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Thermodynamic Destabilization of N-Centered Radical Cations by a γ-Keto Group

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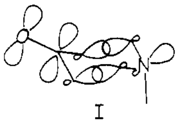
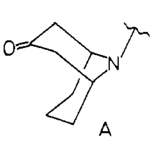
Abstract: Vertical ionization potentials measured by PE spectroscopy and formal oxidation potentials measured by cyclic voltammetry are compared for several 9-substituted 9-azabicyclo[3.3.1]nonan-3-one derivatives and their nonketo analogues. The compounds studied include hydrazines, 2-tetrazenes, *p*-phenylenediamines, *p-tert*-butylanilines, and *tert*-butylamines. The formal potential for one-electron oxidation is raised 3.2–7.4 kcal/mol by the presence of the keto group, depending on the amount of positive charge at N_9 in the radical cation. In contrast, the formal potential for 3-oxobutyltrimethylhydrazine is only 0.5 kcal/mol higher than that of butyltrimethylhydrazine, although the change in vertical ionization potential is as large in the acyclic as in the bicyclic hydrazine.

Cookson and co-workers[1a] pointed out the generality of σ-coupled π,π and n,π interactions in affecting the UV spectra of compounds in which two π systems or a π system and a lone pair each overlap well with a carbon–carbon single bond connecting the two functional groups. Hoffmann[1b] has discussed such interactions in simple MO terms. An example of a σ-coupled nitrogen lone pair and carbonyl group which is particularly pertinent to this work is the 4-ketopiperidine system, for which the orbitals of interest are shown diagrammatically in I. The geometry is excellent for σ-coupled n,π (C=O) interaction through two equivalently disposed CC σ bonds when the nitrogen substituent is axial, as shown. A long-wavelength UV band (λ_{max} about 230–250 nm) which is not present in compounds containing the isolated chromophores has been assigned to the σ-coupled charge-transfer transition, and observed in many β-amino ketones having favorable geometry.[2] Other spectral influences of σ coupling include changes in the carbonyl IR stretch[2f] and higher energy nitrogen lone pair ionization potential in the photoelectron (PE) spectrum.[3] The basicity of the nitrogen is also decreased.[2d,f,h]

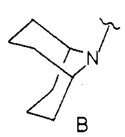


I

We have prepared several σ-coupled β-amino ketones containing the 9-azabicyclo[3.3.1]nonan-3-one system (9-ABN-3-one, **A**) in the course of making their nonketo analogues, 9-ABN derivatives, **B**.[4] Derivatives of **B** have Bredt's rule protected CH bonds α to nitrogen, and far longer lifetimes when the nitrogen has only one unshared electron (and hence a positive charge) than analogous but nonprotected compounds, which rapidly deprotonate α to nitrogen. The long $B^{+\cdot}$ lifetimes allow measurement of their relative $\Delta G°$ for electron removal in solution by determining the formal potential for one-electron oxidation ($E°'$), using cyclic voltammetry (CV). The keto group of **A** will destabilize $A^{+\cdot}$. We hoped that the kinetic stabilization provided by the **B**redt's rule effect would provide long enough lifetimes to permit measurement of the thermodynamic destabilization of the **A**,$A^{+\cdot}$ electron transfer equilibrium relative to the **B**,$B^{+\cdot}$ equilibrium. This would establish the magnitude of the effect of introducing the carbonyl group at C_3, in kcal/mol, for radical cation formation, a reaction which should be especially sensitive to the carbonyl substitution.



A



B

Table I. UV Spectral Data for 1–6 in Acetonitrile

compd	λ_{max}, nm (log ε, M^{-1} cm^{-1}
1AA	257 (3.3)
1AB	sh ~260 (2.9); 280 (3.0)
1BB	sh ~240 (2.2)
2AA	273 (4.2), sh 320 (3.3)
2BB	279 (4.1), 340 (3.1)
3AA	sh 260 (3.8); 288 (4.0)
3BB	sh 264 (3.7); 293 (4.0)
4A	sh 224 (3.2)
4B	no sh; log ε 3.0 at 240 nm
5A	254 (4.3); sh 290 (3.5)
5B	261 (4.2); sh 303 (3.2)
6A	234 (3.1); sh 268 (2.8)
6B	sh 254 (2.8)

Table II. PE Spectral Data for 1 and 4–6

compd	vertical ionization potentials,[a] eV
1AA	7.77; 8.77; 9.07 (n(C=O)); ~10.1[b]
1AB	7.66; 9.25 (n(C=O)); ~9.8[b]
1BB[c]	6.94; 9.07
4A	8.03; ~9.0;[d] 9.09 (n(C=O)); ~10.1–10.2[b]
4B[e]	7.53; 8.42; ~9.5–9.6
5A	7.34
5B[c]	6.94; 8.64 (π); 9.23 (n(C=O) + π?)
6A	7.76; 8.95 (9.08[f]) (n(C=O))
6B[c]	7.30
7	8.59; 9.38
8	ca. 9.0 (very broad)[g]
9	8.12; 8.66

[a] Maxima of GFIT Gaussians (see Experimental Section). Lone pair combination orbitals, except for peaks marked n(C=O) or π, which are assigned to carbonyl oxygen π lone pairs or aromatic π electrons. [b] Position uncertain because of overlap with σ ionizations. [c] From ref 4. [d] Position uncertain; overlap with the 9.09-eV peak. [e] From ref 6. [f] 9.04 (half-width 1.49 eV) when fit with a single Gaussian. [g] Requiring two peaks to fit the experimental data gave IPs of 8.97 and 9.14 eV, with half-widths at half-height of 1.09 and 1.45 eV, respectively.

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Table III. Comparison of Formal Potentials for Electron Transfer of 1–8

compds	substituent	$E^{\circ\prime b}(\Delta E^{\text{pp}\,c})$	9-ABN-3-one deriv $E^{\circ\prime b}(\Delta E^{\text{pp}\,c})$	9-ABN deriv $E^{\circ\prime\, b}(\Delta E^{\text{pp}\,c})$	a(N), G^d
1AB; **1BB**	-9-ABN	0.22(68) [1.33(80)]^e	−0.01(62) [1.18(70)]^e	0.23 [0.15]^e	13.15^a
1AA; **1AB**	-9-ABN-3-one	0.45(69) [1.59(110)]^e	0.22(68) [1.33(80)]^e	0.23 [0.26]^e	
2AA; **2BB**	$-(C_6H_4)-$	0.29(70) [0.79(82)]^e	0.02(68) [0.60(78)]^e	0.14^f [0.10]^{e,f}	7.4^a
3AA; **3BB**	–N=N–	0.75(81) [1.61(73)]^e	0.40(72) [1.36(65)]^e	0.18^f [0.13]^{e,f}	11.1^a
4A; **4B**	$-NMe_2$	0.32(77)	0.11(62)	0.21	
5A; **5B**	$-C_6H_4$-4-*t*-Bu	0.84(78)	0.65(77)	0.19	
6A; **6B**	-*t*-Bu	0.95(72)	0.63(71)	0.32	19.5^a
7; 9		0.34(100)	0.32(88)	0.02	
8; 9		~0.55(240)	0.32(86)	~0.23	

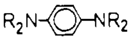
^{a} From ref 4. ^{b} In CH_3CN containing 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte, reported in V vs. SCE. ^{c} The difference in oxidation and reduction peak potentials, reported in mV. ^{d} Nitrogen ESR splitting for the 9-ABN derivative radical cation. ^{e} The numbers in brackets are for the second electron transfer $(\ )^{+\cdot} - e \rightarrow (\ )^{2+}$. ^{f} Per 3-keto substituent.

Results

We report here a comparison of spectral properties and $E^{\circ\prime}$ for **1AA**–**6A** with those for their noncarbonyl analogues **1BB**–**6B**.

R_2NNR_2

1



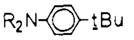
2

$R_2NN{=}NNR_2$

3

R_2NNMe_2

4

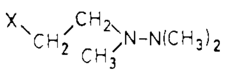


5

R_2N*t*Bu

6

Suffix **A** indicates that R_2N is the 3-keto-9-azabicyclo[3.3.1]nonyl group shown as **A** above, and suffix **B** compounds have the carbonyl replaced by CH_2, as shown in **B**. All **A** derivatives were prepared by double Michael addition of the appropriate amine derivative to 2,7-cyclooctadienone,[5] which Wiseman and coworkers[2h] had already shown is successful even for the very hindered **6A**. Acyclic hydrazines **7** and **8**, which have an electron-withdrawing β substituent but lack the special alignment of this group favoring σ coupling, were compared with the saturated alkyl analogue **9** in hopes of seeing if special alignment effects for **A** would be revealed. UV data, vapor phase vertical ionization potentials measured by PE spectroscopy, and formal oxidation potentials ($E^{\circ\prime}$) measured by CV are collected in Tables I–III.



7 $X= C(=O)CH_3$

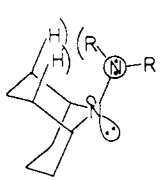
8 $X= C{\equiv}N$

9 $X= CH_2CH_3$

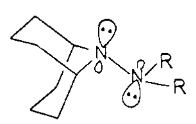
Discussion

UV and PE Spectra. Bands attributable to lone pair, C=O charge transfer absorption cannot be picked out in the conjugated systems **2**, **3**, and **5**, which have other bands in the near UV. The saturated systems **1BB** and **6B** show shoulders in the near UV, and such shoulders also appear in the spectra of **1AB** and **6A**. The presence of extra absorption, presumably caused by charge-transfer bands, is apparent for **1AB**, **1AA**, **4A**, and **6A**.

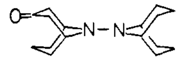
The vertical IP data of Table II provide an estimate of the homo energy of these compounds which is of interest in comparing their ease of oxidation in solution. Introduction of a 3-keto group raises IP_1 by 0.50 for **4**, 0.45 for **5**, and 0.36 eV for **6**. The trend is much less regular in **1**, where introduction of the first 3-keto group raises IP_1 0.7 eV, but the second only raises it an additional 0.1 eV. We suggest that the explanation for this anomaly lies in conformational changes in these molecules. **1BB** is exclusively in the lone pair–lone pair dihedral angle θ = 180° anti conformation in the solid state,[6] and its PE spectrum is consistent with only this conformation being observed in the vapor phase. Sterically less hindered hydrazines exist in $\theta \sim 90°$ conformations.[7] The 9-ABN system forces an N_9 substituent to be axial to one piperidine ring, causing steric interaction of one of the R groups of 9-R_2N-9-ABN with this ring when θ is near 90° (see II). Such interaction is relieved in the anti conformation III. The 9-Me_2N-substituted compounds **4A** and **4B**[8] exhibit PE ionizations for both anti and gauche conformations, implying that these conformations are similar in energy. The piperidine rings of the 9-ABN system are flattened relative to those of a monocyclic piperidine,[6] and N_9 would presumably also flatten to relieve congestion in II. We suggest that the electronic destabilization of the θ = 180° anti conformation III relative to a gauche conformation is on the order of 3–4 kcal/mol, from the near equality of the energies of the diequatorial and axial, equatorial conformations of dimethylhexahydropyridazine[9] and the 2.5–3.0 kcal/mol greater stability for equatorial than axial *N*-methylpiperidine.[10] The bis-9-ABN systems **1** have two steric interactions like II, and, if each is any large fraction of 3 kcal/mol, there will be no detectable amount of gauche (II) conformations. However, the 3-keto-9-ABN ring is flattened compared to its saturated analogue.[11] The PE spectrum of **1AA** shows both anti and gauche conformation peaks, in contrast to both **1BB** and **1AB**. The first observed peak for **1AA** as well as **4A** therefore consists of unresolved IP_1 peaks for both gauche and anti conformations, and the crowded gauche conformation probably has significantly flattened nitrogens. Such flattening will lower IP_1. IP_1 for **6B** is 0.31 eV lower than it would be if N_9 were not flattened.[4c] Considerable uncertainty as to the vapor-phase IP_1 for especially **1AA** and **4A** results from these overlap problems.



II



III



1AB

$E^{\circ\prime}$ Values. The effect of 3-keto substitution on $E^{\circ\prime}$ for a 9-ABN system is quite substantial despite the two saturated

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carbons intervening between the nitrogen and the carbonyl group. For the hydrazine system, $E^{\circ\prime}$(**1AB**) - (**1BB**) = 0.23 V, or 5.3 kcal/mol, so the equilibrium constant for the reaction

$$(\mathbf{1AB})^{+\cdot} + \mathbf{1BB} \rightleftarrows \mathbf{1AB} + (\mathbf{1BB})^{+\cdot} \qquad (1)$$

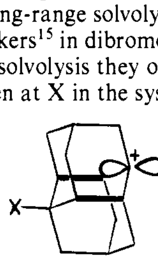
is 8.5×10^3. $\Delta E^{\circ\prime}$ for **1AA** is 0.46 V (10.6 kcal/mol). The effect of a second keto group is additive in solution, in contrast to the nonadditive effect on IP_1 in the vapor phase. The fact that **1AA** has two conformations of similar energy but different degrees of flattening at nitrogen has a significant perturbation on the PE spectrum, but $E^{\circ\prime}$ is only sensitive to the thermodynamic energy gap between neutral and radical cation, which is experimentally twice that for **1AB** vs. **1BB**. The magnitude of the effect of 3-keto substitution on $E^{\circ\prime}$ is not constant, but varies from a maximum of 0.32 V (7.4 kcal/mol) for the *tert*-butylamine system **6** to a minimum of 0.14 V (3.2 kcal/mol) per keto group for the *p*-phenylenediamine system **2**. The amount of positive charge at N_9 is greatest in the amine and least in the *p*-phenylenediamine system, which has the largest π system for charge delocalization. An experimental measurement related to charge density at N in the radical cation is the nitrogen ESR splitting constant, a(N). a(N) is proportional to total spin density directly at the nitrogen nucleus and not to charge density itself, and changes in either the degree of spin delocalization off N into attached π systems or the amount of hyperconjugative spin delocalization will decouple spin and charge delocalization. Nevertheless, there is experimentally an excellent linear correlation between $\Delta E^{\circ\prime} = E^{\circ\prime}$(9-ABN-3-one) - $E^{\circ\prime}$(9-ABN) derivative and a(N). The average $\Delta E^{\circ\prime}$ deviation observed from the least-squares correlation which includes the origin as a point, $E^{\circ\prime}(\mathrm{V}) = 0.0164a(\mathrm{N}) + 0.0043$, is 0.009 V, about the reproducibility of the $E^{\circ\prime}$ measurements. A large fraction of the vapor-phase ΔIP_1 for the **A** and **B** substituted molecules appears in the solution-phase $\Delta E^{\circ\prime}$; $\Delta E^{\circ\prime}/\Delta IP_1$ is 0.42 for the hydrazine **4**, 0.48 for the anilines **5**, and 0.70 for the *tert*-butylamines **6**. Only small $\Delta E^{\circ\prime}/\Delta IP_1$ values of about 0.15 were observed when the ease of oxidation of tetraalkylhydrazines was altered by changing the length of the alkyl groups.[12] This behavior is consistent with the majority of the IP_1-lowering effect of alkyl group homologation being a polarizability effect which disappears in solution,[13] although solvation effects (less stable radical cations with longer nonpolar alkyl groups) are also present and also contribute to the low ratio. Because the major reasons for an IP_1 increase in **A** substituted amino compounds compared to **B** substituted ones is destabilization of the radical cation by the keto group, a polar effect which does not disappear in solution, it seems reasonable that $\Delta E^{\circ}/\Delta IP_1$ is rather large.

The acyclic β-acetyl- (**7**) and β-cyano- (**8**) hydrazines were compared with their saturated analogue **9** to see if having β electron-withdrawing groups which are not required to be specially aligned would lead to substantially different effects than having them aligned as in **A**. The PE spectra of **7** and **8** exhibit significantly broader low-energy ionization bands than do acyclic tetraalkylhydrazines such as **9**. The lowest energy Gaussian curves of the best two Gaussian fit to the data for **7** and **8** have half-widths at half-height of 0.9 and 1.1 eV, respecitvely, compared to 0.5 for **9**. This could be a result of greater anisotropy for interaction of a CH_2CH_2X group with the nitrogen lone pair when X is the electron-withdrawing acetyl and cyano than when it is ethyl.

The size of IP_1(**7**) - IP_1(**9**), 0.45 eV, is about the same as for **A** vs. **B** derivatives (0.50 for the hydrazine comparison, **4A**–**4B**), although in the bicyclic case the carbonyl is fixed in position for rather good through-bond overlap, and there are also two σ band pathways between the carbonyl and nitrogen. There are, of course, significant geometry differences between **A** and the expected predominant conformations of **7**. A larger ΔIP_1 for **8** vs. **9** (0.90 eV observed) than for **7** vs. **9** is reasonable, because a cyano group is a considerably stronger electron-withdrawing group than is acetyl, by such criteria as σ_I value.[14]

The observed $\Delta E^{\circ\prime}$ for **7** vs. **9** is only 10% as large as that for **4A** vs. **4B**, although their ΔIP_1 values are similar. $E^{\circ\prime}$ is an adiabatic energy difference, reflecting the energy gap between the most stable forms of the neutral and cation radical species. These geometries could be significantly different for the acyclic case, but not very different for the **A** system. In the **A** system, the electron-deficient p orbital at nitrogen of the radical cation is fixed in position for overlap with the CC bonds which are in turn fixed for effective overlap with the electron-deficient p orbital of the carbonyl carbon. In an acyclic system, rotations which decrease the overlap could occur, decreasing the interaction of the electron-deficient centers, leading to a stabilization compared with the aligned bicyclic case. Thus $\mathbf{7}^{+\cdot}$ should be able to seek out a conformation in which N–carbonyl interaction is minimized, rationalizing the small $\Delta E^{\circ\prime}$ observed relative to the bicyclic case. The increase in $E^{\circ\prime}$ for the cyanohydrazine **8** compared with the tetraalkylhydrazine **9** is ten times the size of that for the acyclic ketohydrazine **7** compared with **9**. In addition to cyano being more electron withdrawing than acetyl, the $N{\equiv}CCH_2CH_2N$ interaction is inherently less anisotropic than the $CH_3(O{=}C)CH_2CH_2N$ interaction because of the cylindrical symmetry of the cyano group. We are, of course, unable to evaluate the solvation difference contribution, which might also be larger in the cyano case.

σ-Inductive and σ-Conjugative Effects. The large $E^{\circ\prime}$ difference for the acyclic and aligned bicyclic ketohydrazines is consistent with a significant geometry-dependent interaction between the CO group and the electron-deficient oxidized nitrogen being transmitted by their mutual overlap with the intervening CC σ bonds. The large effect we see on $E^{\circ\prime}$ is similar in character to the large long-range solvolysis rate effects observed by Schleyer and co-workers[15] in dibromodiamantane systems. The increases in $\Delta G^{\ddagger}$ for solvolysis they observe upon substitution of bromine for hydrogen at X in the systems ionizing to **10** and **11** were 4.4 and 2.7 kcal/mol, respectively. It is useful, however, to carefully distinguish between cases in which polar effects are transmitted via orbital interactions, which might be termed a "σ-conjugative effect", from the "σ-inductive effect".[16] As Stock and co-workers have shown in careful studies of substituted bicyclic acid ionization constants,[17] and as is also clear from molecular orbital calculations[18] such as those by Topsom[18b] on the effect of fluorine for hydrogen substitution on vapor phase proton transfer reactions of amines, there is not a significant transmission of polar effects through several σ bonds, even when an electron-withdrawing substituent is lined up with them as in **12**. The σ-inductive effect falls off far more rapidly than was once believed.[16-18] Even for aligned β-amino ketones analogous to those studied here, the effect of the keto group on basicity, in solution, is quite small. **13** is only 2.4_7 pK units less basic than **14**,[2d] corresponding to a ΔG° dif-



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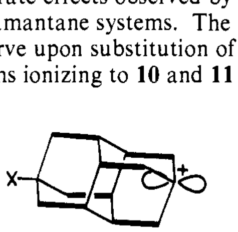

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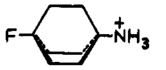

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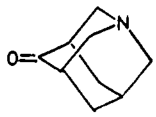

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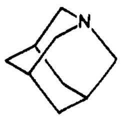

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ference of 1.8 kcal/mol, which is not significantly larger than the basicity changes seen for nonaligned analogues.[2d] Large "σ-conjugative" effects are seen in solution when the electronic demand for stabilization of an unfilled orbital is present, as in Grob fragmentations,[19] solvolyses in systems like **10** and **11**, and the one-electron oxidations discussed here.

Conclusion

Introduction of a 3-keto group into the 9-ABN system in going from **B** to **A** as a dialkylamino substituent maintains the kinetic stabilization of the radical cation, but destabilizes it thermodynamically by 7.4–3.2 kcal/mol, depending upon the amount of positive charge at nitrogen in the radical cation. The tenfold greater change in $E^{\circ\prime}$ upon introduction of a 3-keto group on the 9-Me_2N-9-ABN system than upon the butyltrimethylhydrazine system indicates that the σ-conjugative alignment forced by the bicyclic system is important in causing the rather large thermodynamic destabilization by a keto group isolated from the nitrogen by two carbon atoms. We suggest that the most potentially useful aspect of this work is that it provides a series of electron-transfer couples which resemble each other sterically, have both oxidized and reduced forms that are long lived, and extend over a range of 27 kcal/mol in $E^{\circ\prime}$ (37 kcal/mol if cation radical–dication pairs are included). These compounds should prove useful in electron transfer rate studies.

Experimental Section

Preparations of several of the compounds used here have been published: **1BB**, **3BB**;[6] **2AA**, **2BB**, **5A**, **5B**, **6B**;[4c] **4A**, **4B**;[12a] **6A**;[2h] **9**.[12a]

9-(9-Azabicyclo[3.3.1]nonyl)azabicyclo[3.3.1]nonan-3-one (1AB). A solution of 131 mg (1.07 mmol) of 2,7-cyclooctadienone and 150 mg (1.07 mmol) of 9-amino-9-azabicyclo[3.3.1]nonane in 2 mL of methanol was stirred under nitrogen for 3 days. Filtration of the white precipitate, which was washed with cold methanol, gave 89 mg (32%) of **IAB**, mp 148–151 °C.[17] ^{1}H NMR: δ 3.75 (br s, 2 H), 3.28 (br s, 2H), 2.83 (d of d, *J* = 7, 16 Hz, 2 H), 1.3–2.3 (m, 2 H). IR: no NH, 1700 cm^{-1} (CO).

9,9′-Bis-9-azabicyclo[3.3.1]nonan-3-one (1AA). A mixture of 2.5 g (20.5 mmol) of 2,7-cyclooctadienone, 0.51 g (10.2 mmol) of hydrazine hydrate, and 4 mL of methanol was stirred for 24 h and filtered, and the precipitate washed with cold methanol to give 1.01 g (36%) of **1AA**, after crystallization from acetone mp 258–259 °C.[7] ^{1}H NMR: δ 3.84 (br s, 4 H), 2.81 (d of d, *J* = 7, 16 Hz, 4 H), 2.13 (d, *J* = 16 Hz, 4 H), 1.7–2.0 (m, 8 H), 1.3–1.6 (m, 4 H). IR ($CHCl_3$): no NH, 1700 (C=O), 1100 cm^{-1}.

9-Amino-9-azabicyclo[3.3.1]nonan-3-one. An equimolar mixture of cycloocta-2,7-dienone and hydrazine hydrate in methanol (1 mL/mmol) was stirred at room temperature for 48 h and concentrated, and the residue crystallized from ether, giving 57% of a white solid, mp 72–73 °C.[17] ^{1}H NMR ($CDCl_3$): δ 3.29 (m, 4 H), 2.89 (dd, *J* = 7, 15 Hz, 2 H), 2.32 (br s, 1 H), 1.2–2.2 (m, 7 H). IR ($CHCl_3$): 3300 (NH), 1700 cm^{-1} (C=O).

Azo-9-azabicyclo[3.3.1]nonan-3-one (3AA). A solution of iodine (0.32 g, 1.3 mmol) in 10 mL of methylene chloride was added dropwise to an ice-cooled solution of 195 mg (1.3 mmol) of 9-amino-9-azabicyclo-[3.3.1]nonan-3-one in 10 mL of methylene chloride containing 0.5 mL of diethylamine. Addition was stopped when the iodine color persisted. After the mixture was washed with 2 × 20 mL of sodium thiosulfate solution and dried over magnesium sulfate, concentration gave a yellow solid which was crystallized from methanol to give 135 mg (68%) of white crystals, mp 215–217 °C dec.[17] ^{1}H NMR ($CDCl_3$): δ 4.60 (br s, 2 H), 2.68 (dd, *J* = 7, 17 Hz, 2 H), 2.44 (s, 1 H), 1.5–2.3 (m, 7 H). IR ($CHCl_3$): 1720 cm^{-1} (C=O).

3-Oxobutyltrimethylhydrazine (7). A mixture of 1.78 g (24 mmol) of trimethylhydrazine[18] in 5 mL of Et_2O and 10 drops of methanol was stirred for 50 h with 2.20 g (31.4 mmol) of freshly distilled methyl vinyl ketone. After concentration under vacuum, distillation gave 1.25 g (8.7 mmol) of **7** as a colorless oil, bp 45–51 °C (21 mm).[17] ^{1}H NMR: δ 2.74 (t, *J* = 6 Hz, 2 H), 2.54 (t, *J* = 6 Hz, 2 H), 2.23 (s, 3 H), 2.22 (s, 6 H), 2.15 (s, 3 H). IR: no NH, 1725 cm^{-1} (C—O).

2-Cyanoethyltrimethylhydrazine (8). A mixture of 2.6 g (23 mmol) of 2-(2-cyanoethyl)-1,1-dimethylhydrazine,[19] 6.0 g (200 mmol) of formalin solution, and 2.18 g (51.3 mmol) of sodium cyanoborohydride in 35 mL of acetonitrile was stirred under nitrogen, and 5–7 drops of acetic acid added every 20 min until the pH reached 5–6 (moist pH paper). After the mixture was stirred for 18 h, 10 mL of concentrated hydrochloric acid was added slowly, and the mixture was concentrated to a residue under vacuum. The residue was dissolved in 100 mL of H_2O, made basic with KOH pellets, and extracted with ether, and the organic layer dried over potassium carbonate. Concentration and distillation gave **7** as a colorless liquid, bp 78–85 °C (0.2 mm), 2.18 g (74.8%). ^{1}H NMR ($CDCl_3$): δ 2.63 (m, 4 H), 2.29 (s, 6 H), 2.28 (s, 3 H). IR (CCl_4): no NH, 2265 cm^{-1} (C≡N).

The PE and cyclic voltammetry equipment and data analysis have been previously described.[4]

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