

Crystallographic Characterization of the Geometry Changes upon Electron Loss from 2-*tert*-Butyl-3-aryl-2,3-diazabicyclo[2.2.2]octanes[†]

Stephen F. Nelsen,^{*,‡} Asgeir E. Konradsson,[‡] Rustem F. Ismagilov,[‡] and Iliia A. Guzei[§]

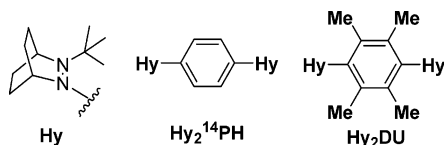
Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, and Molecular Structure Laboratory, Chemistry Department, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396

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ABSTRACT: Crystal structures of 2-*tert*-butyl-3-(2,3,5,6-tetramethylphenyl)-2,3-diazabicyclo[2.2.2]-octane radical cation nitrate (**HyDU**⁺**NO**₃⁻) [**Hy** = (2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl); 2-*tert*-butyl-3-(1-naphthyl)-2,3-diazabicyclo[2.2.2]octane radical cation hexafluoroantimonate (**Hy**¹**NA**⁺**SbF**₆⁻); 2-*tert*-butyl-3-(2-naphthyl)-2,3-diazabicyclo[2.2.2]octane radical cation hexafluoroantimonate (**Hy**²**NA**⁺**SbF**₆⁻); 1,5-bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)naphthalene dication bis(tetraphenylborate) (**Hy**₂¹⁵**NA**²⁺(**Ph**₄**B**⁻)₂); and 2,7-bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)naphthalene dication bis(hexafluoroantimonate) (**Hy**₂²⁷**NA**²⁺(**SbF**₆⁻)₂·**CH**₃**CN**) are reported, and the geometries about the oxidized **Hy** units compared with literature data for neutral **Hy**-substituted analogues and the geometry changes upon electron loss for these compounds, which have a lone pair, lone pair twist angle in the neutral form ($\theta(0)$) in the range 122–130°, are compared with those for tetraalkylhydrazines that have $\theta(0)$ values near 180, 90, and 0°.

Introduction

We have used 2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl (**Hy**) groups as the charge-bearing units in charge-localized aryl-bridged intervalence radical cations.



Charge-localized intervalence compounds (Robin-Day Class II systems)¹ may be symbolized as $n\mathbf{M}-\mathbf{B}-\mathbf{M}^{n+1}$ compounds, in which the charge-bearing units **M** differ in charge by one unit and are linked to a bridge. They are the simplest electron-transfer systems ever devised because the bridge controls the distance and orientation of the **M** groups, and when they are symmetrical in lower or higher oxidation levels, ΔG° for electron-transfer is zero. The intervalence compound concept was devised for compounds with transition metal-centered **M** units, and most studies have been of such compounds.^{2,3} We were particularly interested in making organic-centered intervalence compounds to test the classical Marcus–Hush theory assumption that the electron-transfer barrier could be accurately predicted from the intervalence band of Class II compounds, using the energy of the band maximum as Marcus’s reorganization energy λ ^{4,5} and the Hush eq 1

$$H_{ab} = (\mu_{12}/\Delta\mu)\lambda \quad (1)$$

for evaluation of the off-diagonal matrix element, H_{ab} , where μ_{12} is the transition dipole moment, usually evaluated using Hush’s Gaussian approximation,^{6,7} and $\Delta\mu$ is the change in dipole moment, estimated as $e d_{ab}$, where d_{ab} is often taken as the separation between the **M** group centers.⁸ The ESR spectra of **Hy**-centered radical cations provide an experimental means of measuring the electron-transfer rate constant for dinitrogen-centered intervalence radical cations, although the range of rate constants that can be measured is rather narrow, about a factor of 10 centered at about $10^8 \text{ M}^{-1} \text{ s}^{-1}$, so most intervalence compounds have rate constants that are either too fast or too slow to measure.⁹ The parent **Hy**₂¹⁴**PH**⁺ has an electron-transfer rate constant that is too large to measure in any pure solvents that we have tried.¹⁰ However, the rate constant could be tuned to lie within the range necessary for accurate measurement by increasing the N–Ar twist angles (ϕ) by placing substituents on the *p*-phenylene group, as in **Hy**₂²⁷**DU**⁺, because H_{ab} is, as expected, approximately proportional to $\cos \phi$.⁷ Our studies led to compounds for which rate constants could be measured, and in certain cases, crystal structures could be obtained that allowed us to compare the oxidized and reduced **Hy** units in their intervalence oxidation level with those at the 0 and 2+ level or with monohydrazine model compounds.¹¹

The most important structural quantities for consideration of electron transfer are the quantities that change the most upon electron removal, the NN and NC_{Ar} bond distances, the pyramidalicity at nitrogen, and the twist angles θ and ϕ at the hydrazine unit. Here we use $\Delta\alpha_{av}$, the difference of the average of the bond angles at nitrogen from the 120° for planarity as our measure

[†] Dedicated to Professor Michael McBride on the occasion of his 65th birthday.

^{*} To whom correspondence should be addressed. E-mail: nelsen@chem.wisc.edu.

[‡] Department of Chemistry.

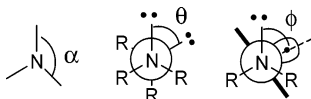
[§] Molecular Structure Laboratory.

Table 1. Hy⁺ Units of HyDU Systems

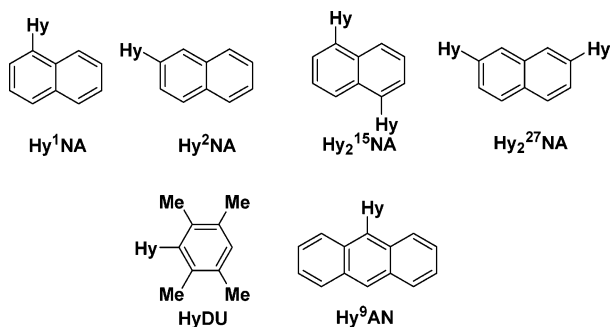
	HyDU ⁺ NO ₃ ⁻ (1+ unit) ^a	HyDU ⁺ Ph ₄ B ⁻ (1+ unit) ^b	Hy ₂ Du ²⁺ Ph ₄ B ⁻ (1+ unit) ^b
<i>d</i> (NN), Å	1.3548(12)	1.346(2)	1.356(3)
<i>d</i> (NC _{Ar}), Å	1.4503(13)	1.455(3)	1.443(3)
Δα _{av} (N _{Ar}), °	1.53(8)	1.0(2)	1.5(3)
Δα _{av} (N _{tBu}), °	1.23(8)	1.4(2)	1.5(2)
φ°, °	63.84(14)	(-66.2(3))	(-63.6(4))
θ°, °	(-158.33(9))	156.6 ₅ (2)	156.1 ₅ (3)
∠C _{tBu} NNC _{Ar} , °	45.14(14)	(-44.8(3))	(-48.0(4))

^a This work. ^b Ref 10.

of pyramidal geometry because Δα_{av} is nearly linear with fractional s orbital character and hence lone pair ionization potential all the way from planarity to being bent past tetrahedral (Δα_{av} > 10.5°). We assume that the lone pair and p orbital axes bisect the CXC angles in Newman projections down the NN or NC_{Ar} bonds in calculating θ and φ from the structural data.



In this work, we compare structural data for the neutral and radical cation oxidation levels of the α (1) and β (2)-Hy-substituted naphthalenes, as well as dications of the 1,5- and 2,7-substituted systems and compare their geometries about the hydrazine units with previously published as well as new data on the phenylene- and durene-bridged and anthracene¹² systems.



Results and Discussion

Disorder problems are severe for neutral Hy-substituted aromatics, especially for the disubstituted compounds. The relative orientation of the hydrazine units does not affect their energy in solution and three of the four possible diastereomers were found in the crystal structure of Hy₂Du⁰,¹¹ which results in poor quality for the structure (so it is not included in the discussion here). Although we had obtained a structure for HyDU⁰, it was too disordered to be useful here and is not reported. However, the structure of HyDU⁺ is reported because it gives a third oxidized Hy unit for comparison with that of Hy₂Du⁺ (see Table 1).

The Hy⁰ and Hy⁺ units of HyPH systems are compared in Tables 2 and 3, respectively. The very short lifetime of Hy₂PH²⁺ precludes obtaining data exactly analogous to that of Table 1 for Hy₂Du²⁺, but if we compare the available data it is clear that the methyls do indeed increase φ for Hy⁺ by about 18°, which leads to the significant difference in H_{ab} that is observed (the cos φ₊ values are 0.67 for HyPH⁺ and 0.40 for HyDU⁺).

Table 2. Hy⁰ Units of HyPH Systems

	Hy ₂ ¹⁴ PH ⁰ (0 unit) ^a	Hy ₂ ¹⁴ PH ⁺ (0 unit) ^a
<i>d</i> (NN), Å	1.461(2)	1.454(3)
<i>d</i> (NC _{Ar}), Å	1.440(2)	1.426(3)
Δα _{av} (N _{Ar}), °	6.9(1)	6.4(2)
Δα _{av} (N _{tBu}), °	8.0(1)	7.3(2)
φ°, °	-37.5(2)	-32.6(3)
θ°, °	124.1 ₇ (1 ₃)	121.6(3)
∠C _{tBu} NNC _{Ar} , °	-105.8(1)	-107.3(3)

^a Ref 10.

Table 3. Hy⁺ Units of HyPH Systems

	HyPH ⁺ (HC≡C) ₄ B ⁻ (1+ unit) ^a	HyPH ⁺ NO ₃ ⁻ (1+ unit) ^b	Hy ₂ ¹⁴ PH ⁺ Ph ₄ B ⁻ (1+ unit) ^b
<i>d</i> (NN), Å	1.355(2)	1.351(2)	1.359(3)
<i>d</i> (NC _{Ar}), Å	1.440(2)	1.443(3)	1.436(3)
Δα _{av} (N _{Ar}), °	0.9(1)	0.7(2)	1.3(2)
Δα _{av} (N _{tBu}), °	3.0(1)	2.8(2)	3.8(2)
φ°, °	(-59.2(2))	53.1(3)	47.6(3)
θ°, °	(-146.4(2))	152.8(3)	142.3 ₅ (2)
∠C _{tBu} NNC _{Ar} , °	(-53.6(2))	57.5(3)	67.3(3)

^a Ref 10. ^b Ref 10.

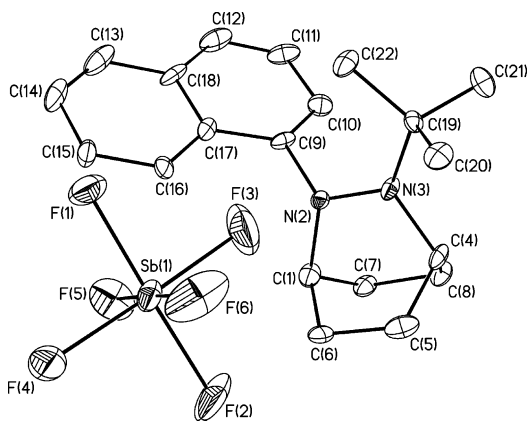


Figure 1. Molecular drawing of Hy¹NA⁺(SbF₆⁻) (30% probability ellipsoids).

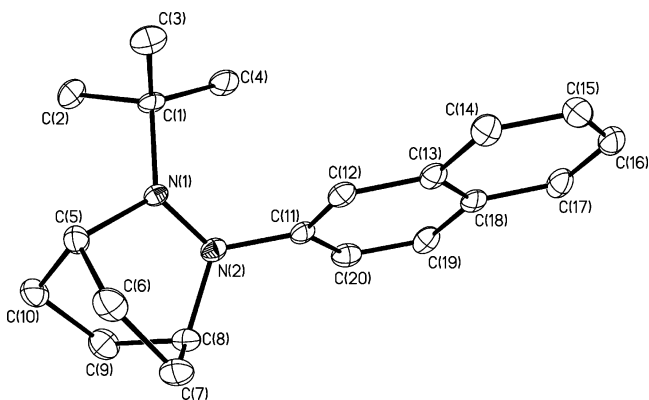


Figure 2. Molecular drawing (50% probability ellipsoids) of the cation portion of Hy²NA⁺(SbF₆⁻).

Because we have obtained crystal structures for both 0¹³ and +1 oxidation states of Hy¹NA and Hy²NA (for molecular drawings of the radical cations, see Figures 1 and 2) as well as Hy⁹NA,¹² the changes in their geometrical parameters upon electron loss may be directly compared (see Table 4).

These compounds are the first mono-*N,N'*-bicyclic hydrazines for which the changes in geometric parameters upon electron loss are experimentally available, and they provide data for hydrazines with θ(0) in a

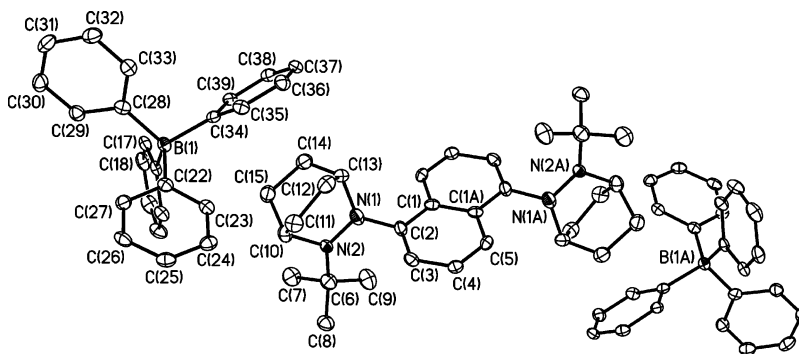


Figure 3. Molecular drawing (50% probability ellipsoids) of the crystal structure of $\text{Hy}_2^{15}\text{NA}^{2+}(\text{Ph}_4\text{B}^-)_2$. The molecules rest on a center of inversion.

Table 4. Changes in Geometry at Nitrogen for Hy^1NA , Hy^2NA , and Hy^9AN

^1NA	Hy^1NA^0 ^a	$\text{Hy}^1\text{NA}^+\text{SbF}_6^-$ ^b	change
$d(\text{NN})$, Å	1.446(6)	1.348(8)	-0.098 (6.8%)
$d(\text{NC}_{\text{Ar}})$, Å	1.442(6)	1.461(8)	+0.019 (1.3%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{Ar}})$, °	9.3(4)	0.9(6)	-8.4° (80%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{tBu}})$, °	6.8(4)	3.1(6)	-3.7° (35%)
ϕ , °	(-)-50.2(6)	64.7(9)	+14.5°
θ , °	129.8(4)	153.3(6)	+23.5°
$\angle\text{C}_{\text{tBu}}\text{NNC}_{\text{Ar}}$, °	(-)-101.7(5)	53.3(9)	-48.4
^2NA	Hy^2NA^0 ^a	$\text{Hy}^2\text{NA}^+\text{SbF}_6^-$ ^b	
$d(\text{NN})$, Å	1.458(2)	1.347(4)	-0.111 (7.6%)
$d(\text{NC}_{\text{Ar}})$, Å	1.495(2)	1.437(4)	-0.058 (3.8%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{Ar}})$, °	7.8(1)	1.1(3)	-6.7° (36%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{tBu}})$, °	6.3(1)	2.9(3)	-3.4° (32%)
ϕ_{CN} , °	37.1(2)	53.4(4)	+16.3°
θ , °	122.49(12)	149.3(3)	+26.8°
$\angle\text{C}_{\text{tBu}}\text{NNC}_{\text{Ar}}$, °	105.92(12)	53.5(4)	
^9AN	Hy^9AN^0 ^c	$\text{Hy}^9\text{AN}^+\text{Ph}_4\text{B}^-$ ^c	
$d(\text{NN})$, Å	1.452(4)	1.358(2)	-0.094 (6.5%)
$d(\text{NC}_{\text{Ar}})$, Å	1.466(3)	1.445(2)	-0.021 (1.4%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{Ar}})$, °	5.3(2)	1.5(1)	-3.8° (36%)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{tBu}})$, °	7.7(3)	0.9(1)	-6.8° (65%)
ϕ_{CN} , °	43.2(4)	66.7(2)	+23.5
θ , °	126.8(3)	157.0(1)	+30.2
$\angle\text{C}_{\text{tBu}}\text{NNC}_{\text{Ar}}$, °	-89.7(3)	44.9(2)	

^a Ref 12. ^b This work. ^c Ref 11.

range different than that for previously studied compounds for which both 0 and +1 oxidation level crystal structures are available, which were all tetraalkylhydrazines.

Additional structural information for Hy^+ groups arises from the 2+ oxidation level of disubstituted compounds, which contain two Hy^+ groups. Crystal structures are only available for the 1,5-bridged α -substituted (Figure 3) and 2,7-bridged β -substituted (Figure 4) dications because of short lifetimes for both the 1,4- and the 2,6-substituted isomers, which decompose with half-lives of hours. Tables 5 and 6 compare the hydrazine units of α - and β -substituted naphthalene-bridged monohydrazine radical cations with those of the dihydrazine dication. As we point out elsewhere, the shorter dication lifetimes correlate with the larger electronic couplings for the radical cations.¹³ In addition, we suggested that this electronic coupling in the diradical dication corresponds to charge separation, to $\text{Hy}^{2+}-\text{Ar}-\text{Hy}^0$ in the dication, and the dicationic oxidation state of Hy is extremely unstable, resulting in de-tert-butylation.¹⁴ Two nonidentical Hy^+ units are present in the crystal of $\text{Hy}_2^{27}\text{NA}^{2+}(\text{SbF}_6^-)_2\cdot\text{CH}_3\text{CN}$, leading to the

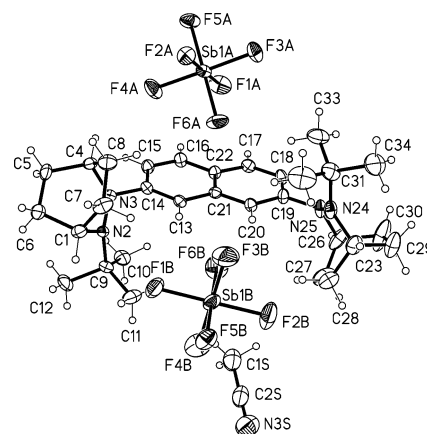


Figure 4. Molecular drawing (50% probability ellipsoids) of the crystal structure of $\text{Hy}_2^{27}\text{NA}^{2+}(\text{SbF}_6^-)_2\cdot\text{CH}_3\text{CN}$.

Table 5. Comparison of the Hy^+ Units of Mono- and Di- α -substituted Naphthalenes

	$\text{Hy}^1\text{NA}^+\text{SbF}_6^-$	$\text{Hy}_2^{15}\text{NA}^{2+}(\text{Ph}_4\text{B}^-)_2$
$d(\text{NN})$, Å	1.348(8)	1.342(3)
$d(\text{NC}_{\text{Ar}})$, Å	1.461(8)	1.444(4)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{Ar}})$, °	0.9(6)	0.9(2)
$\Delta\alpha_{\text{av}}(\text{N}_{\text{tBu}})$, °	3.1(6)	3.2(2)
ϕ , °	64.7(9)	71.6(4)
θ , °	153.3(6)	148.9(3)
$\angle\text{C}_{\text{tBu}}\text{NNC}_{\text{Ar}}$, °	53.3(9)	-57.8(4)

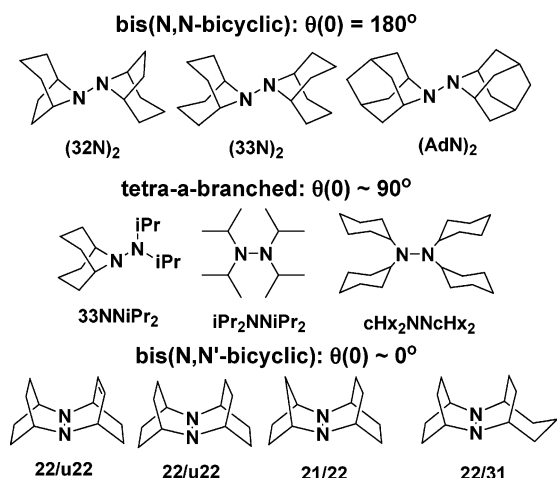
Table 6. Comparison of the Hy^+ Units of Mono- and Di- β -substituted Naphthalenes

	$\text{Hy}^2\text{NA}^+\text{SbF}_6^-$	$\text{Hy}_2^{27}\text{NA}^{2+}(\text{SbF}_6^-)_2\cdot\text{CH}_3\text{CN}$
$d(\text{NN})$, Å	1.347(4)	1.353(4)[A] 1.334(5)[B]
$d(\text{NC}_{\text{Ar}})$, Å	1.437(4)	1.434(5)[A] 1.430(5)[B]
$\Delta\alpha_{\text{av}}(\text{N}_{\text{Ar}})$, °	1.1(3)	0.9(3)[A] 1.1(4)[B]
$\Delta\alpha_{\text{av}}(\text{N}_{\text{tBu}})$, °	2.9(3)	3.4(3)[A] 2.9(4)[B]
ϕ_{CN} , °	53.4(4)	59.0(5)[A] (-)-53.2(6)[B]
θ , °	149.3(3)	147.8(4)[A] 146.3(4)[B]
$\angle\text{C}_{\text{tBu}}\text{NNC}_{\text{Ar}}$, °	53.5(4)	-59.1(5)[A] -60.1(6)[B]

two sets of parameters in Table 6. The structure of $\text{Hy}^1\text{NA}^+\text{SbF}_6^-$ is not very accurate, and there is a larger deviation between the parameters obtained for it and for the dihydrazine.

For the structures of tetraalkylhydrazines for which crystal structures are available for both 0 and 1+

Scheme 1. Structures of R_4N_2 for which Both 0 and 1+ Oxidation Level Crystal Structures Are Available^a



^a See Supporting Information for details.

Table 7. Changes in Geometry upon Electron Loss for Hydrazines of Four Structural Types

quantity	bis(- N,N -bicyclic)	HyAr (Tables 4–6)	tetra- α -branched)	bis(N,N' - bicyclic)
$\Delta d(\text{NN})$, %	9.8–10.5	6.5–7.6	4.0–5.2	9.9–11.8
$\Delta\alpha_{\text{av}}(0)$, °	11.7–12.1	6.3–7.7	2.3–4.7	7.2–10.0
$\Delta\alpha_{\text{av}}(+)$, °	3.3–4.4	0.9–3.1	0.1–3.1	0.9–1.4
$\theta(0)$	180	122–130	86–89	0–15
$\theta(+)$	180	146–157	0–23	0–6

charged oxidation levels, grouped by size of $\theta(0)$, see Scheme 1. The geometrical parameters of these compounds are compared in Table 7. The bicyclo-[2.2.2]-octyl ring of **HyAr** derivatives cannot twist very much, and the bulky *tert*-butyl group of **Hy** ensures trans-fused Ar and *t*Bu, making $\theta(0)$ near 126° , and $\theta(+)$ is 149 – 157° , corresponding to pyramidalities at N between 14 and 30% of the way from planar to tetrahedral. The $\Delta d(\text{NN})$ values for these compounds of intermediate θ value are $7.2 \pm 0.6^\circ$, clearly intermediate between the $10.2 \pm 0.4^\circ$ range found for $\theta(0) = 180^\circ$ hydrazines and $10.9 \pm 1.0^\circ$ range of $\theta(0) \sim 0$ hydrazines, which have the largest lone pair, lone pair energy differences (over 2.3 eV as measured by photoelectron spectroscopy) and the $\theta(0) \sim 90^\circ$ acyclic compounds that have the smallest (under 0.6 eV).¹⁵ $\theta(0)$ is the most important factor in determining the size of the Marcus reorganization energy λ , which is the principal factor in causing the huge range of intrinsic reactivities for electron transfer for hydrazines that have been measured using stopped-flow kinetics for electron transfer between different 0,1+ couples.¹⁶

Conclusions

The changes in NN distance and the pyramidalities at nitrogen upon electron loss for **HyAr** compounds ($\theta(0)$ near 126°) are intermediate between those of acyclic tetra- α -branched compounds, which have a small lone

pair lone pair interaction because $\theta(0)$ is near 90° , and the bis-bicyclic compounds that have large interactions because $\theta(0)$ is near 0° (bis- N,N' bicyclic) or 180° (bis- N,N -bicyclic). The radical cations of **HyAr** compounds have their lone pair axes twisted about 30 ± 6 degrees from having maximum interaction (180°), which is more than for the tetraalkylhydrazine studied, presumably because of nonbonded interactions between the large *tert*-butyl and phenyl substituents.

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Note Added after ASAP Publication

An earlier version of this paper posted ASAP on the web on July 14, 2005, contained two errors in the compound names on lines 15 and 16 of the abstract. The names have been corrected in this new version posted September 30, 2005.

Supporting Information Available: Summary of the data used to give the ranges in Table 5. Crystal structural data for **HyDU**+ NO_3^- , **Hy¹NA**+ SbF_6^- , **Hy²NA**+ SbF_6^- , **Hy²NA**+ SbF_6^- , **Hy²NA**+ SbF_6^- , **Hy²NA**+ SbF_6^- , **Hy²NA**+ SbF_6^- , and **Hy²NA**+ SbF_6^- · CH_3CN . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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