the five-membered ring,[8] **5Htee** and **5Htaa**, and we suggest that a similar conformational mixture may well be present for **5**.



5Htee 5Htaa

N,N'-Diacylhydrazine **6** has its nitrogen lone pairs approximately perpendicular (see below) and shows several ill-resolved bands in its photoelectron spectrum below 11 eV, but **7–9**, which have restricted NN rotational angles and hence large N lone pair,lone pair interactions, show a single low-IP band attributable to the antibonding lone-pair combination.

Platinum was used as the working electrode for most of the CV work because of the high potentials necessary for oxidation, and quite large oxidation, reduction peak potential separations were observed. Tetraalkylhydrazines show smaller peak separations at gold working electrodes than they do at platinum, partially because of faster heterogeneous rate constants,[9] but also because electrode fouling is more serious at platinum, and better data are easier to obtain at gold. Only **7–9**, which give long-lived cation radicals, gave near-theoretical peak-to-peak separations; the other compounds give rather short-lived radical cations and distorted peak shapes. Lowering the temperature and scanning faster to decrease decomposition increased the broadening. The number reported for **5** is at gold because much poorer behavior was seen at platinum, as indicated in footnote *c* in Table I. $\mathbf{6}^+$ decomposed especially rapidly, and we had to go to acidic solvent as indicated in footnote *d* to obtain any reduction wave.

Oxidation of **3–5** gives the radical cations, which are easily detected by ESR but which have complex spectra that we have not been able to analyze. We have not obtained the ESR spectrum of the very short-lived $\mathbf{6}^+$. The spectrum of $\mathbf{7}^+$ shows $a(2N)$ = 10.2 G, $a(4H)$ = 16.5 G, and $a(4H)$ = 2.15 G at room temperature, that of $\mathbf{8}^+$ shows $a(2N)$ = 9.8 G and $a(4H)$ = 14.8 G at −60 °C; and that previously reported[3] for $\mathbf{9}^+$ is $a(2N)$ = 9.6 G and $a(4H)$ = 2.9 G, with unresolved smaller couplings clearly present for both $\mathbf{8}^+$ and $\mathbf{9}^+$.

To enable comparison of the effect of rings upon ionization behavior for acylated hydrazines with that for tetraalkylhydrazines, we show literature data[10–12] for the tetraalkyl analogues of the compounds of Table I in Table II. We designate the tetraalkyl compounds that have C=O replaced by CH_2 groups with a suffix H. Within each series, substantial differences in ionization behavior are observed when the connectivity of the nitrogen substituents is changed. This can be seen in the graphic comparisons of the vIP and $E^{\circ\prime}$ data shown in Figures 1 and 2, respectively. Understanding why these differences occur requires a knowledge of how the geometries of the neutral and cationic forms of the acylated compounds differ from those of the all-alkylated ones. We shall first consider the geometries of the neutral acylated hydrazines.

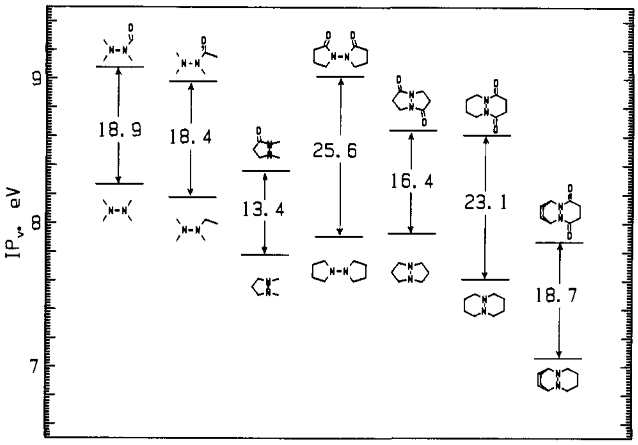


Figure 1. Comparison of vIP for acylated hydrazines with their alkyl analogues having C=O replaced by CH_2. The numbers given are differences in vIP in kcal/mol.

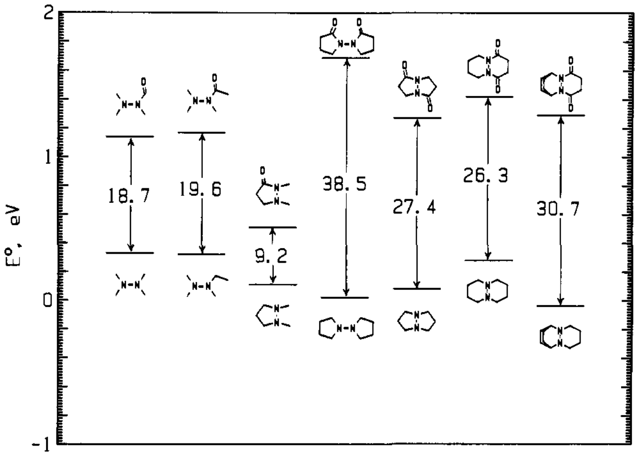


Figure 2. Comparison of $E^{\circ\prime}$ for acylated hydrazines with their alkyl analogues having C=O replaced by CH_2. The numbers given are differences in $E^{\circ\prime}$ in kcal/mol.

Rotational Barrier for 6 and Structures of 6 and 7. Figures 1 and 2 demonstrate substantial lowering in both vIP and $E^{\circ\prime}$ upon N,N' five-membered ring closure for both acylated (**4** → **5**) and all-alkyl hydrazines (**4H** → **5H**). This presumably occurs principally because NN rotation in both neutral forms is required to be quite different from the optimum value of θ near 90° which occurs for **3**, **4**, and **6**. Delocalization of the nitrogen lone-pair electrons onto the carbonyl groups in acylated hydrazines might have been postulated to decrease the lone pair,lone pair interactions which cause a substantial rotational barrier in R_4N_2, but it was already known that some N,N'-diacylated hydrazines have a large NN rotational barrier. Several groups[13] found high NN rotational

---

[7] The MNDO minimum we obtained for **5**, ΔH_f −19.05 kcal/mol, has both nitrogens strongly pyramidal (α(av) 114.4° for the acylated N, 111.5° for the dialkylated N) and a 99.4° CH_3N,NCH_3 torsional angle despite little ring torsion, OCN,NCH_2 angle 2.8°. The calculated vIP for this structure was 8.98(RHF), 8.83(UHF) eV. We do not doubt that the acylated nitrogen is calculated to be too bent, and requiring it to be planar raised ΔH_f 3.3 kcal/mol, and lowered vIP to 8.74(RHF), 8.56(UHF) eV, closer to the experimental value. These calculations gave first and second ionization potential separations of 1.18 and 1.54 eV, respectively, with the shomo dominated by the n_O orbital, as expected.

[8] Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6987.

[9] Kinlen, P. J.; Evans, D. H.; Nelsen, S. F. *J. Electroanal. Chem.* **1979**, *97*, 265.

[10] Nelsen, S. F.; Rumack, D. T.; Meot-Ner, M., in preparation.

[11] Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269.

[12] Nelsen, S. F.; Hollinsed, V. E.; Grezzo, L. A.; Parmelee, W. P. *J. Am. Chem. Soc.* **1981**, *101*, 7347.

[13] (a) Bishop, G. J.; Price, B. J.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1967**, 672. (b) Korsch, B. H.; Riggs, N. V. *Tetrahedron Lett.* **1966**, 5897. (c) Foucaud, A.; Roudant, C. R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 726.

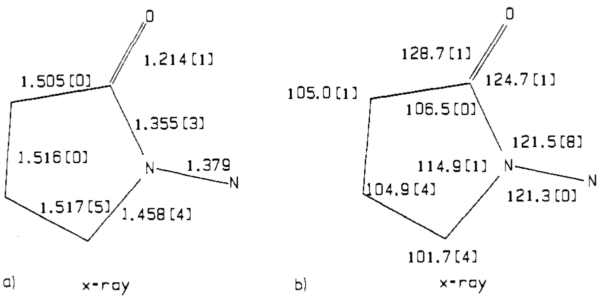


Figure 3. (a) X-ray crystallographic bond lengths for **6**. (b) Bond angles for **6**. Numbers in brackets are differences in the last place between chemically equivalent quantities in the crystal.

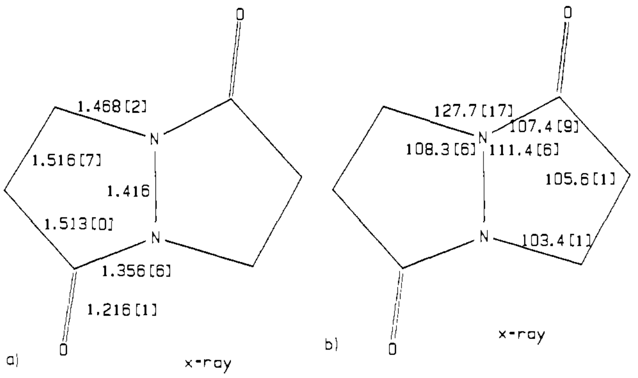


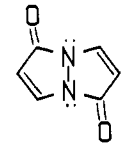
Figure 4. (a) X-ray crystallographic bond lengths for **7**. (b) Bond angles for **7**. Numbers in brackets are differences in the last place between chemically equivalent quantities in the crystal.

barriers for acylated hydrazines, and Sutherland and co-workers[13a] report barriers fof 23.3–23.5 kcal/mol for symmetrical dibenzyl, diacylhydrazines with acetyl, carbomethoxy, and carbobenzyloxy as the acyl groups. It has never been clear to us how much of these barriers is steric, imposed by the necessity of having N–CO rotation to force the alkyl groups past the acyl groups. Dewar and Jennings[14] were the first to discuss the effects of acylation on hydrazine NN rotational barriers in detail. They pointed out that rehybridization of the lone pair of an acylated hydrazine to essentially pure p character increases it overlap with an adjacent lone pair, leading to a higher NN rotational barrier because of increased lone pair,lone pair interaction compared to the case for alkylhydrazines, which have considerably more s character in their lone-pair hybrids, and lower overlap. **6** is a good case to examine for consideration of the rotational barrier of an *N,N'*-diacylhydrazine because it is not nearly as sterically hindered as previous examples,[15] and if its barrier is higher than for a tetraalkylhydrazine, the increase ought to be attributable to an electronic effect. The methylene group next to nitrogen does freeze out to two different chemical shifts at low temperature in a ^{1}H NMR spectrum. The adjacent CH_2 group led to a simple AB pattern with $J = 8.8$ Hz, and extrapolation of the observed $\Delta\nu$ (21.9 Hz at −90 °C, 27.6 Hz at −67.5 °C, and approximately linear at three intermediate temperatures) gave $\Delta\nu = 32.3$ at the observed coalescence temperature of −48 °C at 270 MHz, yielding an NN rotational barrier of 11.4 kcal/mol. This is indeed substantially higher than would be predicted for the tetraalkylhydrazine analogue. The rotational barrier of tetramethylhydrazine has recently been measured at 6.0 kcal/mol (−137 °C),[16] and we would expect a similar value for **6H**.

The different chemical shifts for the CH_2 hydrogens next to N of **6** require that the molecule be twisted about the NN bond in solution. X-ray crystal structures of both *N,N'*-diformyl- and *N,N'*-diacetylhydrazine have their heavy atoms in a single plane (α(av) = 120°, θ = 0/180°),[17a] while crystalline tetraformylhydrazine has perpendicular planar $N(CHO)_2$ groups.[17c] It seems likely that hydrogen bonding is holding the disubstituted compounds planar, which is consistent with the fact that the hydrate of *N,N'*-diacetylhydrazine has the planes containing the *N*-acetyl groups twisted 135° (θ = 45/135°).[17b]

We have determined X-ray crystal structures of **6** and **7** to see how the geometry about the nitrogens is affected by changing from bis-N,N to bis-N,N' five-membered rings. Figure 3 shows the bond lengths and bond angles of **6**. Two crystallographically different molecules (A and B), each at a special site with a C_2 axis bisecting the NN bond, are present in the unit cell, and the numbers shown in brackets are differences in the last place for the quantity in these two molecules. The nitrogen atoms are nearly planar, α(av) = 119.1 and 119.3°, respectively, and the lone pairs are nearly perpendicular, θ being 95.2 and 91.9° for A and B, respectively.

The bond lengths and bond angles of **7** determined by X-ray crystallography are given in Figure 4. The C_2 axis bisecting the NN bond that might have been present is lacking, and the numbers in brackets show differences in the last place between the quantities for chemically equivalent bonds. The N,N' rings do not allow substantial twisting of the lone pairs out of coplanarity. The H_2CN,NCO dihedral angles are 18.6 and 21.2° in the two rings, so θ is about 19.9°. As expected from work on structurally related triazolinedione Diels–Alder adducts,[4] the nitrogens of **7** are substantially nonplanar, α(av) being 115.8°. Thus **7**, for which the N,N' rings force the NN rotational angle to be about 20°, responds to this unfavorably large lone pair,lone pair interaction by significantly bending the nitrogen atoms from planarity, presumably to decrease the lone pair,lone pair overlap. There is also about a 22.8° twist angle between the nitrogen lone-pair orbital axis and the carbonyl carbon p orbital axis, another sign of strain in **7**. X-ray studies of several bis-unsaturated analogues of **7** such as **10** (bimanes, in Kosower's nomenclature) have been carried out by Kosower and co-workers.[18] Unless structurally constrained, the heavy atoms of bimanes lie in a plane (α(av) = 120, ± = 0/180°). The NN distance is considerably shorter than in **7** (1.384 Å for **10**), and as expected, the bond lengths next to the double bond of **10** are much shorter than those near the CH_2CH_2 carbons of **7**. The N–CO bond of 10 is 1.390 Å, which is considerably longer than that of **7**, while the C=O bond is only marginally longer, at 1.219 Å. N–CO resonance in **10** appears to be inhibited, perhaps because delocalization of the nitrogen lone pairs onto the oxygen atoms makes the bicyclic system an antiaromatic 8π one.



10

The X-ray structure of **8** has been published elsewhere,[4] but is useful to compare with that of **6** and **7** here. In contrast to **7**, **8** has nearly planar nitrogen atoms (α(av) = 119.5°). Part of this is doubtless caused by less restriction of the NNC angles, which are in six-membered rings in **8** but five-membered rings in **7**, but an additional factor is that the larger bridges of **8** allow more twisting about the NN bond, and θ is 138.2° (that is, the

---

(14) (a) Dewar, M. J. S.; Jennings, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 3655. (b) Dewar, M. J. S.; Jennings, W. B. *Tetrahedron Lett.* **1970**, 339. (c) Dewar, M. J. S.; Jennings, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 1562.

(15) Although Allinger's MM2 program is not completely parameterized for hydrazines or acylated hydrazines, we used the latest provisional parameter set (9/30/86) for CNNC and NCO groups with unknown torsional parameters set equal to zero to investigate the assertion that a large steric component should not be present for **6**; the barrier obtained was under 4 kcal/mol, in agreement with this assertion.

(16) Lunazzi, L.; Maccantelli, D. *Tetrahedron* **1985**, *41*, 1991.

(17) (a) Tomiie, Y. *Acta Crystallogr.* **1958**, *11*, 875. (b) Shintani, R. *Acta Crystallogr.* **1960**, *13*, 609. (c) Hinderer, A.; Hess, H. *Chem. Ber.* **1974**, *107*, 492.

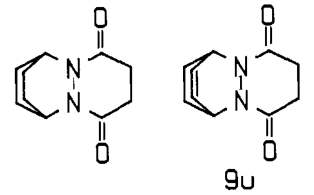
(18) Goldberg, I.; Bernstein, J.; Kosower, E. M.; Goldstein, E.; Pashenchevsky, B. *J. Heterocycl. Chem.* **1983**, *20*, 903.

Table III. Comparison of Experimental X-ray Structures with Those Calculated by MNDO and AM1

compd	quantity	X-ray	MNDO	AM1
6	d(N—N), Å	1.379	1.361	1.364
	d(N—CO), Å	1.355	1.441	1.437
	d(C═O), Å	1.214	1.221	1.237
	α(av), deg	119.2	117.1	116.2
	θ = dih OCN,NCH$_2$, deg	95.2, 91.5^a	95.1	72.9
	dih OCN,NCO, deg	65.4, 71.7^a	49.8	66.6
	dih H$_2$CN, NCH$_2$, deg	101.4, 104.5^a	120.0	147.6
	ΔH_f, kcal/mol		−70.8	−41.0
7	d(N—N), Å	1.416	1.388	1.407
	d(N—CO), Å	1.356	1.440	1.456
	d(C═O), Å	1.216	1.219	1.231
	α(av), deg	115.8	115.6	112.0
	θ = dih OCN,NCH$_2$, deg	18.6, 21.2^b	1.8	9.3
	dih OCN,NCO, deg	125.4	141.4	120.2
	dih H$_2$CN,NCH$_2$, deg	165.2	145.0	138.8
	ΔH_f, kcal/mol		−57.8	−21.0
8c	d(N—N), Å	1.416	1.372	1.373
	d(N—CO), Å	1.357	1.433	1.405
	d(C═O), Å	1.216	1.223	1.243
	α(av), deg	119.5	119.5	119.96
	θ = dih OCN,NCH$_2$, deg	138.2	128.5	144.7
	dih OCN,NCO, deg	55.9	64.6	39.6
	dih H$_2$CN,NCH$_2$, deg	27.7	38.3	31.1
	ΔH_f, kcal/mol		−55.8	−41.3
9u^c	d(N—N), Å	1.418		
	d(N—CO), Å	1.341		
	d(C═O), Å	1.216		
	α(av), deg	119.2		
	θ = dih OCN,NCH, deg	159.8		
	dih OCN,NCO, deg	37.3		
	dih HCN,NCH, deg	3.0		

^{a}For molecules A and B in the unit cell, respectively. ^{b}No crystallographic C2; for the two rings. ^{c}X-ray data from ref 4.

lone-pair axes are twisted 41.8° from being coplanar) for **8**. The X-ray structure of **9** has not been run, but the closely related **9u**,



9u

differing only by having a double bond in the bicycloalkyl portion of the molecule has,[4] and these data are included in Table III. As for **8**, the nitrogens are almost planar. The bicyclic ring holds the alkylated CN,NC dihedral angle nearly eclipsed and results in θ of 159.8°, so the lone pairs are twisted 20.2° out of coplanarity, roughly half the twist of **8**.

Discussion

Semiempirical Calculations on Acylated Hydrazines. We have carried out semiempirical calculations using Dewar's MNDO[19] and AM1[20] methods on **6**–**8** to see how well these calculations are able to handle the ring size and connectivity differences between these compounds, the compare some results with the X-ray structures in Table III. Generally speaking, both MNDO and AM1 are rather disappointing for the amide linkages,[21] as they yield a CN bond far too long, indicating that the interaction between the nitrogens and the C═O group is calculated to be tco small, although AM1 does yield a shorter CN bond than MNDO. As is the case for tetraalkylhydrazines,[22] both methods give NN bond lengths for acylated hydrazines that are too short. Nevertheless, the CO bond lengths, changes in the amounts of bend at nitrogen, and the θ value changes in the series **6**–**8** are rather better reproduced by MNDO than by AM1. We believe it is noteworthy that AM1 is not an improvement over MNDO for obtaining the structures of these acylated hydrazines, despite the fact that AM1 is an obvious improvement over MNDO for most types of compounds,[20] including tetraalkylhydrazines.[22]

The calculations do get the NN bond rotational angle about right for **6**. Although the amount of N,C═O interaction is clearly calculated to be too low, it might not change much with NN rotation, so we also calculated the NN rotational barrier. This is a more complicated problem than we had imagined at first. The CH$_2$N,NCH$_2$ dihedral angle was fixed at various values by using the PATH option in the calculations, and the rest of the structure was optimized in C_2 symmetry (for syn bent nitrogens) or inversion symmetry (for anti bent nitrogens). More than one structure occurs for a given CH$_2$N,NCH$_2$ dihedral angle, depending upon the relative direction of pyramidalization of the nitrogens, which was found to vary depending on the size of the steps employed and the direction of the PATH steps chosen. As expected from both electronic and steric effects, the greatest destabilization occurs near θ values of 0 and 180°. MNDO gets a $\Delta H^{\ddagger}$ near 180° of about 17.3 kcal/mol, which is significantly higher than the experimental value of $\Delta G^{\ddagger}(-48\ °\mathrm{C})$ = 11.4 kcal/mol; it is known that nonbonded interactions are overemphasized in MNDO calculations. AM1 obtains a $\Delta H^{\ddagger}$ of about 6.3 kcal/mol near θ = 14°, which is substantially too low. The NN rotational curves are distressingly different by MNDO and AM1,[23] and neither is really close enough to the observed value to make these calculations look good enough for predicting rotational barriers in acylated hydrazines.

Acylated Hydrazine Cation Radicals. Our only experimental evidence bearing directly on the cation radicals consists of the ESR spectra for **7**$^+$–**9**$^+$ reported above. Comparing to their R$_4$N$_2$ analogues with both C═O groups replaced by CH$_2$, **7H**$^+$–**9H**$^+$, a(2N) values for **7**$^+$–**9**$^+$ correspond to 42, 29, and 29% decreases.[24] These decreases in a(2N) cannot be directly equated to decreases in spin density at nitrogen for the acylated cations, because the R$_4$N$_2$ analogues are certainly more bent at nitrogen, which increases a(2N) compared to less bent compounds in a rather complex manner.[1] The β-hydrogen splittings (at NCH$_2$) are 4% and 6% higher for **7**$^+$ and **8**$^+$ than for **7H**$^+$ and **8H**$^+$. An increase in $a(\mathrm{H}_\beta)$ is expected if the nitrogens are more planar and the nitrogen spin density is the same because $a(\mathrm{H}_\beta)$ has hyperconjugation as an important component. The ESR spectra of these cation radicals are consistent with only modest delocalization of the spin from the nitrogen atoms onto the carbonyl groups and with acyl groups not removing much more spin density from nitrogen than alkyl groups remove.

An antibonding electron is removed from an orbital that is poorly handled by semiempirical calculations when a hydrazine is oxidized, and the cation radical structures are calculated better than are those of the neutral hydrazines. Both the amounts of bend at nitrogen and inversion barriers at nitrogen for bis-bicyclic tetraalkylhydrazine cation radicals are calculated surprisingly well by AM1,[22b] although MNDO makes these species significantly too flat at nitrogen. We summarize MNDO and AM1 results on acylated hydrazine cation radicals **6**$^+$–**8**$^+$ in Table IV. Both methods agree that the nitrogen atoms are essentially flat (α(av) = 120.0° for flat nitrogens) for all three species, which as pointed out above, is consistent with the observed ESR splitting constants.[25]

---

(19) Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(21) (a) We have also noted that the six-membered rings of **8** are calculated much better by MNDO than by AM1. Neither method is able to reproduce the NN twist of **7**, which seems to be a rather general problem for these methods, as they also do not get the tetrahydro analogue, **7H** twisted, as it is known to be.[21b] (b) Rademacher, P. *J. Mol. Struct.* **1975**, *28*, 97.

(22) (a) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* **1986**, *42*, 1769. (b) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.*, in press.

(23) Plots of calculated energy vs. NN rotational angle obtained by MNDO and AM1 are given in the Supplementary Material.

(24) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916.

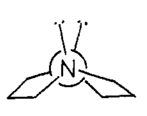
(25) Although the calculated spin densities are qualitatively consistent with the ESR spectra reported, a quantitative comparison will not be attempted because of the complexities in doing so, the limited amount of ESR data, and the rather poor geometrical results of the calculations for these compounds.

Table IV. Comparison of MNDO and AM1 Calculated Structures for Acylhydrazine Cation Radicals

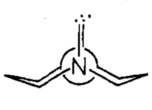
compd	quantity	MNDO	AM1
6^+	d(N—N), Å	1.303	1.299
	d(N—CO), Å	1.512	1.487
	d(C=O), Å	1.204	1.221
	α(av), deg	120.0	120.0
	θ = dih deg OCN,NCH$_2$, deg	26.3	0.3
	dih OCN,NCO, deg	157.4	178.0
	dih H$_2$CN,NCH$_2$, deg	150.0	177.5
	ΔH_f, kcal/mol	119.4	132.0
7^+	d(N—N), Å	1.307	1.316
	d(N—CO), Å	1.505	1.494
	d(C=O), Å	1.199	1.212
	α(av), deg	120.0	119.3
	θ = dih OCN,NCH$_2$, deg	0.6	1.5
	dih OCN,NCO, deg	177.7	164.8
	dih H$_2$CN,NCH$_2$, deg	178.9	167.7
	ΔH_f, kcal/mol	127.3	168.1
8^+	d(N—N), Å	1.311	1.307
	d(N—CO), Å	1.508	1.481
	d(C=O), Å	1.208	1.223
	α(av), deg	120.0	119.8
	θ = dih OCN,NCH$_2$, deg	142.1	168.7
	dih OCN,NCO, deg	35.9	2.7
	dih H$_2$CN,NCH$_2$, deg	40.0	19.9
	ΔH_f, kcal/mol	129.4	132.9

The MNDO and AM1 calculations differ substantially in how twisted about the NN bond the acylated hydrazine cation radicals are predicted to be. AM1 calculations make 6^+ stablest with essentially coplanar lone pairs (θ = 0.3; see Table III), and 8^+ was calculated to have about an 11° twist from coplanarity (θ = 168.7°). In contrast, MNDO gets 6^+ stablest with θ of about 26°, and about a 38° twist from coplanarity for 8^+ (θ = 142.1°). As for the neutral compounds, a large difference in rotational curves is calculated by the two methods. AM1 gets a stronger NN π bond for 6^+ ($\Delta\Delta H_f(\theta = 60°) = 20.0$ kcal/mol) than it does for the parent $H_4N_2^+$ ($\Delta\Delta H_f(\theta = 60°) = 15.9$ kcal/mol). In contrast MNDO makes 6^+ significantly twisted, and gets $\Delta\Delta H_f(\theta = 60°) = 7.6$ kcal/mol, although it gets a larger $\Delta\Delta H_f(\theta = 60°)$ value for $H_4N_2^+$ (16.6 kcal/mol) than does AM1. The unreasonably large nonbonded steric interactions obtained by MNDO[20] are probably responsible for the rather different results. In summary, semiempirical calculations get even diacylated hydrazine cation radicals to have essentially a full three-electron π bond between the nitrogens and almost no delocalization onto the carbonyl groups. The ESR nitrogen splitting constants suggest that this conclusion is exaggerated and that modestly more delocalization of spin onto the acyl groups occurs, but are also consistent with the picture of the cation having a large amount of three-electron π bonding and the carbonyl groups only delocalizing a modest amount of spin.

Changes in Oxidation Properties of Acylated and Alkylated Hydrazines. Complex changes in vIP and $\Delta G°$e occur in both the acylated and alkylated hydrazines as their alkyl groups are linked into rings (Figures 1 and 2). First we consider the vIP changes. Closure of an N,N′ five-membered ring in going from **4** to **5** lowers vIP 0.62 eV, but the same structural change in going from **4H** to **5H** lowers vIP only 0.40 eV. The flatter acylated nitrogen raises the lone pair,lone pair interaction for a given five-ring torsional interaction. **7** (θ = 20°, α(av) = 115.8°) has a 0.38-eV-lower vIP than does **6** ($\theta \sim 93°$, α(av) = 119.2°). **7Htw** both is more twisted and has more-pyramidal nitrogens (θ = 38°, α(av) = 107.7°[21b]) than **6H** and has vIP only 0.02 eV different from **6H**. The N,N′ bis-six-membered ring closure in comparing **8** to **6** lowers vIP 0.41 eV, while **8H** has a 0.30-eV-lower vIP than **6H**. The nearly planar nitrogens of **8** cause its lone pairs to be twisted almost 48° out of coplanarity, while those of **8H** are expected to be coplanar like those of model compound **11**, but strongly pyramidal (α(av) = 107.7 for **11**).[26] A significantly larger vIP lowering is observed for **9** vs. **6** (1.15 eV) than **9H** vs. **6H** (0.85 eV), presumably caused by greater flattening at N in the bis-acylated compound.



7Htw



7Hecl

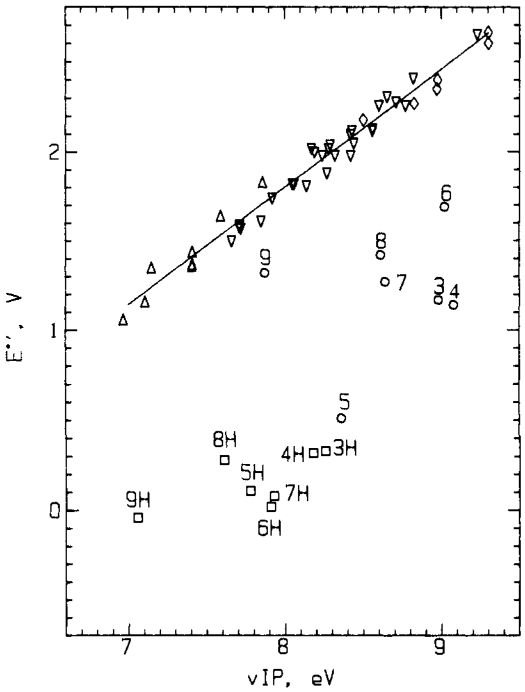


Figure 5. Plot of $E°'$ vs. vIP. The triangles are fused-ring aromatic hydrocarbons, the inverted triangles are alkylated benzenes, and the diamonds are bicyclic peroxides; the line is the least-squares line through these points. The circles are acylated hydrazines and the squares, their tetraalkylhydrazine analogues with C=O replaced by CH$_2$.

11

The changes in $E°'$ upon acyl substitution (Figure 2) only roughly mirror those in vIP. $E°'$ changes include both radical cation relaxation energy differences and solvent stabilization difference effects. For R_4N_2, gas-phase equilibration studies have shown that solvent stabilization differences are not sensitive to θ and show a regular decrease with increasing size of the alkyl groups,[10] so we do not expect that the principal reason for the different patterns of Figures 1 and 2 is mostly caused by solvent stabilization differences. The larger $E°'$ difference for **4** and **4H** than for **3** and **3H** despite the opposite trend in vIP differences, however, is most likely to be caused by poorer solvation for the acetylated cation radical than for the formylated cation radical.

The points in an $E°'$ vs. vIP plot lie on a single straight line for compounds as different as fused-ring aromatics (where the number and connectivity of C(sp) 2p orbitals changes vIP), polyalkylated benzenes (where the number of "inductively electron-releasing" alkyl groups changes vIP), and bicyclic θ = 0° peroxides.[27] Despite the fact that three different solvents were used to obtain the $E°'$ data (which may well hide significant solvation energy differences between the classes of compounds), the 41 points follow the regression line of eq 2 with r = 0.987,

$$E(\text{reg}),\ \text{V} = 0.659\text{vIP} - 3.466 \qquad (2)$$

---

[26] Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461.

[27] Nelsen, S. F.; Teasley, M. F.; Bloodworth, A. J.; Eggelte, H. J. *J. Org. Chem.* **1985**, *50*, 3299.

Table V. Deviations of $E^{\circ\prime}$ Values of Some Alkylated and Acylated Hydrazines from the $E^{\circ\prime}$,vIP Line of Eq 3

compd type	compd	$\delta\Delta Ge$, kcal/mol
tetraalkyl	**3H**	37.9
	4H	36.9
	5Htee	35.7
	6H	39.7
	7Htw	38.6
	8H	29.1
	9H	28.2
monoacyl	**3**	31.7
	4	29.4
	5	35.3
N,N'-diacyl	**6**	18.1
	7	22.0
	8	18.1
	9	9.1

average deviation from the line of 1.2 kcal/mol. About the only structural feature the above compounds have in common is that the electron is removed from a pure p MO, so that relaxation due to rehybridization upon electron removal cannot be present. Hydrazines fall far below the line in such a plot, and the deviations $\delta\Delta Ge$ (eq 3) are listed in Table V. The reason for trying to use

$$\delta\Delta Ge\text{, kcal/mol} = 23.06[E(\text{reg}) - E^{\circ\prime}(\text{obsd})] \qquad (3)$$

such a line to understand our data is that we believe that the principal reason for tetraalkylhydrazines being easier to oxidize than the regression line for the above classes of compounds is that they undergo a large geometry change upon electron removal and hence have a large relaxation energy. The relaxation energy has been shown[10] to be extremely sensitive to θ, and hence to vIP (see Table II for how sensitive vIP is to θ for different conformations of **5H** and **7H**). The effects of changing the alkyl group structures on both vIP and $E^{\circ\prime}$ are well worked out for R_4N_2, but too complex to summarize properly in a sentence or two. In general, vIP is very sensitive to ΔIP and hence to θ, and also to lone-pair s character (α(av)). The relaxation energy has significant contributions from both enthalpy and entropy changes when the vertical cation relaxes to the adiabatic one. An obvious difficulty in any vIP,$E^{\circ\prime}$ correlation is that vIP is an enthalpy, but $E^{\circ\prime}$ a free energy; when entropy changes are important (and they are easily detectable in R_4N_2 ionization[10]), direct comparison is going to be a problem. Nevertheless, the observed $\delta\Delta Ge$ values are 35.7–39.1 kcal/mol for the acyclic and five-membered-ring cyclic R_4N_2 compounds here (**3H**–**7H**), but significantly smaller at 29.1 and 28.2 kcal/mol for **8H** and **9H**, respectively. These numbers are somewhat larger than the differences between the vIP values and the gas-phase relaxation free energies at room temperature for the compounds studied in the gas phase:[10] **3H** (33.4), **5H** (27.1), **6H** (35.7), **7H** (34.1), and **8H** (23.9). The differences between the solution-phase $\delta\Delta Ge$ values (Table V) and these gas-phase vIP, relaxation free energies are rather constant, at 4.5, 8.6, 4.0, 4.5, and 5.2 kcal/mol, respectively. We are unable to rationalize the larger difference for **5H** than for the other compounds, but believe that the comparison shows that the major reason for R_4N_2 showing large $\delta\Delta Ge$ values is indeed the geometry relaxation that accompanies electron loss, which is phase independent.

3, **4**, and **6** share the structural features of having perpendicular lone pairs in the neutral forms and planar acylated nitrogens. The $\delta\Delta Ge$ values observed for **3** and **4** are 31.7 and 29.4 kcal/mol, respectively, 16 and 20% smaller than $\delta\Delta Ge$ for **3H** and **4H**, while $\delta\Delta Ge$ for the N,N'-diacylated compound **6** is 54% smaller than for **6H**, but still a substantial 18.1 kcal/mol. The N,N'-diacylated compounds **8** and **9** also have nearly planar nitrogens. The fact that they and their R_4N_2 analogues **8H** and **9H** have substantial and different lone pair,lone pair interactions makes direct comparison less valid, but $\delta\Delta Ge$ for **8** is observed to be 38% smaller than for **8H**, and that for **9** 68% smaller than for **9H**. Although these numbers include solvent stabilization differences of unknown size, we think it is clear that electron removal from a planar acylated nitrogen is associated with a substantial relaxation energy, despite the fact that rehybridization associated with flattening at nitrogen cannot be a factor.

A major change in bonding must occur upon electron removal, even though the nitrogen stays planar. A neutral amide nitrogen lone pair ($n_{N'}$) has a large electronic interaction with π(CO); amide rotational barriers approach 20 kcal/mol. After electron removal, the $n_{N'}$,π(CO) electronic interaction will, however, be small. Feller, Davidson, and Borden[28] have pointed out that on the basis of high-level ab initio calculations, heteroallyl radicals with electronegative atoms at the ends (which certainly characterize amide cation radicals) have insignificant allyl stabilization. The same conclusion is obtained from semiempirical calculations. As pointed out above, the amide bond is poorly treated by semiempirical calculations, and AM1 only gets a 10.1 kcal/mol rotational barrier for formamide,[20] but it correctly estimates the barrier to essentially disappear in the cation radical. The planar (HN,CO dihedral angle $\phi = 0°$) form remains the energy minimum, but $\phi = 90°$ is now a second minimum only 0.3 kcal/mol higher than $\phi = 0°$, and the maximum occurs near 45°, 0.6 kcal/mol higher in energy. $N^{+\bullet}$,π(CO) interaction is estimated to be very small, only 0.3 kcal/mol better than the $N^{+\bullet}$,σ(CH) and σ(CO) hyperconjugative interaction which maximizes at $\phi = 90°$. The $n_{N'}$ orbital is less stabilized in $H_2NNH\text{-}CHO^{+\bullet}$, so more allylic stabilization is obtained, but a rotational barrier of only 2.9 kcal/mol is calculated; for $Me_2NMeN\text{-}CHO$ ($3^{+\bullet}$), steric interactions are larger, and the stablest form is calculated to have a 90.5° NN,CO angle, with the 180° form 3.7 kcal/mol higher in energy. Although AM1 calculations are certainly rather inaccurate for compounds having amide nitrogens, these calculations do qualitatively agree with our ESR results, which indicate that even when the NN,CO dihedral angle is held near 180° by structural constraints, little spin delocalization into the carbonyl groups occurs. They also give a $\Delta\Delta H_f$ of relaxation between the vertical cation radical and the geometry-optimized, UHF cation of $3^{+\bullet}$ at 28.1 kcal/mol, which is consistent with the substantial relaxation energies inferred from the large $\delta\Delta Ge$ values observed.

Conclusion

Carbonyl substituents on hydrazines cause the nitrogens to flatten completely when the nitrogen lone pairs can be substantially twisted from coplanarity, but for *N,N'*-cycloalkyl cases in which the hydrazine is incorporated in a five-membered ring, substantial deformation of the nitrogens from planarity occurs, and for **7**, α(av) is 115.8°. The p-rich nitrogen lone pairs in *N,N'*-diacylhydrazines cause substantially higher electronic components to NN rotational barriers than for tetraalkylhydrazines, and **6** has an 11.4 kcal/mol rotational barrier. Electron removal from acylated hydrazines is far more difficult than from tetraalkylhydrazines, but the cation radicals formed have NN three-electron π bonds, and delocalize little spin into the CO groups even when these are held in position for maximum electronic interaction with the three-electron π bond. Amide resonance has largely disappeared in the cation radicals. Although the vertical cation radicals of acylated hydrazines have smaller relaxation energies than those of tetraalkylhydrazines of comparable substitution, substantial relaxation energy is present even when the nitrogens are planar in both the neutral forms and the cation radicals. A paper on alkylated and acylated hydroxylamine cation radicals that agrees with these conclusions will appear soon.

Experimental Section

3 and **4** were prepared by acylation of trimethylhydrazine,[29] and **6**,[30] **7**,[31] **8**,[32] and **9**[12] were also prepared by literature methods.

1,2-Dimethyl-3-ketopyrazolidine (5) was prepared by refluxing a mixture of 1.0 g (7.5 mmol) of 1,2-dimethylhydrazine dihydrochloride

---

[28] Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347.

[29] Beltrami, R. T.; Bissel, F. R. *J. Am. Chem. Soc.* **1956**, *78*, 2467.

[30] Stetter, H.; Findeisen, K. *Chem. Ber.* **1965**, *98*, 3228.

[31] Stetter, H.; Spangenberger, h. *Chem. Ber.* **1958**, *91*, 1982.

[32] Nelsen, S. F.; Clennan, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4004.

in 15 mL of ethanol with 0.75 mL (0.9 mmol) of methyl acrylate and 2.5 mL of triethylamine for 3 h, cooling and concentrating to a solid residue, washing with ether, and concentrating to an oil. Chromatography on base-washed alumina (CHCl$_3$ eluant) gave **5** as a clear oil in 22% yield: ^{1}H NMR δ (CDCl$_3$) 3.54 (s, 3 H), 2.60 (t, 2 H), 2.35 (t, 2 H), 2.05 (s, 3 H); empirical formula determined by high-resolution mass spectroscopy.

VT NMR of **6** (^{1}H NMR δ (CDCl$_3$) 3.60 (t, NCH$_2$), 2.42 (t, OCCH$_2$), 2.15 (pent, CCH$_2$C)) was determined on a Bruker WP-270 in CH$_2$Cl$_2$. The AB pattern at δ 3.6 observed at low temperature when the δ 2.15 siganl was decoupled showed below coalescence at -90 °C (J_{AB} = 8.9 Hz, $\Delta\nu$ = 21.91 Hz), -86.8 (8.8, 22.7$_3$), -84.5 (8.7, 22.2$_6$) -79.0 (8.8, 24.4$_3$), -67.5 (8.6, 27.6$_4$), and coalescence was achieved at -48 °C, where $\Delta\nu$ was extrapolated to 32.3 Hz, leading to $\Delta G^{\ddagger}(-48\ °\mathrm{C})$ of 11.36 kcal/mol.

Photoelectron spectra were determined on a rebuilt[10] Varian IEE-15, ESR spectra on a Varian E-15, and cyclic voltammograms on Parr equipment.[10] Calculations were carried out on VAX 8600 and IBM PC-XT equipment.

Crystal Structure Data. Intensity data were measured with a Philips PW 1100 four-circle, computer-controlled diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The crystal structures were solved either by MULTAN 80[33] or by SHELX 76[34] and refined by SHELX 76 with anisotropic vibrational parameters for O, N, and C atoms and isotropic parameters for H atoms. The scattering factors for O, N, and C atoms are from Cromer and Mann[35] and those for H from Stewart et al.[36]

6, C$_8$H$_{12}$N$_2$O$_2$; monoclinic $P2/n$ space group; a = 12.683 (6) Å, b = 5.282 (3) Å, c = 12.509 (6) Å, β = 92.48 (2)°; 1479 reflections measured, 1450 used in the refinement, R = 0.058, R_w = 0.079. There are two molecules in the asymmetric unit, each occupies a twofold-axis special position.

7, C$_6$H$_8$N$_2$O$_2$; monoclinic $P2_1/n$ space group; a = 10.722 (5) Å, b = 6.110 (3) Å, c = 10.321 (5) Å, β = 110.57 (2)°; 1291 reflections measured, 1153 used in the refinement, R = 0.050, R_w = 0.061.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8025111, CHE-8415077, and CHE-8401836), the Technion VPR Fund, and the Lawrence Deutsch Research Fund for partial financial support of this work.

Registry No. 3, 3645-44-1; **4**, 6261-36-5; **5**, 18714-58-4; **6**, 60769-64-4; **7**, 19720-72-0; **7**$^+$, 109669-74-1; **8**, 3661-10-7; **8**$^+$, 109669-75-2; **9**, 72282-81-6; **9**$^+$, 84960-96-3.

Supplementary Material Available: Listing of atomic coordinates, anisotropic temperature factors, and bond lengths and angles for **6** and **7**, photoelectron spectra for **3**–**9**, MNDO and AM1 bond lengths and bond angles for comparison with Figures 3 and 4 for **6**, **7**, and **8**, and plots of NN twisting barriers for **6** and **6**$^{\bullet +}$ by MNDO and AM1 (17 pages). Ordering information is given on any current masthead page.

---

[33] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, S.-P.; Woolfson, M. M. Multan 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; Universities of York, England, and Louvian, Belgium.

[34] Sheldrick, G. M. Shelx, Program for Crystal Structure Determination, University of Cambridge, 1976.

[35] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A*: *Cryst. Phys. Diffr. Theor. Gen. Crystallog.* **1968**, *A24*, 321.

[36] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Anionic Rearrangements of *syn*- and *anti*-7-Cyclopentenyl-7-hydroxynorbornenes. The Case for Sequential Ring Cleavage and Intramolecular Michael Addition

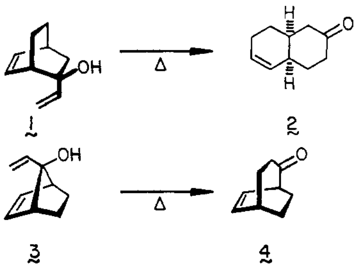
Leo A. Paquette,* Francis Pierre, and Charles E. Cottrell[1]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210.

Received February 23, 1987

Abstract: Oxyanion formation within several *anti*-7-norbornenols is shown to foster rearrangement predominantly via formal antarafacial-retention [1,3]-sigmatropic bridgehead carbon migration. To a lesser extent, oxy-Cope bond reorganization takes place. Under the same conditions, the epimeric syn alcohols undergo exclusively the first of these processes, but with regiochemical and stereochemical characteristics identical with those observed in the first series. The favored mechanism for the [1,3]-shift pathway involves heterolysis of a norbornene bridgehead/apical bond, proper conformational alignment within the resulting 3-cyclohexenyl anion intermediate, and intramolecular Michael addition under kinetic (and thermodynamic) control. The presence of a 2-methyl group induces an avoidance to the positioning of this substituent at one of the allyl anion termini, for obvious energetic reasons. In contrast, the oxy-Cope process gives every indication of occurring concertedly in a boat transition state. The 2-methyl substituent, when present, directs rebonding to the second (unsubstituted) norbornenyl trigonal center in order to avoid generation of a quaternary carbon. Despite the concert with which [3,3]-sigmatropy takes place, it never is the dominant pathway, probably because of the somewhat distorted geometry required in the relevant transition states.

The rapid elaboration of polycyclic ketones with good stereochemical control is an important objective in organic synthesis. That 3-hydroxy-1,5-hexadienes can be made to undergo thermal oxy-Cope rearrangement with formation of such carbonyl compounds was first described by Berson and Jones in 1964.[2] In these reports, the conversion of **1** and **3** principally to **2** and **4**, respectively, was detailed. Both reactions were considered to proceed stepwise via diradical intermediates. Preferred operation within **3** of the so-called "single-inversion" pathway was attributed to the less than ideal proximity of its diene termini. The geometric



---

[1] Campus Chemical Instrument Center.

[2] (a) Berson, J. A.; Jones, M., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5017. (b) Berson, J. A.; Jones, M., Jr. *Ibid.* **1964**, *86*, 5019.

0002-7863/87/1509-5731$01.50/0