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9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonane and Tetraisopropylhydrazine: Isolable Radical Cations from Hydrazines with Nearly Perpendicular Lone Pairs

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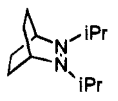
Abstract: Cuprous iodide catalyzes the addition of isopropyl Grignard reagent to triisopropyldiazenium cation (**6**) to give tetraisopropylhydrazine (**3**), a reaction which produces mostly the hydride transfer and deprotonation products of **6** in its absence. 9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonane (**2**), its 3-keto analogue (**4**), and **3** each give isolable radical cations. Crystal structures are reported for **2**, $2^+NO_3^-$, $3^+OTs^-CH_3CN$, and **4**. 2^+ has its isopropyl groups in different rotamers, and 3^+ is nearly isostructural with tetraisopropylethylene (**11**), with each isopropyl methyne hydrogen roughly bisecting the C(Me$_2$) unit of an adjacent isopropyl group. The first dynamic NMR experiments reported on radicals demonstrate that 2^+ occupies the same conformation in solution as in the crystal, and allow rough estimation of the barriers for isopropyl group interconversion in 2^+ and 3^+ at ~11 kcal/mol. Cyclic voltammetry and photoelectron spectroscopic data are reported for **2** and **3**.

Introduction

We recently reported that 2,3-diisopropyl-2,3-diazabicyclooctane (**1**) gives an isolable radical cation.[1] Nonbonded steric interactions force its isopropyl groups to assume conformations with small π(N),C$_\alpha$H overlap, which provides kinetic protection from decomposition by the C$_\alpha$−H bond cleavage reaction which hydrazine radical cations with other singly attached alkyl groups undergo. If only α-branching is required to protect an alkyl group of a hydrazine radical cation, the *N,N*-diisopropyl **2** and tetraisopropyl **3** should also give isolable radical cations. The reason for our interest in them is that their neutral forms are predicted to have lone pair, lone pair dihedral angle θ values near 90°. All previously studied isolable hydrazine radical cations have neutral forms with θ near 0 or 180°, which has precluded detailed study of electron transfer (ET) for hydrazines which should have the slowest ET. The intrinsic barrier for ET, λ in Marcus theory,[2] is the energy difference between a neutral compound and its vertical radical cation, and the rate constant for self-ET, electron exchange between a neutral compound and its own radical cation, is directly proportional to $\exp(-\lambda/4RT)$ in Marcus theory. Large geometry changes between neutral and radical cation oxidation states cause large λ values and hence slow ET. Gas phase measurements have shown that the difference between the vertical and adiabatic ionization potential,[3] $\Delta H_{\rm rel}$ = vIP − aIP, is strongly dependent upon θ, and is a maximum at θ = 90°, which is the electronically preferred value for hydrazines. Semiempirical calculations which are surprisingly successful at calculating $\Delta H_{\rm rel}$ predict it to be about half of the enthalpy contribution to λ.[4] In this work the solid state, solution, and gas phase conformations of **2** and **3** and their radical cations are studied by a variety of experimental techniques. It is established that the neutral forms are in θ ~90° conformations, the geometry changes upon electron removal are estimated, and isopropyl rotation in the radical cations is probed by dynamic NMR.



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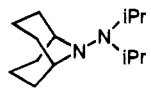

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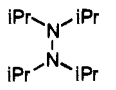

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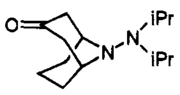
Results

Double Michael addition of 1,1-diisopropylhydrazine to cycloocta-2,7-dienone gave 9-(diisopropylamino)-9-azabicyclo-[3.3.1]nonan-3-one (**4**), which was reduced to **2** in poor yield under Wolff−Kishner conditions at 225 °C. Reductive alkylation of 1,1-diisopropylhydrazine under a variety of conditions only added one more isopropyl group, producing triisopropylhydrazine (**5**). Oxidation of **5** by nitrosyl hexafluorophosphate gave the triisopropyldiazenium salt $6^+PF_6^-$, which we hoped to convert to **3** by adding an isopropyl organometallic to the $(N{=}N)^+$ bond.[1] Reaction of $6^+PF_6^-$ with both isopropyllithium



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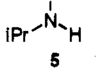

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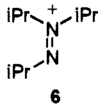

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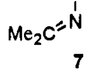

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Table 1. Comparison of Neutral and Radical Cation X-ray Geometries at Nitrogen

	neutral		radical cation	
	4	**2**	$\mathbf{2}^{\cdot+}NO_3^-$	$\mathbf{3}^{\cdot+}TSO^-{\cdot}CH_3N$
d(NN), Å	1.415(2)	1.420(2)	1.346(3)	1.333(4)
$\alpha(C_bNN)$, deg	114.4, 121.3	113.8, 121.2	120.9, 119.5	
$\alpha(C_iNN)$, deg	121.5, 111.7	121.4, 111.5	119.9, 119.3	122.5, 120.1, 112.5, 119.4
$\alpha(C_bNC_b)$, deg	111.3	110.8	112.6	
$\alpha(C_iNC_i)$, deg	117.9	117.7	117.2	117.1;116.9
$\alpha_{av}(N_9)$, deg	115.7	115.3	117.7	
$\alpha_{av}(NiP_2)$, deg	117.0	116.9	118.8	119.9;119.6
dihedral CNNC, deg	123.3, 47.8, −98.7, -90.1_5	125.0, 46.8, −98.8, −89.4	162.0, 152.7, -49.2_5, +3.9	174.6, 169.6
θ,[a] deg	85.6	85.9	22.7	7.9
dihedral HC_iNN[b]	24.8, 166.3	26.2, 168.4	−29.7, 150.4	−170.0, −6.2, −179.9, +9.0

[a] Lone pair, lone pair dihedral angle, calculated assuming the lone pair bisects the CNC angle in a Newman projection down the NN bond. [b] Calculated from $\angle NN'C_iMe$ twist angles assuming the C_iH bond bisects the MeC_iMe angle in a Newman projection down the C_iN' bond: $\phi_{av} = (\angle NN'C_iMe + \angle NN'C_iMe')/2$; $\angle HC_iN'N = \phi_{av}$ or $(\phi_{av} - 180°)$.

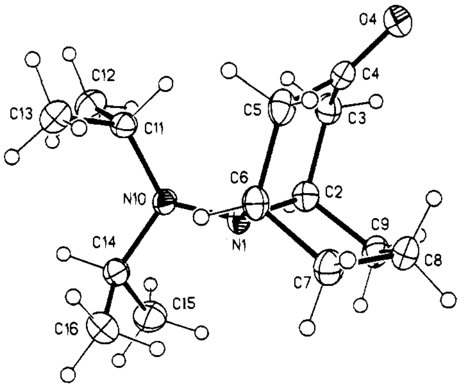


Figure 1. Thermal ellipsoid drawing of the X-ray structure of **4** (50% probability).

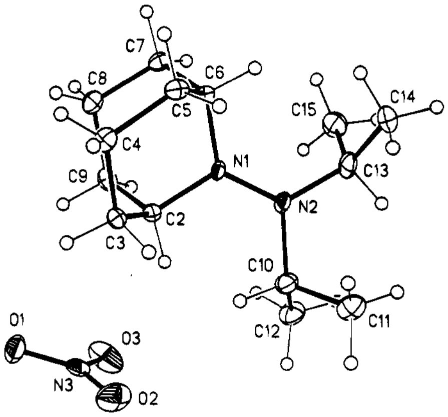
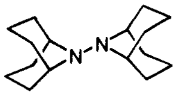


Figure 2. Thermal ellipsoid drawing of the X-ray stucture of $\mathbf{2}^+NO_3^-$ (50% probability).

and isopropylmagnesium chloride in ether, however, produced complex product mixtures. The Grignard reagent gave principally the hydride transfer product **5** and the deprotonation product **7**, accompanied by a small amount of a compound later shown to be **3**; the approximate relative amounts of **5**:**7**:**3** were 43:45:12. Fortunately, carrying out the reaction in the presence of 10% CuI nearly eliminated the formation of **5** and substantially reduced that of **7**, **5**:**7**:**3** changing to trace:29:71, from which **3** was isolated by column chromatography in 26% yield. The reaction mixture should contain principally the Grignard, and the isopropylcopper species formed is apparently both a less active hydrogen donor and transfers isopropyl to $\mathbf{6}^+$ significantly more rapidly than does the Grignard. **2**, **3**, and **4** all gave isolable radical cations upon oxidation with nitrosyl hexafluorophosphate.

X-ray structures were determined for both **4** (Figure 1), which crystallizes in the N_9 inversion form having the $N(iPr)_2$ group *syn* to the keto bridge, and **2**. They have very similar geometries at nitrogen (see Table 1), and nearly perpendicular lone pairs.



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Their NN bond rotational angles are very different from the apparently structurally similar **8**, for which only the θ = 180° rotamer is present in the crystal (by X-ray crystallography) and the gas phase (from photoelectron spectroscopy measurements).[5] The isopropyl groups for both **2** and **4** assume conformations with different orientations relative to the NN bond; one has the HC_i,NN dihedral angle ϕ near 25° (which we shall call an **inner** isopropyl group rotamer), while the other has it near 167° (which we shall call **outer**). **8** is constrained to conformations with **i** rotamers for all its alkyl groups and has more pyramidal nitrogens, which apparently causes the difference in θ. We failed to obtain X-ray quality crystals for the low-melting **3** despite many attempts. X-ray structures were obtained for both $\mathbf{2}^+NO_3^-$ (Figure 2) and $\mathbf{3}^+NO_3^-$, but in the latter case the cation was disordered so that the NN bonds assume two perpendicular orientatons, for which the isopropyl atom positions were not resolved, so that details of the isopropyl group positions could not be obtained. The tosylate crystallized with a mole of acetonitrile, but without such disorder, and the structure of $\mathbf{3}^+TsO^-{\cdot}CH_3CN$ (Figure 3) is compared with that of $\mathbf{2}^+NO_3^-$ in the summary of geometries at nitrogen in these species which appears in Table 1.

ESR hyperfine splitting constants can provide information about the conformations of the radical cations in solution. Only hyperfine structure corresponding to the large nitrogen splitting was clearly resolved by ESR for both $\mathbf{2}^+$ and $\mathbf{3}^+$: a(2N) is about 13.8 G (room temperature), 13.5 G (190 K) for $\mathbf{2}^+$, and 13.2 G (room temperature), 13.2_5 G (190 K) for $\mathbf{3}^+$, so no structural information was available. We were unable to obtain an ENDOR spectrum of $\mathbf{2}^+$. Proton NMR spectroscopy allows determination of ESR hyperfine splitting constants a_H for radicals having small a_H from the paramagnetic chemical shift, $\Delta\delta_H = \delta_H(\text{cation}) - \delta_H(\text{neutral})$ for a radical cation, and is

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Table 2. Comparison of the $\mathbf{2}^{\cdot+}$ with $\mathbf{8}^{\cdot+}$ and Low-Temperature Spectrum of $\mathbf{2}^{\cdot+}$

	$\mathbf{8}^{\cdot+\,a}$ (T = 298 K)	2 (T = 298 K)	$\mathbf{2}^{\cdot+\,b}$ (T = 298 K)		$\mathbf{2}^{\cdot+\,b}$ (T = 260 K)	
hydrogen	a(H_{NMR}), G	δ(neu), ppm	$\delta(\mathrm{cat})_o$, ppm	a(H_{NMR}), G	$\delta(\mathrm{cat})_o$, ppm	a(H_{NMR}), G
H(3e)	+1.54	1.63	$+111.4_5$	+1.49	$+119.9_4{}^c$	$+1.39^c$
H(2e)	+1.27	1.44	$+104.5_2$	+1.40	$+119.9_4{}^c$	$+1.39^c$
H(1)	+0.97	2.96	$+87.1_8$	+1.14	$+95.2_2$	+1.08
H(3a)	+0.28	1.98	$+19.9_5$	+0.24	$+22.6_1$	+0.24
H(2a)	−0.55	2.07	-39.0_5	−0.56	-46.0_8, -49.2_9	−0.57, −0.60
Me(iPr)		1.02	(~-8)	−0.12	$+16.0_9$, -28.7_4	+0.18, −0.35

[a] From ref 1; studied as the PF_6^- salt. [b] Studied as the NO_3^- salt. [c] The H(3e) and H(2e) signals were not resolved at 260 K.

Table 3. Variable Temperature NMR Studies of Isopropyl Group Interconversion

	δ(Me) [$\nu_{1/2}$,ppm]		
temp, K	$\mathbf{2}^{\cdot+}NO_3^{-\,a}$	$\mathbf{3}^{\cdot+}TsO^-\cdot CH_3CN^b$	$\mathbf{3}^{\cdot+}NO_3^{-\,c}$
340		+5.19 [13.3]	
330	−1.89 [6.7]	+5.03 [16.1]	+6.6 [8.9]
320	−1.89 [10.0]	+4.5 [21.6]	+6.4 [13.4]
310	−2.82 [16.3]	~+3.2 [29.9]	+5.8 [24.7]
305			~6 [35.3]
300	~−4.3 [32.9]	~+17, ~−7	+17.19, −6.12
295	+8.61, −16.74		
290	+13.65, −19.87	+23.09 [19.1], −11.57 [15.4]	+24.67 [14.4], −10.07 [12.0]
280	+16.25 [10.7], −23.08 [10.3]	+25.85 [18.3], −13.32 [13.5]	+27.03 [11.6], −12.22 [9.0]
270	+16.94 [8.3], −25.04 [7.2]	+27.44 [18.0], −15.23 [11.3]	+28.70 [10.2], −13.61 [6.6]
260	+17.80 [7.1], −26.38 [6.6]	+28.74 [20.5], −16.41 [10.8]	+30.12 [10.2], −14.78 [5.1]
250		+30.45 [22.2], −17.43 [10.9]	

[a] 42.1 mg in 400 μL of CD_3CN: 0.37 M. [b] 20.7 mg in 400 μL of CD_3CN: 0.13 M. [c] 33.1 mg in 400 μL of CD_3CN: 0.32 M.

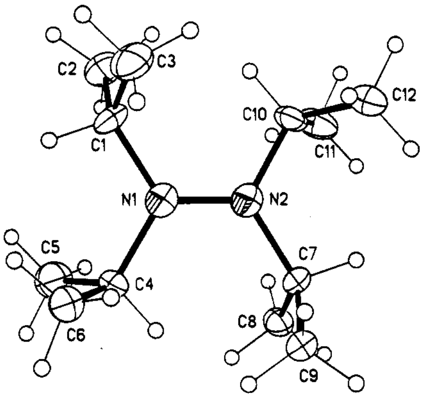

Figure 3. Thermal ellipsoid drawing of the X-ray structure of $\mathbf{3}^+TsO^-$ (50% probability).

directly proportional to a_H (eq 1).[6] NMR measurements have far more resolution than ESR, and NMR studies proved

$$\Delta\delta_H(\mathrm{ppm}) = [2.213 \times 10^4/T(\mathrm{K})]a_H(\mathrm{gauss}) \qquad (1)$$

particularly revealing for these species. The room temperature NMR spectrum of $\mathbf{2}^+$ exhibits six signals, five corresponding to bicyclononyl unit a_H values, as shown by the comparison with the $\mathbf{8}^+$ values[6] shown in Table 2, and one corresponding to an averaged isopropyl methyl group signal. It is not clear whether the isopropyl CH signal is hidden under the three bicyclic ring signals in the δ 87−111 region or is too large to measure by NMR. The methyl signal was noticeably broadened at room temperature, and lowering the temperature caused it to separate into positive and negative chemical shift peaks. Addition of di-*tert*-butylnitroxide at 260 K allowed measurement of more accurate a(H) values by allowing determination of the chemical shift at zero radical concentration, $\delta(\mathrm{cat})_0$,[6] and provided sufficient sharpening of the H(2a) signal that it could be resolved into two components. Variable-temperature experiments on $\mathbf{2}^+$ are summarized in Table 3. All the peaks show increasing $|\delta(\mathrm{cat})|$ values as the temperature is lowered because $\Delta\delta_H/a_H$ is proportional to T^{-1} (eq 1).

Simulations of the unresolved ESR spectrum of $\mathbf{3}^+$ indicated that in addition to the two small 12 H methyl splittings which were easily detected by NMR (see below), the the average of the splittings for the four isopropyl CH hydrogens was not larger than 0.9 G. The ENDOR spectrum of $\mathbf{3}^+$ proved exceptionally difficult to obtain, but a pair of signals for each of the four different types of hydrogen present was finally observed for the TsO^- salt in toluene containing a trace of ethanol at low concentration, in the narrow temperature range of 200−215 K. The splitting constants are +0.79 (CH), +0.56 (CH), +0.33 (CH_3), and −0.19 (CH_3) G at 200 K. The ENDOR doublets corresponding to the +0.33 and −0.19 G splittings are far more intense than the other two, and clearly correspond to the methyl splittings. The methyl signals were not clearly resolved at 210 K, and the CH splittings are slightly larger, 0.85 and 0.60 G. The NMR spectrum of $\mathbf{3}^+$ shows that room temperature is slightly below T_c for the methyl group interconversion. $\mathbf{3}^+$ unfortunately reacts with di-*tert*-butylnitroxide too rapidly to allow its addition to narrow the CH signals enough for their detection, but the low-temperature chemical shifts correspond to a_H(Me) of +0.33, a_H(Me) = −0.20 G, in excellent agreement with the ENDOR data. Variable-temperature experiments are summarized in Table 3, and spectra for the NO_3^- salt are shown in Figure 4. In contrast to the behavior of several bis-*N,N'*-bicyclic hydrazines and **8**, mixtures of the neutral and +1 oxidations states of **1**,[1] **2**, and **3** show no line broadening because of ET; the self-ET rate constant is clearly much smaller for all three compounds than is necessary to observe line broadening.

Photoelectron spectroscopy and cyclic voltammetry data on **1**−**3** are summarized in Table 4. Even for solutions of $\mathbf{2}^+$ or $\mathbf{3}^+$, so that the basic neutral form is not present, the cation, dication CV wave is totally irreversible in acetonitrile even at 50 V scan rates at −40 °C. Isopropyl groups clearly do not successfully kinetically protect hydrazine dications.

Discussion

X-ray Geometries. Despite both being *N*-bis-α-branched-alkylamino derivatives of 9-azabicyclo[3.3.1]nonane, **2** and **8** are in very different geometries about the nitrogen atoms, which we suggest is principally caused by their very different θ values, 85.9° for **2** and 180° for **8**. The twist, NN bond length, and pyramidality of hydrazines are significantly interdependent.[7] When the lone pairs of hydrazines are closer to being coplanar

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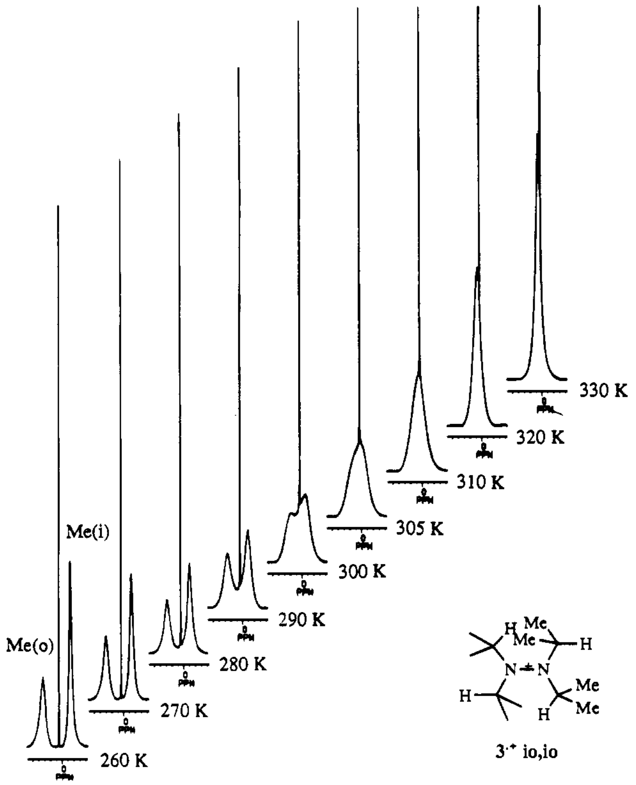


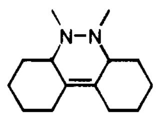
Figure 4. Variable-temperature NMR series for $3^+NO_3^-$.

Table 4. Photoelectron Spectroscopy and Cyclic Voltammetry Data for **1**−**3**

	PE spectrum[a]		cyclic voltammetry[b]		
compd	vIP_1	vIP_2-vIP_1	electrode	$(E_p^{ox} - E_p^{red})/2$	$(E_p^{ox} - E_p^{red})$
1[c]	7.34	1.31	Au	−0.04	0.08
			Pt	−0.04	0.37
1M[d]	7.46	1.82	Pt	+0.07	0.09
2	7.23	0.50	Au	+0.07	0.10
			Pt	+0.12	0.42
2M[e]	7.53	0.89	Au	+0.11	0.06
3	7.35	0.38	Au	+0.26	0.14
			Pt	+0.27	0.34
3u[d]	7.65	0.72	Au	+0.29	
3s[d]	7.92	0.52	Au	+0.29	

[a] Reported in electronvolts. [b] In acetonitrile containing 0.1 M tetrabutylammonium perchlorate, at room temperature, scan rate 200 mV/s, reported vs SCE, in volts. [c] Reference 1. [d] Reference 16a. [e] Reference 16b.

and there is large lone pair, lone pair interaction, the nitrogens pyramidalize more, which decreases this interaction. **4** and **2** are the first tetra-α-branched hydrazines with θ values near 90° for which structural information is available, allowing determination of the range of the geometry changes which occur. The difference in α_{av} (the average of the bond angles at nitrogen, which is nearly linear with formal lone pair hybridization) for the bicyclononyl nitrogens of **2** (115.3°) and **8** (108.3°) is 7.0°, so the bicyclononyl nitrogen of **8** is more pyramidal than that of **2** by 67% of the 10.5° between a planar and a tetrahedral nitrogen. Even the diisopropylamino nitrogen of **2**, α_{av} = 116.9°, is more planar than the nitrogens of **8**, although it is significantly more pyramidalized (22% of 10.5°) than the nearly planar nitrogen of triisopropylamine, α_{av} = 119.2°.[8] The 1.420 Å NN bond length of **2** is 0.085 Å shorter than that of **8**, which is a substantial change, larger than the 0.074 Å decrease in NN bond length which occurs upon removal of an electron from **2**. Despite being tetra-α-branched, **2** and **4** have the shortest NN bond lengths reported for hydrazines, presumably because their θ is near 90° and they also have flattened nitrogens; flattening increases s hydbridization in the N−N bond, resulting in detectable bond shortening. For comparison, the bis-α-branched **9** has θ = 65.4°, an NN distance of 1.450(3) Å, and α_{av} of 110.7 and 112.2° at the methyl pseudoaxial and pseudoequatorial nitrogens, respectively.[7]



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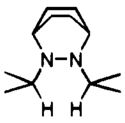
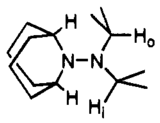
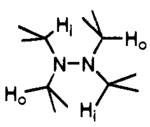
Removal of an electron from a hydrazine changes the lone pair orbital occupancy from four to three, which has a large effect on the preferred geometry about the nitrogens. Hydrazine radical cations have α_{av} close to 120° and $\theta \sim 0$ or 180°.[9] Differing nonbonded steric interactions make different isopropyl group rotamers the most stable for *N,N'* bicyclic compounds such as 1^+ and 2^+ or 3^+. Only a symmetrical conformation, assigned as 1^+**ii**, was observed for this compound,[1] while crystalline 2^+ is in the **i,o** and 3^+ is in the **io,io** conformation.



1⁺ii



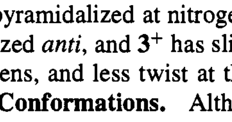
2⁺i,o



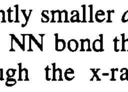
3⁺io,io

The nitrogens of 2^+ are flatter than those of neutral **2** (by 23% of 10.5° for the bicyclic nitrogen and 18% for the diisopropyl nitrogen) and the NN bond is shorter by 0.074 Å (5.2%). These changes in α_{av} and d(NN) are small compared to previously examined θ ~0° bis-*N,N'*-bicyclic hydrazines and 180° bis-*N,N*-bicyclic bicyclic ones such as **8** ($\Delta\alpha_{av}$ = 8.3°, 79% of 10.5°, and Δd(NN) = −0.146, 9.8%),[5b] because neutral **2** has flatter nitrogens and a shorter NN bond length. Both 2^+ and 3^+ are slightly *syn* pyramidalized at nitrogen, in contrast to 8^+, which is pyramidalized *anti*, and 3^+ has slightly smaller d(NN), more planar nitrogens, and less twist at the NN bond than does 2^+.

Solution Conformations. Although the x-ray crystallographic studies establish the conformations of solid **2**, 2^+, and 3^+, especially bond rotational angles are rather "soft", and the possibility always exists that these conformations are imposed by crystal packing forces, and do not represent the global energy minima in their absence. The photoelectron spectra of **2** and **3** show that only θ ~90° conformations are detectably occupied in the gas phase as well as in crystals. The low-temperature NMR specta of 2^+, which have signals with two different a_H values for both the isopropyl methyl groups and the γ-axial hydrogens of the bicyclic ring, require that it is present in solution in the **i,o** conformation, as it is in crystals. The **i** isopropyl methyl splitting constant is +0.17 G for 1^+ at 298 K, and that for its *tert*-butyl, isopropyl analogue **10** is +0.25 G, while the *tert*-butyl splitting constant for the latter compound, which represents an averaged methyl group splitting, is −0.08



2⁺



10

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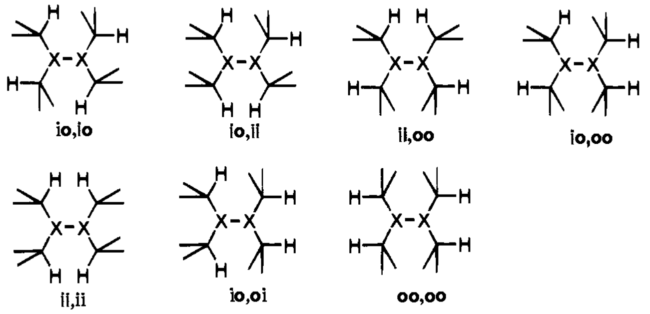
(8) Bock, H.; Göbl, I.; Havlas, Z.; Liedle, S.; Oberhammer, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *29*, 187.

(9) Nelsen, S. F. Stereodynamics of Open Shell Nitrogen Systems. In ref 7, Chapter 7, p 245.

Chart 1



G.[1] We conclude that the positive a_H(Me) value of 2^+ probably corresponds to the **i** isopropyl group, and the negative one to the **o** isopropyl group.

We were initially surprised to observe isopropyl rotation dynamics with coalescence temperatures near room temperature for these compounds, because far lower temperatures are required to freeze out alkyl rotation by NMR for neutral compounds. The formula relating the barrier $\Delta G^{\ddagger}_c$ at the coalescence temperature T_c for equilibrating equal intensity singlets when the transmission coefficient $\kappa = 1/2$ is shown in eq 2.[10] Interconversion of the methyl groups in 2^+ requires

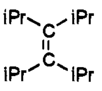
$$\Delta G^{\ddagger}_{c} = 4.57T_{c} = [9.67 + \log(T_{c}/\Delta\delta)] \qquad (2)$$

rotation of both isopropyl groups about their N−iPr bonds and would be expected to proceed by single isopropyl group rotation to produce an undetected symmetrical intermediate (2^+**ii** or 2^+**oo**). If $\Delta\nu$ were in the range 20−60 Hz (which is significantly higher than would be expected for isopropyl rotamers) a $\Delta G^{\ddagger}_c$ of 10.8 kcal/mol would give T_c in the range of −53 to −43 °C; one would not see dynamic effects of isopropyl group rotation in the temperature range studied. However, the paramagnetic shifts of radical cations produce large chemical shift differences, especially because the signs of the splitting constants for **i** and **o** isopropyl methyl hydrogens are opposite. From extrapolations of the 260, 270, and 280 K methyl group shifts vs T^{-1} to 300 K, $\Delta\delta_{Me}$ values of 36.6_3 ppm (1.78 × 10^4 Hz at 500 MHz) are obtained. T_c for these signals is >295 °C, and eq 2 gives $\Delta G^{\ddagger}_{300}$ ~ 10.8. This number is certainly approximate, because it assumes equal line widths for the signals undergoing conformational interconversion, while the two signals for 2^+ are of different widths because the a_H(Me) values are different; the line width for a paramagnetic species increases approximately as $\Delta\delta_H{}^2$.[11] These problems make the barrier of 10.8 uncertain, but we doubt that it is overestimated by using eq 2; the factors we have thought of complicating the situation lead to extra line broadening near T_c, which would make the estimated barrier too high. The isopropyl rotation barrier for **10** was estimated as 8.4 kcal/mol (at 180 K) by the temperature of maximum broadening method;[1] we would expect the flatter nitrogens and shorter NN bond of 2^+ to raise the barrier at least slightly.

Table 5. Comparison of Calculated $iPr_4N_2{}^{\cdot+}$ and iPr_4C_2 iPr Rotamer Energies

	$iPr_4N_2{}^{\cdot+}$(AM1 calcd)		iPr_4C_2 [AM1 and mol mech[a]]	
rotamer[b]	$\Delta\Delta H_f$, kcal/mol	θ, deg	$\Delta\Delta H_f[\Delta V]$, kcal/mol	θ, deg
io,io	0.00	23.8	0.00 [0.00]	0.7 [0.0]
io,ii	2.75	21.7	2.06 [2.10]	9.3 [7.8]
ii,oo	3.73	42.5	6.89 [9.39]	18.3 [10.1]
io,oo	4.74	47.2	9.10 [11.79]	12.9 [9.4]
ii,ii	4.92	23.9	2.92 [2.23]	14.0 [12.2]
io,oi	5.10	25.5	5.40 [6.77]	7.7 [8.0]
oo,oo	9.34	62.4	21.46 [22.00]	28.5 [15.3]

[a] The first number is calculated by AM1, and the second number [in brackets] is calculated by molecular mechanics, taken from ref 14. [b] See Chart 1.



11

As indicated in Table 3, the coalescence temperature and $\Delta\nu$ values are rather similar for 2^+ and 3^+. Estimation of the isopropyl group interconversion barrier for 3^+ using eq 2 gives $\Delta G^{\ddagger}$(310±5 K) ~ 11.2 ± 0.3 kcal/mol. The isopropyl group interconversion process for 3^+ might be expected to be comparable to that for the nearly isostructural tetraisopropylethylene (**11**), which has been extensively studied. **11** is also most stable in the **io,io** isopropyl group rotamer in solution[12] and crystallizes in this conformation.[13] The barrier to isopropyl group interconversion for **11** is 17 kcal/mol by proton NMR,[12] ~6 kcal/mol higher than that estimated above for 3^+. Despite the uncertainty in extracting $\Delta G^{\ddagger}$ for 3^+ from its NMR data, its isopropyl interconversion barrier is unquestionably significantly lower than that for **11**. From their X-ray structures, the NN and NC bond lengths of 3^+ are shorter than the C=C and C_vC lengths of **11** by 1.0 and 2.3%, respectively, which might have been predicted to raise the interconversion barrier for 3^+ relative to **11** instead of lowering it. Ermer carried out an extensive computational study of isopropyl group rotation in **11** by molecular mechanics[14] including all seven isopropyl rotamers shown in Chart 1, showing that the isopropyl groups rotate independently, and concluding that the rate limiting barrier for interconversion of **io,io** to **oi,oi** (the process observed by NMR) involves conversion of the second lowest energy conformation, **io,ii**, to the fourth, **io,oi**, which has a calculated potential energy difference of 17.6 kcal/mol (calculated barrier of 19.6 kcal/mol). As summarized in Table 5, the higher energy conformations (as well as the transition states,[14] not calculated by us) are characterized by higher C=C twist angles. Twist about the 3e−π bond[9] of 3^+ is far easier than about the π bond of **11**, which we suggest is principally responsible for the lower isopropyl group rotation barrier in 3^+. Table 5 also shows the relative enthalpies calculated by AM1 for both compounds. The differences between the results of Ermer's molecular mechanics force field and AM1 for the rotamers of **11** is small enough that the order of energies of the conformations is the same. The most interesting difference between the relative enthalpies calculated for 3^+ and **11** is that the **ii,oo** and **io,oo** conformations are predicted to be far more stable relative to **io,io** for 3^+ than for **11**, and are even more stable than **ii,ii**. This rather clearly occurs because $(NN)^+$ twist is easier than C=C twist. This suggests that isopropyl rotation routes through these conformations might be comparable in energy to that through **io,oi** or

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(10) (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 223. (b) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

(11) Because the line widths as well as δ values depend upon temperature, and because of possible coupling between the electron and proton spins, simulations of the temperature variation of the NMR spectra for 2^+ and 3^+ have proven to be a problem. We are collaborating with Gideon Fraenkel's group at Ohio State University in attempts to obtain quantitative barriers for these processes from the experimental spectra, but have not yet been successful in this endeavor.

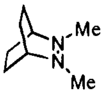
(12) (a) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777. (b) Bomse, D. S.; Morton, T. H. *Tetrahedron Lett.* **1975**, 781.

(13) Casalone, G.; Pilati, T.; Simonetta, M. *Tetrahedron Lett.* **1980**, *21*, 2345.

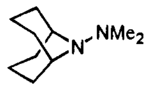
(14) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 998.

ii,ii for $\mathbf{3}^+$. Despite their structural similarity, $\mathbf{3}^+$ and **11** might well have different pathways for interconversion of **io,io** and **oi,oi** because of their significantly different central bond rotational barriers and pyramidalization energies.[15]

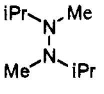
Electron Loss from 1−3. The photoelectron spectroscopy and cyclic voltammetry data for **1−3** are compared with literature values[16] for analogues with two isopropyl groups replaced by methyls (designated **1M−3M**, structures shown below) in Table 4. Both vIP_1 and $\mathrm{vIP}_2 - \mathrm{vIP}_1$ are significantly smaller for **1−3** than for **1M−3M**, as expected because of the flattening which accompanies bis-α-branched-alkyl substitution at nitrogen. It is not clear that even the 0.51 eV $\mathrm{vIP}_2 - \mathrm{vIP}_1$ difference for **1** and **1M** is caused by a significant change in θ. AM1 calculations predict θ values of 129.3 and 129.0° (which are almost certainly too large because they do not get enough twist in the bicyclic ring, but suggest that the values are probably similar); and X-ray data are not available for these species. $\mathrm{vIP}_2 - \mathrm{vIP}_1$ is especially large for the unsymmetrical compounds **2M** and **3Mu** because the lone pairs are of different energy even in the (hypothetical) absence of the lone pair, lone pair interaction which gives rise to the splitting in symmetrical hydrazines. **1−3** show slightly lower $E^{\circ\prime}$ values than their methylated analogues, indicating that vicinal isopropyl, isopropyl interaction in the radical cations does not significantly destabilize these species. The isopropyl groups must assume specific relative orientations to achieve this, and heterogeneous electron transfer is quite slow for **1−3**, as indicated by the very large wave separations at a platinum electrode for these compounds. Electron loss from **1** has been argued to produce a high-energy conformation of $\mathbf{1}^+$ because of isopropyl group interactions as the nitrogens flatten (gearing). The high-energy conformation converts to $\mathbf{1}^+$**ii** rapidly on the time scale of cyclic voltammetry, resulting in broadening of the wave.[1] **2** and **3** show very similar behavior to **1**, most probably for the same reason. AM1 calculations predict such behavior for **3**, where removal of an electron from the most stable conformation of the neutral compound is predicted to give unstable conformations of the radical cation, but because AM1 does not handle neutral hydrazine conformations very well the details of these calculations will not be reported here. Self-ET rate constants are probably even smaller for the θ ~90° **2** and **3** than for **1** (θ ~120°). As indicated in the Results section, all show too slow ET for measurement by NMR line broadening. Cross rate studies in collaboration with the group of Pladziewicz have allowed estimation of the rate constant for $\mathbf{1}^{0/+}$ ET at 75 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is a factor of 13 smaller than that estimated for the 180° $\mathbf{8}^{+/0}$ by the same method, and a factor of 247 smaller that measured by NMR for the θ ~0° *N,N'*-bis-bicyclic compound **12**.[5b] It will be especially interesting to measure self-ET rate constants for $\mathbf{2}^{0/+}$ and $\mathbf{3}^{0/+}$, which will allow finding out how large the θ effect actually is. Experiments designed to do this are in progress, and will be reported soon.



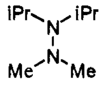
1M



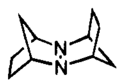
2M



3Ms



3Mu



12

Experimental Section

9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonan-3-one (4). A solution of cycloocta-2,7-dienone[17] (3.05 g, 0.025 mol) and diisopropylhydrazine (3.05 g, 0.026 mol) in MeOH (10 mL) was stirred at room temperature under N_2 for 9 days and solvent was removed on a rotary evaporator to give a creamy yellow solid which crystallized after 3−4 days. Purification by column chromatography (silica gel, 1:1 ether−hexane) gave 3.64 g (61.1%) of yellow crystalline **4** (R_f = 0.53), mp 68−69 °C. ^{1}H NMR ($CDCl_3$): δ 3.51 (s, 2H), 3.31 (hept, 2H, J = 6.6 Hz), 2.73 (dd, 2H, J = 17.3, 6.9 Hz), 2.26 (d, 2H, J = 17.3 Hz), 2.04−1.96 (m, 2H), 1.53−1.36 (m, 4H), 1.07 (d, 12H, J = 6.6Hz). ^{13}C NMR ($CDCl_3$): δ 212.56 (C=O), 58.69 (CH), 50.58 (CH), 45.44 (CH_2), 31.76 (CH_2), 22.86 (CH_3), 16.36 (CH_2). MS: *m/e* 238.2051 (calcd for $C_{14}H_{26}N_2O$ 238.2045, 44.8%), 195.1487 (100%), 153.1034 (21.2%).

9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonan-3-one Radical Cation Hexafluorophosphate ($\mathbf{4}^{\cdot+}\mathbf{PF_6}^-$). A solution of $NOPF_6$ (81.4 mg, 0.47 mmol) in CH_3CN (1 mL) was added to a stirred solution of **4** (111.9 mg, 0.47 mmol) in CH_3CN (12 mL) at −35 °C under Ar, the solution was stirred at −35 °C for 10 min, and ice-cold ether (200 mL) was added to precipitate a white solid, which was washed with ether (2 × 100 mL) and dried under N_2 to give 131.7 mg (73.9%), 172−3 °C dec.

9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonane (2). Diethylene glycol (30 mL) and 85% KOH (1.18 g, 0.021 mol) were briefly heated to 100−130 °C to dissolve the KOH and cooled, and hydrazine hydrate (0.85 mL, 0.88 g, 0.0176 mol) and **4** (0.75 g, 0.00315 mol) were added. The stirred mixture was heated at 140 °C for 2 h, the temperature was raised from 140 to 225 °C over 1 h and maintained at 220−225 °C while volitile products were allowed to distill through a 4 in. Vigreux column equipped with a distillation head. After cooling overnight, the mixture was poured into 100 mL of H_2O and extracted with pentane (3 × 100 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (silica gel, 1:2 ether−hexane) gave 178.6 mg (25.2%) of **2** as a white solid (R_f = 0.7), mp 45 °C. ^{1}H NMR ($CDCl_3$): δ 3.42 (hept, 2H, J = 6.5 Hz), 2.96 (s, 2H), 2.11−1.94 (m, 6H), 1.64−1.61 (m, 2H), 1.44 (dd, 4H, J = 13.08, 6.55 Hz), 1.02 (d, 12H, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 56.06 (CH), 50.24 (CH), 29.34 (CH_2), 22.82 (CH_3), 20.57 (CH_2). MS: *m/e* 224.2251 (calcd for $C_{14}H_{28}N_2$ 224.2252, 22.4%), 181.1710 (100%).

9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonane Radical Cation Hexafluorophosphate ($\mathbf{2}^{\cdot+}PF_6^-$). $NOPF_6$ (86.5 mg, 96%, 0.47 mmol) was added in one portion to a stirred solution of **2** (98.8 mg, 0.44 mmol) in deaerated CH_2Cl_2 (5 mL) at −35 °C under Ar. The resulting mixture was stirred at −35 °C for 30 min, ice-cold ether (200 mL) was added, and stirring was continued at −35 °C for 30 min to let the solid aggregate. After the surpernatant was removed by cannulation, the solid was washed with ether (2 × 100 mL) and dried under a N_2 stream to give 106.8 mg (61.2%) of crude $\mathbf{2}^{\cdot+}PF_6^-$, which was recrystallized from CH_3CN under an ethereal atmosphere to give yellow crystals, mp 187−8 °C (the crystals began to split into small pieces above 170 °C).

9-(Diisopropylamino)-9-azabicyclo[3.3.1]nonane Radical Cation Nitrate ($\mathbf{2}^{\cdot+}\mathbf{NO_3}^-$). A solution of $AgNO_3$ (62.6 mg, 0.37 mmol) in deaerated CH_3CN (8 mL) was added dropwise to a stirred solution of **2** (82.0 mg, 0.37 mmol) in deaerated CH_3CN (22 mL) at 0 °C under argon. After the solution was stirred at 0 °C for 1 h, a yellow solution formed along with the silver precipitate. The mixture was filtered through Celite under Ar, and ether (220 mL) was added to the filtrate to precipitate a yellow solid, which was washed with ether (2 × 100 mL), dried under N_2, and recrystallized from CH_3CN under an ethereal atmosphere to give 48.1 mg (46.0%) of $\mathbf{2}^{\cdot+}NO_3^-$ as yellow crystals, mp 168−9 °C.

1,1,2-Triisopropylhydrazine (5). $NaBH_3CN$ (8.42 g, 0.134 mol) was added to a solution of 1,1-diisopropylhydrazine (7.98 g, 0.0687

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[15] Ermer did not consider the pathway through these conformations for conformational interconversion of **11**, because of the high energies of these intermediates. We have not tried to calculate relative barriers for the $\mathbf{3}^+$ pathways by AM1, which would be very time consuming, because we can think of no way of experimentally determining the pathway actually taken.

[16] (a) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269. (b) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

[17] Garbisch, E. W. *J. Org. Chem.* **1965**, *30*, 2019.

mol) and acetone (23.51 g, 0.405 mol) in CH_3CN (150 mL). The resulting mixture was heated to reflux under N_2, glacial acetic acid (13.5 mL) was added dropwise over a period of 2 h, and reflux was continued for 14 h. After the solution was cooled to room temperature, 15% NaOH (150 mL) was added and the mixture was extracted with pentane (4 × 220 mL). After drying ($MgSO_4$) and evaporation, distillation through a 4 in. Vigreux column (63 °C, 25 mmHg) gave **5** as a colorless liquid (8.51 g, 7.83%). ^1H NMR ($CDCl_3$): δ 2.89–2.97 (m, 3H), 2.23 (s, 1H), 0.99 (d, 12H, $J = 6.4$ Hz), 0.94 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 51.61 (2 CH), 49.33 (CH), 21.84 (2 CH_3), 20.11 (CH_3, broad). MS: *m/e* 158.1779 (calcd for $C_9H_{22}N_2$ 158.1783, 27.3%), 115.1261 (57.9%), 73.0766 (100%).

Triisopropyldiazenium Hexafluorophosphate ($6^+PF_6^-$). A solution of **5** (1.35 g, 0.00853 mol) in CH_3CN (8 mL) was added dropwise to a stirred solution of $NOPF_6$ (3.21 g, 0.0179 mol) in CH_3CN (10 mL) at −35 °C under N_2. After the solution was stirred at −35 °C for 30 min, ether (200 mL) was added to precipitate a solid which gradually turned a light red. Washing with ether (2 × 100 mL) and drying under vacuum gave 2.28 g (88.4%) $6^+PF_6^-$ as a light red powder. ^1H NMR (CD_3CN): δ 5.29 (hept, 1H, $J = 6.4$ Hz), 5.21 (hept, 1H, $J = 6.6$ Hz), 4.65 (hept, 1H, $J = 6.2$ Hz), 1.59 (d, 6H, $J = 6.6$ Hz), 1.47 (d, 6H, $J = 6.2$ Hz), 1.42 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR (CD_3CN): δ 68.89 (CH), 67.34 (CH), 64.78 (CH), 23.51 (CH_3), 20.53 (CH_3), 19.98 (CH_3).

Tetraisopropylhydrazine (3). A solution of isopropylmagnesium chloride in THF (2 M, 9 mL, 18 mmol) was added dropwise to a stirred mixture of CuI (0.34 g, 1.79 mmol) in THF (20 mL) at 0 °C under N_2. This mixture was cannulated into a stirred mixture of $6^+PF_6^-$ (2.28 g, 7.54 mmol) in THF (20 mL) at 0 °C under N_2. After being stirred at 0 °C for 1 h and at room temperature for 0.5 h, the mixture was poured into H_2O (100 mL) and extracted with pentane (6 × 100 mL). After drying ($MgSO_4$) and solvent evaporation, column chromatography (silica gel, 1:4 ether–hexane, $R_f = 0.75$) gave **3** as a white solid (390.8 mg, 26%). ^1H NMR ($CDCl_3$): δ 3.18 (hept, 4H, $J = 6.6$ Hz), 1.06 (d, 24 H, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 50.50 (CH), 23.14 (CH_3). MS: *m/e* 200.2260 (calcd for $C_{12}H_{28}N_2$ 200.2252, 65.9%), 157.1702 (66.4%), 115.1225 (99.9%), 73.0767 (100%).

Tetraisopropylhydrazine Radical Cation Tosylate ($3^{\cdot+}TsO^-$). A solution of AgOTs (125.8 mg, 0.45 mmol) in deaerated CH_3CN (5 mL) was added dropwise to a stirred solution of **3** (88.5 mg, 0.44 mmol) in deaerated CH_3CN (27 mL) at −35 °C under Ar. The resulting mixture was warmed to room temperature and stirred for 3 h, and silver was removed bt filtration through Celite under Ar. Concentration under vacuum to gave $3^{\cdot+}TsO^-$ as a yellow solid (147.8 mg, 90.1%), which was recrystallized from CH_3CN under an ethereal atmosphere to give orange crystals.

Tetraisopropylhydrazine Radical Cation Nitrate ($3^{\cdot+}NO_3^-$). A solution of $AgNO_3$ (56.6 mg, 0.333 mmol) in deaerated CH_3CN (7 mL) was added dropwise to a stirred solution of **3** (67.4 mg, 0.336 mmol) in deaerated CH_3CN (20 mL) at 0 °C under Ar. After the solution was stirred at 0 °C for 1 h and filtered through Celite under Ar, ether (220 mL) was added and the white solid was washed with ether (2 × 100 mL) and dried under N_2. Recrystallization from CH_3CN under an ethereal atmosphere gave 35.8 mg (40,6%) of $3^{\cdot+}NO_3^-$ as light yellow crystals, mp 146–7 °C (the crystals turned red at 120 °C and broke into small pieces at 140 °C).

Crystal Structures. The crystal of **2** was grown by sublimation (ambient temperature, 0.2 mmHg) and that of **4** by slow crystallization from the reaction mixture after the solvent was removed. Crystals $2^+NO_3^-$ and $3^+TsO^-\cdot CH_3CN$ were grown by vapor diffusion of ether into an acetonitrile solution at −20 °C. Crystal sizes, mm: **2** 0.50 × 0.40 × 0.10, **4** 0.60 × 0.20 × 0.10, $2^+NO_3^-$ 0.50 × 0.50 × 0.20, and $3^+TsO^-\cdot CH_3CN$ 0.50 × 0.50 × 0.40. Intensity data were measured with a Siemans P3f diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54178 Å) and a Wyckoff scan type. All data were collected at 113 K. All structures were solved by the SHELXS-86 program[18a] and refined by the SHELXL-93 program,[18b] which refines on F^2 values. A summary of crystallographic data appears in Table 6.

Table 6. Summary of Crystal Data and Refinement Parameters

	4	2	$2^{\cdot+}NO_3^-$	$3^{\cdot+}TsO^-\cdot CH_3CN$
formula	$C_{14}H_{26}N_2O$	$C_{14}H_{28}N_2$	$C_{14}H_{28}N_3O_3$	$C_{21}H_{38}N_3O_3S$
cryst system	triclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	*Cc*	*Pbca*	$P\bar{1}$
a, Å	6.4392(5)	6.4360(6)	15.634(3)	8.1664(13)
b, Å	8.3935(5)	16.0595(8)	10.7735(11)	11.863(2)
c, Å	13.9871(8)	13.2919(8)	17.947(2)	12.5340(10)
α, deg	86.594(5)	90	90	81.092(9)
β, deg	78.278(5)	97.062(7)	90	82.079(8)
γ, deg	71.206(5)	90	90	87.28(2)
vol, Å^3	700.72(8)	1363.4(2)	3022.9(7)	1187.7(3)
Z	2	4	8	2
density[a]	1.130	1.093	1.259	1.154
F(000)	264	504	1256	450
R/R_w(obs),%	3.66/9.11	3.79/10.81	4.91/13.87	5.49/14.17
R/R_w(all),%	4.14/9.57	3.82/10.87	5.89/14.87	6.16/14.95
gof[b]	1.056	1.055	1.036	1.046

[a] Calculated, g/cm^3. [b] Goodness of fit.

NMR of Radical Cations. All spectra were acquired on an unmodified Bruker AM-500 spectrometer equipped with a 5-mm proton probe. A sweep width of 166 kHz, a size of 16 K, a pulse width of 2.5 μs, and a receiver delay of 1 s were employed. A spectrum of 10% $CHCl_3$ in acetone-d_6 was run prior to each sample, and the methyl resonance of acetone-d_6 was set to 2.04 ppm; it is essential that the recorded radical cation spectrum have the same lock field and SR value as this external standard. Samples were prepared by dissolving 20–50 mg of desired radical cation in 400 or 500 μL of CD_3CN, and then the solution was transferred via a dry syringe to a deaerated 5-mm NMR tube equipped with a septum. After an initial spectrum was obtained, di-*tert*-butylnitroxide (5.96 M) was added in 10–20 μL aliquots until a total radical concentration (radical cation plus DBNO) of about 1 M was reached. The resulting spectra were Fourier transformed (with a line broadening of 20 Hz) and baseline corrected using a spline fit in reverse order (higher concentration first), in order to minimize the possibility that very broad resonances would be lost due to the baseline correction. Plots of δ's vs total radical concentration were extrapolated to zero radical concentration to give the δ_0 values.

ESR, ENDOR, and **triple-resonance** spectra were measured using a Brucker ESP 300 spectrometer equipped with the ER(ENMR)ENDOR system.

Electrochemistry. Cyclic voltammetry was performed under an N atmosphere in a three-electrode cell containing a sample concentration of approximately 1 × 10^{-3} M in a solution of 0.1 M tetra-*n*-butylammonium perchlorate in CH_3CN. The working electrode was a platinum disk and wire connected by mercury and enclosed in glass. This electrode was polished with 5.0 and 0.3 μm alumina before use. The counter electrode was a coiled platinum wire and the reference electrode was a Corning ceramic junction SCE. Cyclic voltammograms were acquired using a Princeton Applied Research (PAR) 173 Potentiostat/Galvanostat, a PAR 179 Digital Coulomer, and a PAR 175 Universal Programmer. The scans at 50–1000 mV/s were recorded on a Houston Instruments X-Y recorder.

Calculations. AM1 calculations[19] were done using Clark's VAMP programs on a Stardent 3000 computer.[20]

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