Oxidized Phenyl-Substituted Sesquibicyclic Hydrazines

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The effect of α- and β-phenyl substituents on the neutral, +1, and +2 oxidation states of bis-*N,N'*-bicyclic hydrazines **1** and **2** is discussed. An α-phenyl substituent on **2** makes first electron removal 1.8 kcal/mol more difficult, but second electron removal 3.2 kcal/mol less difficult. There is no evidence for significant spin or charge delocalization into the phenyl groups of the +1 oxidation states of these compounds. Exo and endo β-phenyl-substituted hydrazines **xPh-1** and **nPh-1** have electron transfer rate constants between their neutral and radical cation forms which are 85% and 55% as large as that for unsubstituted **1**, which is argued to demonstrate that attaining relative orientations which allow overlap of the dinitrogen π systems at the transition state cannot be important; electron transfer proceeds through the alkyl groups. The dications **xPh-2**$^{2+}$ and **nPh-2**$^{2+}$ decompose in acetonitrile much faster than **2**$^{2+}$ (room temperature lifetimes < 1 s for the phenylated compounds and > 10^4 min for the parent).

Introduction

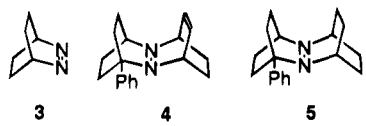
This paper concerns the preparation and properties of the neutral, +1, and +2 oxidation states of bridgehead (α) and methylene (β) phenylated derivatives of the bis-*N,N'*-bicyclic (sesquibicyclic) hydrazines 2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradecene (**1**) and its saturated analogue **2**.

1 **2**

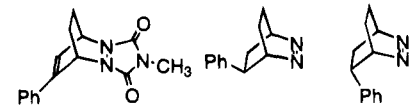
The principal issues considered are the effect of phenyl substituents on the electron transfer rate constant between the neutral and +1 oxidation states and how the phenyls affect the reactivity of the +2 oxidation states.

Results

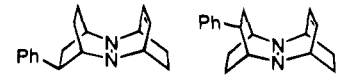
Compound Preparation. The parent compounds were prepared by the proton-driven Diels–Alder reaction of 1,3-cyclohexadiene with protonated 2,3-diazabicyclo-[2.2.2]oct-2-ene (**3**), producing protonated **1**, followed by deprotonation and hydrogenation to give **2**.[1] Because **3** is made from the Diels–Alder adduct of 1,3-cyclohexadiene and an azodicarboxylate, phenylated **1** and **2** can in principle be made by employing a phenyl-substituted cyclohexadiene in either Diels–Alder reaction, but the acid sensitivity of phenylated cyclohexadienes makes the route through phenylated azo compounds much more attractive. The synthesis of the bridgehead phenyl compounds **4** and **5** from 1-phenylcyclohexadiene and the X-ray structure of **5** have been reported previously.[2] The principal discovery in preparing them was that rhodium on alumina is an especially useful catalyst for hydrogenation of double bonds of acylated or protonated hydrazines without getting the CN cleavage products which are the major ones for several other catalysts when a benzylic C–N bond is present. The β-phenyl compounds were prepared from 2-phenyl-1,3-cyclohexadiene. Diels–Alder addition of *N*-methyltriazolinedione gave the expected adduct **6**, and hydrogenation produced predominately the endo phenyl epimer (**n**), i.e. hydrogenation occurs from the exo face, as previously observed for other cyclohexadiene, azodicarboxylate adducts.[3] After chromatographic separation of the hydrogenated adducts, hydrolysis and oxidation gave **xPh-3** and **nPh-3**. Reaction of each protonated azo compound with 1,3-cyclohexadiene gave protonated adducts which were deprotonated to give neutral **xPh-1** and **nPh-1**. **xPh-1** was obtained as a nearly equimolar mixture of the diastereomers having the exo β-phenyl substituted anti (**a**) and syn (**s**) to the unsaturation, shown as **axPh-1** and **sxPh-1**, which were not separated. As expected, the two faces of the **xPh-3-H**$^+$ NN π bond are nearly equivalent. Only



3 **4** **5**



6 **xPh-3** **nPh-3**



axPh-1 **sxPh-1**

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(1) (a) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366. (b) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* **1986**, *42*, 1769.

(2) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hiyashi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(3) Edmunds, A. J. F.; Samuel, C. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1267.

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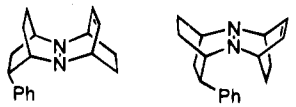
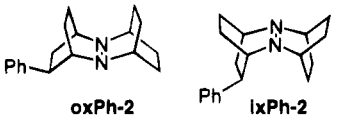
the diastereomer phenylated anti to the unsaturation was detected for **nPh-1**, so the endo phenyl of **nPh-3-H**$^+$ effectively blocks addition from the endo face. For unsubstituted **1**, only the double nitrogen inversion form (invertomer) having the unsaturation at the more crowded, "inner" position relative to the other bicyclic ring (that illustrated for **1**) is detected by ^{13}C-NMR at low temperature. MM2 calculations get the invertomer with the unsaturation "outer" 8.0 kcal/mol higher in steric energy, and AM1 calculations 5.8 kcal/mol higher in ΔH_f. The relative energy of the **nPh-1** invertomers is significant for one aspect of this work, and MM2 and AM1 calculate the **inPh-1** invertomer as lying 10.2 and 9.4 kcal/mol higher in enthalpy.



onPh-1 **inPh-1**

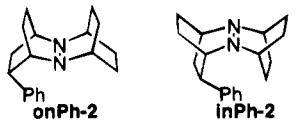
The protonated **Ph-1** derivatives were hydrogenated separately using rhodium on alumina to give **Ph-2** derivatives. **xPh-2** is a single diastereomer on the NMR time scale at room temperature, but the presence of the phenyl group makes its invertomers different in energy.

Double nitrogen inversion is slow on the NMR time scale at 190 K, where a 2.4:1 ratio of **oxPh-2/ixPh-2**



oxPh-2 **ixPh-2**

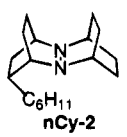
invertomers is present, so $\Delta\Delta G°$ is 0.33 kcal/mol. MM2 and AM1 calculations give $\Delta\Delta H$ values of 0.49 and 0.43 kcal/mol respectively, so the calculated enthalpy difference is not far from the observed free energy difference. Only a single conformation is detected for **nPh-2** even at low temperature, and we assign it as **onPh-2** because



onPh-2 **inPh-2**

the clearly sterically more crowded **inPh-2** invertomer is calculated to lie 2.43 and 2.01 kcal/mol higher in enthalpy by MM2 and AM1 respectively.

In an interesting sidelight of this work, **nPh-1-H**$^+$ was found to undergo hydrogenation of the phenyl group to produce the endo-cyclohexyl compound **nCy-2** when a



nCy-2

hydrogenation was allowed to run overnight. Although rhodium catalysts are well known to be unusually good at hydrogenating aromatic rings,[4] the room temperature, atmospheric pressure hydrogenation of the phenyl group of **nPh-2-H**$^+$ appears to proceed under exceptionally mild conditions, and we suspect that the nearby protonated nitrogen is important for obtaining this result. Reduction

(4) Augustine, R. L. *Catalytic Hydrogenation*; Marcel Dekker: New York, 1965; p. 39.

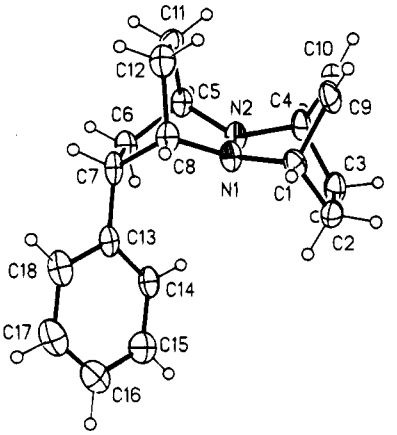


Figure 1. Thermal ellipsoid drawing of the crystal structure of **nPh-1**$^+$.

Table 1. Comparison of Geometry at Nitrogen for nPh-1$^+$PF$_6^-$ and 1$^+$NO$_3^-$

	nPh-1$^+$PF$_6^-$	1$^+$NO$_3^-$ [a]
d(NN), Å	1.343(5)	1.349(1)
α(CNN) uns, deg	113.7,112.6	113.0,113.7
α(CNN) sat, deg	114.6,114.0	114.0,114.1
α(CNC), deg	125.5,125.3	125.5,126.0
α_{av}, deg	117.6,117.4	117.5,117.9
θ, deg	0.6	0.6

[a] Data from ref 13.

Table 2. Splitting Constants (Gauss) from ESR, ENDOR, and Special Triple Experiments for 2$^+$ Derivatives

atom type	2$^+$NO$_3^-$ [a]	**xPh-2**$^+$SbCl$_6^-$ [b]	**nPh-2**$^+$SbCl$_6^-$ [b]
N	15.1(2N)	15.6(2N)	15.2(2N)
exo H	2.80 (8H)	+3.33 (1H)	+4.24 (1H)
		+3.21 (1H)	+4.14 (3H)
		+3.11 (2H)	+1.56 (1H)
		+2.50 (2H)	+1.51 (1H)
		+1.88 (1H)	+1.48 (1H)
			+0.91 (1H)
		[av = 2.81]	[av = 2.77]
endo H	−0.56 (8H)	−0.67 (6 or 8H)	−0.72 (2H?)
			?0.55 (xH)

[a] In toluene at 300 K. [b] In toluene/ethanol (4:1) at 300 K.

of **xPh-1-H**$^+$ under the same conditions did not lead to any phenyl group hydrogenation.

Radical Cations. The radical cation hexafluorophosphates of **nPh-** and **xPh-1** and **-2** were prepared by NOPF$_6$ oxidation and proved isolable. The X-ray structure of **nPh-1**$^+$PF$_6^-$ was obtained (see Figure 1), and as can be seen from the comparison with unsubstituted 1$^+$NO$_3^-$ in Table 1, neither the phenyl substitution nor the counterion change significantly affects the geometrical parameters at nitrogen. Little effect on the geometry about the nitrogens was previously observed for α (bridgehead) phenyl substitution, when the X-ray structures of neutral **5** and **2** were compared.[2]

xPh-2$^+$ and **nPh-2**$^+$ were further characterized in solution by ENDOR and special triple studies of their splitting constants, as summarized and compared with the parent **2**$^+$ in Table 2. The parent equilibrates between two equal energy invertomers, the average H^{exo} splitting is 2.80 G, and the W-plan H^{exo} splitting for one frozen invertomer, **xi** (**ex**o on the **i**nner carbons), lies in

(5) Nelsen, S. F.; Petillo P. A.; De Felippis, J.; Wang, Y.; Chen, L.-J.; Yunta, M. J. R.; Neugebauer, F. A. *J. Am. Chem. Soc.* **1993**, *115*, 5608.

Table 3. Cyclic Voltammetry Data for Phenylated 1 and 2 Derivatives[a]

compound	$E^{\circ\prime}_1$ (ΔE_{pp}), V	$\Delta E^{\circ\prime}_1$	$E^{\circ\prime}_2$ (ΔE_{pp}), V	$\Delta E^{\circ\prime}_2$	$\Delta E^{\circ\prime}$ [b]
1	−0.25(0.065)	≡ 0	+0.95(0.080)	≡ 0	1.20
4(α-Ph-1)	−0.18(0.100)	+0.07	*+0.88 (irr)*[c]		
xPh-1[d]	−0.22(0.078)	+0.03	*+0.99 (irr)*[c]		
nPh-1	−0.25(0.099)	0.00	+1.02(0.080)	+0.07	1.27
2	−0.54(0.069)	≡ 0	+0.86(0.070)	≡ 0	1.40
5(α-Ph-2)	−0.46(0.110)	+0.08	+0.74(0.135)	−0.14	1.20
xPh-2	−0.51(0.159)	+0.03	+0.88(0.103)	+0.02	1.39
nPh-2	−0.52(0.129)	+0.02	+0.93(0.059)	+0.07	1.45
nCy-2	−0.57(0.183)	−0.03	+0.91(0.087)	+0.05	1.47

[a] Conditions: room temperature in CH_3CN containing 0.1 M tetraethylammonium perchlorate, at platinum, 200 mV/s scan rate. [b] $\Delta E^{\circ\prime} = E^{\circ\prime}_2 - E^{\circ\prime}_1$. [c] Irreversible CV wave, for which the oxidation peak potential is quoted. [d] Studied as a mixture of **axPh-1** and **sxPh-1**.

the range 5.5 to 6.25 G, as discussed previously.[5] The lack of symmetry of the phenylated compounds makes their coupling patterns very complex, but five and six signals lying in the range expected for H^{exo} were observed for **xPh-2**$^+$ and **nPh-2**$^+$, respectively. The signals were rather weak, and integration of the special triple signals was not very accurate, but assigning the numbers of hydrogens as shown in Table 2 gives average exo splitting constants of 2.80 and 2.77 G, close to that for the parent, as expected. The larger range of exo splittings for **nPh-2** than for **xPh-2** is expected because its **i** and **o** invertomers will differ more in energy. The exo splitting constants provide a sensitive measure of these energy differences. Use of eqs 4−7 in ref 5 to quantitate the mole fractions of the two invertomers gives an equilibrium fraction of **oPh** of 0.557−0.572 (K_{eq} = 1.34−1.26, ΔG° = −0.14 to −0.11 at 250 K) for **xPh-2**$^+$ and 0.758−0.703 (K_{eq} = 2.82−2.37, ΔG° = −0.50 to −0.42 at 250 K) for **nPh-2**$^+$, the ranges being quoted for the frozen **xi** splitting values of 5.50−6.25 Gauss respectively. AM1 calculations get $\Delta\Delta H_f$ values of −0.07 and −1.08 kcal/mol respectively, underestimating the effect of exo-phenyl substitution and overestimating that of endo substitution, although the calculated values refer to enthalpies and not free energies, and especially for the endo-phenyl compound, the entropy differences between **oPh** and **iPh** invertomers might be significant. We note that the splitting constants show that spin delocalization to the phenyl groups of these γ-phenyl compounds is not significant, a result which is also predicted by AM1 calculations.

Phenyl substitution affects the thermodynamics for electron loss from **1** and **2** very little, as shown by the small changes in formal potentials for electron loss, $E^{\circ\prime}$, measured by cyclic voltammetry (CV) and included in Table 3.

We also determined how phenyl substitution affects k_{ex}, the self-electron transfer (ET) rate constant between the neutral form and its own radical cation. We have argued elsewhere that the k_{ex} values observed for **1**$^{0/+}$ and **2**$^{0/+}$, when considered using Marcus−Hush ET theory and reasonable estimates for inner- and outer-sphere reorganization energies ($\lambda_{in} + \lambda_{out} = \lambda$, the barrier to vertical self-ET), require that the electron transfer is significantly diabatic ("nonadiabatic").[6] This means that the rate constant is argued to be limited by poor overlap between the wave functions for the ET partners at the transition state, i.e. a small V (also called J and H_{ab}) value. The nitrogen atoms of these compounds are hindered by the four α-branched alkyl groups, and we expected that NN-(π) system overlap at the transition state might be difficult to achieve, possibly even requiring the ET to proceed through overlap of the alkyl group wave functions, so that smaller V values might result than for previously studied intermolecular ET systems such as *p*-phenylenediamines[7] and ferrocenes.[8] Both of these systems have relatively unhindered π-system approach available, and Grampp and Jaenicke[7] and Weaver and co-workers[8] have each argued that these systems have ET transition states with face-to-face π-system overlap to achieve maximum V, although each also argues that V is small enough for these systems to show diabatic ET kinetics. If electron transfer through the alkyl groups of **1** and **2** were slow enough, it would seem possible that a phenyl group might even increase the rate of electron transfer for a sesquibicyclic hydrazine by acting as an "antenna" which allows higher V transition states to be attained.

We carried out slow exchange region NMR line broadening studies on neutral compound, cation mixtures in CD_3CN at various temperatures, interpolating the results to 25 °C, as described previously for **1**$^{0/+}$, **2**$^{0/+}$,[9] and several other unsubstituted compounds.[6,9] Because only rate constants measured at 25 °C in CD_3CN will be discussed here, we shall just refer to the values as k_{ex}. Self-ET for the parent **2**$^{0/+}$ has k_{ex} of about 700 M^{-1} s^{-1}, which is near the low end of the range measurable by NMR line broadening (little line broadening is detected as the radical cation is added to the neutral compound), and decomposition of the radical cation by the neutral compound is also a problem. We did not see significant line broadening for either **xPh-2**$^{0/+}$ **or nPh-2**$^{0/+}$. Although radical cation decomposition also appears to be a problem for the phenylated compounds, we are certain that their k_{ex} values are smaller than that of **2**$^{0/+}$. **1**$^{0/+}$ has a higher k_{ex} value of 12 100 $M^{-1}s^{-1}$, and both **xPh-1**$^{0/+}$ and **nPh-1**$^{0/+}$ show comparable, but slightly slower k_{ex} of 10 300 and 6700 M^{-1} s^{-1}, respectively. An "antenna" effect is obviously not significant for these compounds.

Dication Formation and Decomposition. Phenyl substitution greatly decreases dication lifetime, and for the derivatives of the unsaturated system **1**, only the endo-β-substituted compound **nPh-1**$^{2+}$ proved long-lived enough to observe a reversible second oxidation wave (see Table 3 for the CV data). Both of the bridgehead (α) phenyl dications **4**$^{2+}$ and **5**$^{2+}$ are too unstable to obtain NMR spectra even at 240 K in CD_3CN, the conditions under which **1**$^{2+}$ and several other unsubstituted sesquibicyclic dications have been studied.[10]

The methylene(β)-phenylated dications are longer lived, but they decay noticeably during 200 mV/s CV scans at room temperature. The order of stabilities obtained from the relative size of the second reduction wave compared to the second oxidation wave is **nPh-2**$^{2+}$ > **nPh-1**$^{2+}$ > **xPh-2**$^{2+}$ > **xPh-1**$^{2+}$ in lifetime. The derivatives of **2** were

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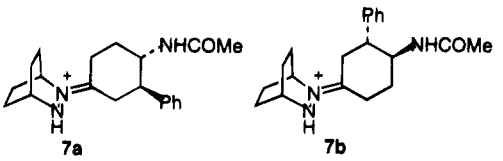
(7) (a) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 325. (b) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 335. (c) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 904.

(8) (a) Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152. (b) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(9) (a) Nelsen, S. F.; Blackstock, S. C. *J. Am. Chem. Soc.* **1985**, *107*, 7189. (b) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

(10) Nelsen, S. F.; Wang, Y. *J. Org. Chem.* **1994**, *59*, 3082.

studied by NMR at 240 K in CD_3CN, where **nPh-2**$^{2+}$ has a half-life of ~60 min and **xPh-2**$^{2+}$ ~30 min. Complete hydrolysis of the reaction mixtures produces **3** but no phenylated **3**, so all of the cleavage occurs at the phenyl-substituted bicyclic ring. We attempted to find out what is involved in the β-phenyl kinetic destabilization of these dications by NMR studies. The ^{1}H-NMR spectra of the decomposition products are so complex that we could tell little, but the ^{13}C-NMR spectra taken after addition of a small amount of D_2O to completely hydrolyze the initially formed acetonitrile trapping products[10] are simpler and show the pattern of chemical shifts expected for a nearly 1:1 mixture of two immonium-alkylated hydrazones (two C_q near 177 and 141 δ, corresponding to C=O and C=N$^+$, four CH between 66 and 55 δ corresponding to CHRN and CHRPh carbons, and seven CH_2 carbons between 21 and 40 δ for each isomer), which we suggest are most likely to be the two C=N$^+$ isomers **7a** and **7b**. We



unfortunately did not observe the trialkyldiazenium cation isomers which we presume are the immediate precursors of **7**. We cannot tell whether the cyclohexane ring substituents are as shown or switched, but the same pair of compounds is produced in similar amounts by both **xPh-2**$^{2+}$ and **nPh-2**$^{2+}$.

Discussion

Electron Transfer Thermodynamics and Kinetics. The CV data of Table 3 shows that the effect of β-phenyl substitution of both **1** and **2** on first electron removal thermodynamics is destabilization by 0.7 kcal/mol or less. When the electron-withdrawing β-phenyl is replaced by the electron-releasing cyclohexyl, slightly easier oxidation is observed, indicating that the small destabilization by β-phenyl is inductive and not steric in origin. The ENDOR data show no evidence for any spin delocalization onto the phenyl groups. The phenyls therefore do not interact significantly with the spin- and charge-bearing hydrazine units of these compounds. We suggest that the similar k_{ex} values for phenylated **1** derivatives to that of the parent have significant implications for the transition state geometry. It has been traditional to estimate the distance between the ET partners for self-ET reactions using the Marcus formula (1) for the solvent reorganization energy, λ_{out}, where r_{eff}

$$\lambda_{out}\,(\text{kcal/mol}) = 332.1\,(1/r_{eff} - 1/d_{eff})\gamma \qquad (1)$$

(Å) is the effective radius of the ET partners and d_{eff} (Å) is the effective distance between the centers at the ET transition state, and γ is a solvent parameter.[7a] (1) is derived for spheres and assumes a dielectric continuum; there has been considerable discussion of how to implement improvements in it.[11] Nevertheless, application of (1) to **1**$^{0/+}$ gives a reasonable r_{eff} value. A solvent effect study on k_{ex} as a function of γ, which uses the assumption that k_{ex} changes in different solvents because λ_{out} changes but does not involve evaluation of the $(1/r_{eff} - 1/d_{eff})$ term, gave λ_{out} = 10.8–12.0 kcal/mol.[6,9] Using $r_{eff} = r_{av}$, the average radius of **1** calculated from the molecular volume of crystalline **1** gives a d_{eff} value of 5.17–5.37 Å, which is about the right size for **1** and **1**$^+$ coming into contact (see below). Contacts between species as complex in shape as **1** are not easy to consider. These molecules are not very close to being spheres, but the van der Waals surfaces of one component at the ET transition state (each **1** molecule between the shape of the two oxidation states) would fit inside a parallelopiped of dimensions 4.36 × 4.78 × 6.69 Å (relative dimensions 1.0 × 1.1 × 1.5). The short dimension is that along the bisector of the N–N bond in the plane of the lone pairs, and the nitrogens are significantly closer to one face of the parallelopiped, which we will call the front face, than the others because they are pyramidalized. The phenyl is roughly directed along the longest axis for **xPh-1** and toward the front face for **nPh-1**.

It has been exceptionally difficult to find out much about the relative orientation of the partners for intermolecular ET reactions, although as noted above, it has been assumed that compounds with π systems show much faster ET for orientations which have the π systems in face-to-face contact because such orientation is expected to lead to higher V values. Because both **1** and **1**$^+$ are pyramidalized at nitrogen, they might be able to achieve overlap of their NN(π) systems by approach of their less-hindered faces.

The first point we shall consider is whether r_{eff} and hence λ_{out} changes significantly when an exo-phenyl is substituted on **1**. Although the phenyl group (C_6H_5) is almost as large as one of the bicyclic alkyl groups flanking the nitrogen (C_6H_{10}), the k_{ex} for **xPh-1**$^{0/+}$ is 85% that of **1**$^{0/+}$. If the only reason k_{ex} changed were an increase in the solvent reorganization barrier, $\Delta\Delta G^{\ddagger}$ increases about 0.1 kcal/mol and λ_{out} about 0.4 kcal/mol. The exo-phenyls of the ET partners are directed well away from each other at the transition state if the face-to-face high π overlap orientation is important for self-ET of these molecules, and we do not see why d_{eff} would be affected significantly. Phenyl substitution presumably could only increase r_{eff},[12] but an increase in r_{eff} without increasing d_{eff} using (1) lowers λ_{out}: an increase in λ_{out} of 0.4 kcal/mol for **1**$^{0/+}$ would require a slight decrease in r_{eff} (from 3.93 to 3.89 Å). We conclude that the observed slight decrease in k_{eff} upon exo-phenyl substitution of **1** is not consistent with expectation if a face-to-face approach is assumed to be important for the ET transition state. The small effect observed upon k_{ex} seems to us to be consistent with the assumption that the phenyl is not involved in the ET reaction and also does not really lower the effective λ_{out} significantly. Its presence presumably blocks close approach of the components from relative orientations along the long axes, which do not contribute very much to the observed rate constant.

We suggest that the small effect on k_{ex} for **nPh-1**$^{0/+}$ (which is 55% that of **1**$^{0/+}$) makes it clear that self-ET for **1**$^{0/+}$ cannot be significantly proceeding through overlap of the NN(π) systems of the ET partners. We have modeled this approach semiquantitatively using AM1 calculations for various orientations of the more sym-

(11) Braunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3659.

(12) If the increase in r_{eff} for phenyl substitution is estimated using the X-ray structure volumes of **2** and **5**, the average molecular radius increases from 3.95 to 4.38 (11%), although the anisotropy of the substitution makes both the use of an average radius and its application using (1) appear unreasonable.

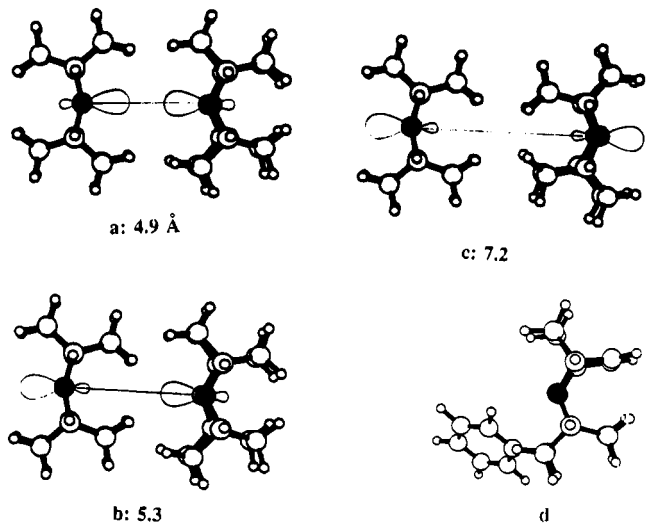
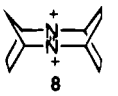


Figure 2. a–c: AM1-calculated $2^0,2^+$ pairs at distances for which ΔH_f starts to increase significantly as the NN bond centers distance decreases for approach along the axis bisecting the NN bonds in the plane of the lone pairs. **d** shows a similar view of **onPh-1**, demonstrating how the phenyl group blocks face approach.

metrical but structurally similar $\mathbf{2},\mathbf{2}^+$ pairs. The enthalpy starts to increase sharply as the distance between the N–N bond centers gets short enough for nonbonded steric interactions to become significant. Figure 2, parts a–c, show the pairs at distances for which the energy starts to increase for approach along the axis bisecting the N–N bond in the plane of the lone pair axes for face–face (4.9 Å), face–back (5.3 Å), and back–back (7.2 Å) relative orientations respectively. Face–face approach would have much higher NN(π) overlap because of the unequal extensions of the π orbitals for the pyramidalized nitrogens (shown only qualitatively on the drawings). Closest approach before serious nonbonded interaction occurs can be achieved with perpendicular N–N bonds in face–face approach (4.1 Å), but this should give a zero NN(π) overlap because of the nodal properties of the lone-pair orbitals. The importance of $\mathbf{nPh\text{-}1}^{0/+}$ for these considerations is that the phenyl clearly blocks the high π overlap face–face approach (see Figure 1 and Figure 2d) in the most stable **onPh-1** invertomer, which greatly predominates. Such approach could be achieved if both neutral and radical cations were in the less stable **inPh-1** conformation, but the **inPh-1** neutral invertomer lies so much higher in energy that if $\mathbf{nPh\text{-}1}^{0/+}$ required the high π-overlap transition state for self-ET, k_{ex} would have become too small to observe because an equilibrium endothermic by approximately 10 kcal/mol would have been incorporated into the ET rate constant expression. This is clearly not the case experimentally, which we suggest should be interpreted as indicating that ET from various relative approaches of the components contribute to the rate constant. This implies to us that most of the orientations involve transfer of the electron through the alkyl substituents. Approaches near the phenyl groups would force the dinitrogen units farther apart and would presumably be much slower, rationalizing a significant amount of the 45% rate decrease observed for endo-phenyl substitution.

Dication Formation and Decomposition. α-Phenyl substitution lowers $E^{\circ\prime}$ by 2.8 kcal/mol for $\mathbf{5}^{0/+}$ relative to $\mathbf{2}^{0/+}$, so some dication stabilizing effect is more powerful than the inductive destabilization from the phenyl group. AM1 calculations on $\mathbf{5}^{2+}$ get the benzylic bond to be substantially stretched, d(NN) = 1.59 Å, 0.079–0.085 Å longer than the other three N–C bonds and substantially longer than the 1.51 Å calculated for $\mathbf{2}^{2+}$ (for which the X-ray distance is 1.47 Å),[13] as well as significant charge delocalization into the α-phenyl group. $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ rather clearly undergo rapid PhC–N^+ cleavage because the C_α–N^+ bond is significantly weakened by the phenyl group. We have no evidence concerning the amount of solvent participation which might accompany this cleavage.

The β-phenyls cause substantial kinetic destabilization of the dications: the parent $\mathbf{2}^{2+}$ has a lifetime of $>10^4$ min at room temperature in CD_3CN [10] and the β-phenylated compounds less than a second, so $\Delta\Delta G^{\ddagger}$ for decomposition is $>\sim 8$ kcal/mol (assuming that the order of the reactions is the same). The CV results show that the second oxidation is only made 1.2–1.6 kcal/mol more difficult by the β-phenyls, suggesting that ground state destabilization toward C–N^+ cleavage is not a plausible reason for the reactivity of these dications. AM1 calculations give slight shortening of the C_α–N^+ distances in the phenylated bicyclic ring for $\mathbf{xPh\text{-}2}^{2+}$ and $\mathbf{nPh\text{-}2}^{2+}$ compared to $\mathbf{2}^{2+}$, so the bonds breaking are not calculated to be inherently weakened by β-phenyl substitution. A β-phenyl group is known to slow S_N1 solvolysis of several alkyl sulfonate derivatives,[14] but the diazabicycloalkyl dication unit is an exceptionally powerful leaving group. Dication **8** has been shown to alkylate acetonitrile by S_N2



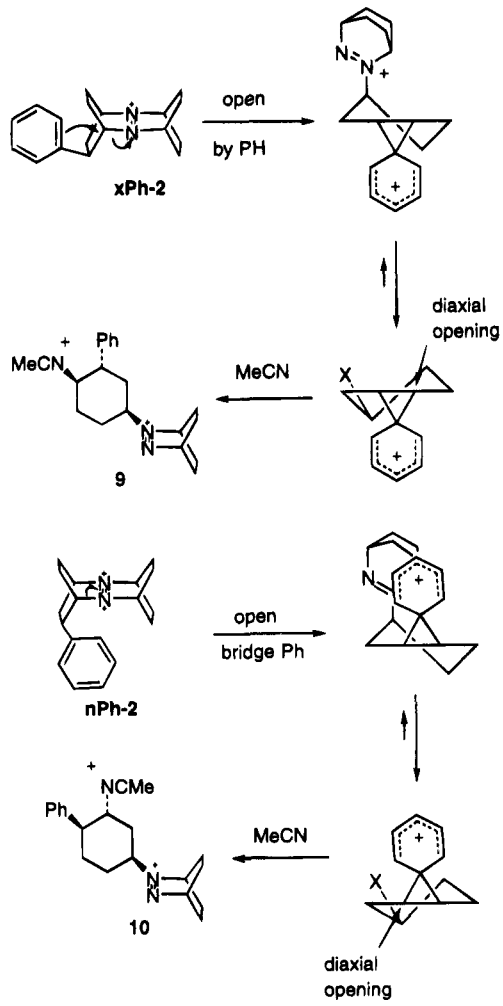
8

attack at the α position of its bicycloheptyl ring with a lower activation energy than does CH_3OSO_2F,[10] despite the position being attacked being hindered, which is known to significantly slow S_N2 reactions. We therefore suggest that it is reasonable to propose intramolecular nucleophilic attack at the bridgehead carbon by the phenyl of $\mathbf{xPh\text{-}2}^{2+}$ as a pathway for its decomposition. As indicated in Scheme 1, the phenonium ion thus formed would be expected to open predominately from one side because the phenonium ion ring reversal forms are very different in energy, and each should undergo diaxial opening. Nucleophilic cleavage of the C–N^+ bond by the phenyl substituent would therefore produce **9**, the trialkyldiazenium precursor of **7a** and **7b**. By the same argument, however, the cleavage of $\mathbf{nPh\text{-}2}^{2+}$ cannot be proceeding through its phenonium ion, because if it did form, cleavage would give predominately **10**, with the phenyl and nitrilium group switched in position, and would not produce the same products. Experimentally, $\mathbf{xPh\text{-}2}^{2+}$ and $\mathbf{nPh\text{-}2}^{2+}$ produce the same products. We suggest that despite the similar rates for their decomposition, $\mathbf{xPh\text{-}2}^{2+}$ and $\mathbf{nPh\text{-}2}^{2+}$ must be following different pathways, which only coincidentally have similar rate constants. The most reasonable pathway for decomposition of the endo compound seems to us to be electrophilic attack on the phenyl group by the powerfully electrophilic diazenium dication group, followed by cleavage as indicated in Scheme 2. Although the cleavage producing **11**

(13) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. *Tetrahedron* **1986**, *42*, 6101.

(14) Lancelot, C. J.; Cram, D. J.; Schleyer, P. R. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, Chapter 27, p 1347.

Scheme 1



initially looks like an unreasonable front-side displacement reaction, it really is not. The trisubstituted nitrogen lone pair can assist breaking the tetrasubstituted N^+–Ar bond at the same time as acetonitrile cleaves the bridgehead C–N^+ bond. **11** and **9** have different stereochemistry at the carbon bonded to the diazenium unit, but both would produce **7a** and **7b**. There is no experimental support for the mechanism written in Scheme 2 except that the same pair of alkylated hydrazonium products is produced by both diastereomers of the dication, which we find difficult to rationalize in other ways.

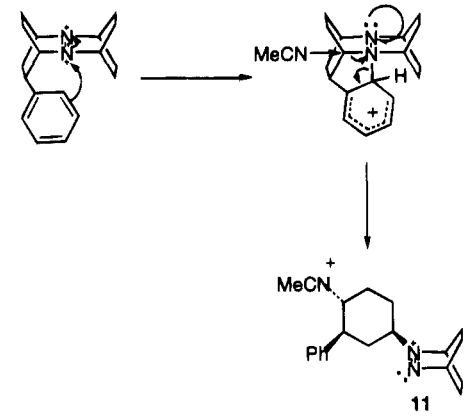
Experimental Section

General Methods and Instrumentation. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. CD_3CN was distilled from CaH_2. CH_3CN used for CV was fractionally distilled from B_2O_3 prior to use. Et_2O and tetrahydrofuran were fractionally distilled from purple sodium benzophenone ketyl under N_2 immediately prior to use, and ethyl acetate was distilled from calcium hydride and stored over 4A molecular sieves. The NMR, ESR, ENDOR, and electrochemical equipment used have been described previously.[10]

2-Phenyl-1,3-cyclohexadiene. A solution of 14.0 g 3-phenyl-2-cyclohexen-1-ol[15] (0.0804 mol) and Et_3N (20 mL, d =1.400, 0.276 mol) in 250 mL anhydrous CH_2ClCH_2Cl was stirred under N_2 for 5 min and 2,4-dinitrobenzenesulfenyl chloride (25.87 g, 96%, 0.105 mmol) was added. The mixture was quickly heated to reflux for 2.5 h under N_2 while stirring and

(15) Reich, H. J.; Wollowitz, S. *J. Am. Chem. Soc.* **1982**, *104*, 7051.

Scheme 2



then poured into 400 mL of pentane after cooling. After filtration and concentration, the residue was passed through silica gel with 5% Et_3N/pentane as an eluting solvent, giving 9.80 g (78.2% yield) of light yellow solid having NMR data consistent with the literature report.[15] The excess of sulfenyl chloride used in the literature[15] does not increase the yield.

8-Phenyl-4-methyl-2,4,6-triazatricyclo[5.2.2.$0^{2,6}$]undec-8-ene-3,5-dione (6). *tert*-Butyl hypochlorite (7.0 g, 0.0644 mol) was added dropwise at 0 °C under argon to a solution of 4-methylurazole (7.53g, 0.0654 mol) in 50 mL of ethyl acetate, producing 4-methyl-1,2,4-triazoline-3,5-dione (MTAD), and after stirring for 30 min at room temperature the solution was cooled below 0 °C while a solution of 2-phenyl-1,3-cyclohexadiene (10.0 g, 83%, 0.0531 mol) in 200 mL of ethyl acetate was added via cannula under argon. The resulting slightly pink solution was washed with saturated $NaHCO_3$ (200 mL) to neutralize HCl and destroy excess MTAD. The ethyl acetate layer was separated, washed with brine, and dried over $MgSO_4$. After filtration and concentration, **6** was obtained as 14.43 g of a white solid containing 7% biphenyl (93.8% yield): ^{1}H NMR ($CDCl_3$, 200.13 MHz) δ 1.65 (br, d, J = 10 Hz, 2H), 2.26 (br, d, J = 12 Hz, 2H), 2.96 (s, 3H), 4.98–5.01 (br m, 1H), 5.30 (br, s, 1H), 6.52 (dd, J = 6.0 2.0 Hz, 1H), 7.35–7.50 (m, 5H). This material was carried on without further purification.

8-*endo*- and 8-*exo*-Phenyl-4-methyl-2,4,6-triazatricyclo-[5.2.2.$0^{2,6}$]undecane-3,5-dione (A and B). A mixture of crude **6** (14.43 g, 93%, 0.0498 mol) in 250 mL of ethyl acetate and 5% Pd/C (400 mg) was hydrogenated at atmospheric pressure until H_2 uptake ceased. The catalyst was removed by filtration through Celite. After concentration the endo/exo mixture (ratio **A**:**B** ~ 6:1) was separated on flash silica gel by eluting with ether, giving 11.60 g endo (**A**) (R_f ~ 0.2) and 1.82 g exo (**B**) (R_f ~ 0.1) as colorless oils, combined yield 99%, which were carried on without further purification.

5-*endo*-Phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (nPh-3). A mixture of **A** (11.60 g, 0.0405 mol) and KOH (85%, 50.0 g) in isopropyl alcohol (600 mL, deaerated with Ar for 1 h) was refluxed for 12 h under N_2 and allowed to cool to room temperature, and excess KOH was filtered off. The filtrate was concentrated, the residue dissolved in 500 mL H_2O, and the pH adjusted to 2–3 by addition of concentrated HCl. A 5 N NH_4OH solution was added to readjust pH of the solution to ~5–6. This solution was then stirred while a 2 M $CuCl_2$ (50 mL) solution was added dropwise over 2 h, while the pH was continually maintained at ~5–6. The brick-red precipitate was collected, stirred with concentrated NH_4OH (200 mL) for 1 h, and extracted with CH_2Cl_2 (4 × 150 mL). The organic layer was washed with brine twice, dried over Mg_2SO_4, filtered, and concentrated. The product was purified by sublimation (room temperature, 0.01 mmHg) to give **nPh-3** as white crystals: mp 69–70 °C: 6.52 g, 86.4% yield; ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.35–1.43 (m, 3H), 1.69–1.77 (m, 2H), 2.18 (ddd, J = 13.5, 11.0, 2.0 Hz, 1H), 3.10 (dd, J = 11.0, 7.0 Hz, 1H), 5.26–5.28 (br, m, 1H), 5.33 (br, s, 1H), 7.05–7.06 (m, 2H), 7.16–7.19 (m, 1H), 7.23–7.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.56 MHz) δ_C 19.56, 22.77, 32.15, 42.11, 62.31, 65.90, 126.48,

127.28, 128.59, 144.21; HRMS calcd for $C_{12}H_{14}N_2$ 186.1157, found 186.1159.

5-*exo*-Phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (xPh-3). The same procedure used for **nPh-3** was used, employing **B** (1.82 g, 6.71 mmol) and KOH (85%, 10.0 g) in isopropyl alcohol (150 mL). The product was purified by sublimation (room temperature, 0.01 mm Hg), giving **xPh-3** as a yellow oil: 0.82 g, 65.7% yield; ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.04−1.09 (m, 1H), 1.34−1.39 (m, 1H), 1.62−1.77 (m, 3H), 1.84 (dd, J = 13.7, 6.7 Hz, 1H), 2.70−2.74 (m, 1H), 5.08 (br, s, 1H), 5.31 (br, s, 1H), 7.26−7.28 (m, 3H), 7.36−7.39 (2H); ^{13}C NMR ($CDCl_3$, 125.56 MHz) δ_C 15.21, 21.94, 25.77, 42.34, 81.84, 87.21, 126.88, 127.93, 128.76, 139.76; HRMS calcd for $C_{12}H_{14}N_2$ 186.1157, found 186.1159.

4-*endo*-Phenyl-2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]dodec-9-ene (nPh-1). A solution of protonated azo compound **nPh-3·HBF$_4$** (0.83 g, 3.03 mmol) and 1,3-cyclohexadiene (0.5 mL, 98%, d = 0.868, 5.30 mmol) in 75 mL of CH_3CN was stirred at 30 °C for 56 h under N_2. The volume of the solution was reduced to 30 mL, and ether (150 mL) was slowly added. The slightly yellow solid **nPh-1·HBF$_4$** was precipitated, collected, washed with ether (3 × 20 mL), and dried by pumping for 5 hours, giving 1.02 g, 95.3% yield. A mixture of **nPh-1·HBF$_4$** (300 mg, 0.847 mmol) and KOH powder (~5.0 g) in 100 mL ether was stirred in an ice bath for 5 h under argon, excess KOH was filtered off through Celite, and the filtrate was concentrated to give **nPh-1** as yellow oil which was recrystallized from pentane at −78 °C, although it melted upon warming to room temperature, giving 125.4 mg, 47.1% yield: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.21 (tt, J = 11.5, 3.0 Hz, 1H), 1.28 (tt, J = 11.5, 3.0 Hz, 1H), 1.56−1.60 (m, 3H), 1.84−2.18 (m, 5H), 2.56 (br, s, 1H), 2.82 (br, s, 1H), 2.87 (ddd, J = 11.5, 6.0, ~2.0 Hz, 1H), 3.15 (br, m, 1H), 3.40 (br, s, 1H), 6.65−6.51 (m, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.56 MHz) δ_C 24.65, 25.63, 26.64, 27.29, 38.66, 46.19, 52.48, 54.17, 54.81, 55.75, 125.72, 127.53, 129.20, 130.17, 130.96, 146.69; HRMS calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1781.

4-*exo*-Phenyl-2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]dodec-9-ene (xPh-1). A solution of protonated azo compound **xPh-3·HBF$_4$** (1.0 g, 3.70 mmol) and 1,3-cyclohexadiene (0.5 mL, 5.30 mmol) in 50 mL of CH_3CN was stirred at 45 °C for 2 days under N_2. The volume of the solution was reduced to 20 mL, and ether (150 mL) was slowly added. The slightly pink oil was collected, washed with ether (3 × 20 mL) and dried by pumping for 5 h, giving 0.9 g **xPh-1·HBF$_4$**, 69.8% yield. This material (260 mg, 0.742 mmol) and KOH powder (~5.0 g) in 70 mL ether were stirred in an ice bath for 5 h under Ar, excess KOH was filtered off through Celite, and the filtrate was concentrated to give a colorless oil which was recrystallized from pentane at −78 °C and melted upon warming to give 150.0 mg, 76.0% yield of **xPh-1** as a mixture of diastereomers **axPh-1** and **sxPh-1**: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ (**a**) 1.32−2.16 (complex, overlapped with **s**), 2.50 (br, t, 1H), 2.67 br, s, 1H), 2.84 (br, s, 1H), 2.87 (br, s, 1H), 3.70 (m, 1H, PhC-H), 6.55 (m, 2H), 7.19−7.32 (complex, overlapped with **s**); (**s**) 1.32−2.16 (complex, overlapped with **a**), 2.70 (br, s, 1H), 3.40 (br, s, 1H, PhC-H), 3.50 (br, s, 2H), 3.56 (br, s, 1H), 6.48 (m, 2H), 7.19−7.32 (complex, overlapped with **a**); ^{13}CNMR ($CDCl_3$, 125.56 MHz) δ_C (**a**) 22.44, 25.89, 28.22, 28.87, 30.13, 40.89, 51.91, 54.51 (2 × CH), 57.36, 125.75, 127.84, 128.28, 130.08; (**s**) 19.03, 25.89, 25.80, 26.18, 35.54, 45.14, 52.02, 54.46, 54.67, 57.45, 125.98, 128.16, 128.20, 130.35; HRMS calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1804.

4-*endo*-Phenyl-2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]dodecane (nPh-2). A mixture of **nPh-1·HBF$_4$** (300.0 mg, 0.847 mmol and 5% Rh/Al_2O_3 (~50 mg) in 100 mL of acetic acid was hydrogenated at atmospheric pressure. The hydrogenation was interrupted after 1 equiv of H_2 was taken up, the catalyst was filtered off through Celite, and the filtrate was concentrated to give ~350 mg of a yellow oil which was stirred with 5 g of KOH powder in ether (250 mL) for 5 h under Ar. After excess KOH was filtered off and concentration and recrystallization from pentane at −78 °C, **nPh-2** was obtained (~140 mg, 61.6% yield) as a slightly yellow solid: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.57 (td, J = 13.5, 5.5 Hz, 1H), 1.64−1.75 (m, 3H), 1.83 (tt, J = 13.5, 3.0 Hz, 1H), 2.11−2.21 (m, 5H), 2.27 (m, 1H), 2.40 (m, 1H), 2.50 (m, 1H), 2.56 (br, m, 1H), 2.58 (m, 1H), 2.63 (br, s, 1H), 2.76 (br, s, 1H), 2.91 (br, s, 1H), 2.95 (dd, J = 10.0, 6.5Hz, 1H), 7.27 (m, 3H), 7.56 (d, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.56 MHz) δ_C 22.77, 23.66, 25.04, 26.17, 26.52, 29.98, 30.51, 46.81, 50.84, 50.90, 52.46, 55.54, 125.73, 127.62, 128.80, 146.66; HRMS calcd for $C_{18}H_{24}N_2$ 268.1939, found 268.2949.

4-*exo*-Phenyl-2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-dodecane (xPh-2). A mixture of **nPh-1·HBF$_4$** (250 mg, 0.714 mmol) and 5% Rh/Al_2O_3 (~50 mg) in 100 mL of acetic acid was hydrogenated and worked up as for the endo isomer, giving ~250 mg of protonated hydrazine as a yellow oil. Deprotonation as for the endo isomer gave **xPh-2** as a yellow solid: mp 62−64 °C, 65 mg (34.0% yield); ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.64−1.76 (m, 6H), 1.99−2.03 (m, 2H), 2.26−2.40 (m, 5H), 2.58 (tt, J = 11.0, 4.0 Hz, 1H), 2.83 (br, s, 2H), 2.86 (br, s, 1H), 2.92 (br, s, 1H), 3.83−3.88 (m, 1H), 7.18−7.22 (m, 1H), 7.32 (br, s, 2H), 7.33 (br, s, 2H); ^{13}C NMR (CD_2Cl_2, 125.56 MHz) δ_C 20.28, 26.45, 27.06, 27.31, 28.50, 28.57, 33.30, 43.76, 51.23, 51.41, 51.85, 57.78, 126.06, 128.16, 128.52, 144.27; HRMS calcd for $C_{18}H_{24}N_2$ 268.1939, found 268.1927.

4-*endo*-Cyclohexyl-2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-dodecane (nCy-2). A mixture of **nPh-1·HBF$_4$** (280 mg, 0.80 mmol) and 5% Rh/Al_2O_3 (~75 mg) in 50 mL of acetic acid was hydrogenated at atmospheric pressure until hydrogen uptake ceased (~18 h). Workup as for **nPh-1** gave a yellow oil which solidified upon standing to give crude **nCy-2** as brown needles: 160 mg (73.1% yield); ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 1.4−2.8 (complex); ^{13}C NMR ($CDCl_3$, 125.56 MHz) δ_C 22.33, 23.53, 25.09, 26.02, 26.31, 26.35, 26.70, 30.21, 30.58, 30.72, 31.44, 36.54, 40.01, 46.98, 50.20, 50.28, 51.41, 52.22.

Dication NMR studies were carried out as previously described.[10] Decomposition of both nPh-2^{2+} and xPh-2^{2+} gave the same pair of products with similar carbon shifts (analyzed after addition of D_2O to complete hydrolysis of the acetonitrile trapping adduct) signals, and DEPT-135 experiments allowed assignments to carbon types: 2 × C_q (177.7, 141.2; 177.3, 141.17; C=O and C=N$^+$ respectively[10]), 4 × CH (65.9, 55.5$_3$, 55.4$_8$, 51.7; 66.1, 56.1, 53.5, 52.5), 7 × CH_2 (38.7, 25.9, 25.5, 25.0, 24.5$_1$, 22.2, 21.2$_2$; 39.9, 26.0, 25.5, 24.5$_4$, 24.4, 22.5, 21.2$_1$). The CD_3 carbons of acetonitrile trapping products are too broad to be detected under our conditions.[10]

Crystal Structure of nPh-1$^+$PF$_6$. Neutral **nPh-1** was oxidized with $NOPF_6$, and the structure was determined at 293(2) K using a 0.4 × 0.4 × 0.5 mm crystal grown by vapor diffusion of ether into acetonitrile, on a Siemens P3f diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54178 Å), Wyckoff scan type, θ range 4.38 to 56.99°. The solution of the structure with direct methods used program SHELXS-86 and the refinement used SHELXL-92, which refines on F^2 values.[16] **nPh-1$^+$PF$_6$** ($C_{18}H_{22}F_6N_2P$, fw 411.35) crystals are monoclinic: space group $P2_1/n$; unit cell dimensions a = 10.695(2), b = 10.6907(13), c = 1.6585(2) Å; β = 108.154(10)°; volume 1801.9(4) Å^3; Z = 4; density (calcd) = 1.516 mg/m^3; absorption coefficient = 1.964 mm^{-1}; reflections collected = 2538, independent reflections 2388 [R(int) = 0.0313], data = 2386; restraints = 1; parameters = 256; goodness-of-fit on F^2 = 1.140; final R indices $R1/wR2$ = 0.0934/0.2661; R indices (all data) $R1$/w$R2$ = 0.1048, 0.2922; extinction coefficient 0.001(1); largest difference peak/hole = 0.820/−0.757 e A^{-3}. The PF_6 group is highly disordered, and the disorder model used 14 F atoms around a single P position.

Self-exchange rate data in CD_3CN were measured and analyzed as previously described.[17] **For nPh-1$^{0/+}$**: (run 1)

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(17) (a) Nelsen, S. F.; Kim., Y.; Blackstock, S. C. *J. Am. Chem. Soc.* **1989**, *111*, 2045. (b) Nelsen, S. F.; Wang, Y.; Ramm, M. T.; Accola, M. A.; Pladziewicz, J. R. *J. Phys. Chem.* **1992**, *96*, 10654. (c) Phelps, D. K.; Ramm, M. T.; Wang, Y.; Nelsen, S. F.; Weaver, M. J. *J. Phys. Chem.*, **1993**, *97*, 181.

[**nPh-1**]^0 = 0.172 M, [**nPh-1**]$^+$ = 8.72 mM [values of T (K), $\Delta\nu$ (Hz), k_{ex} (M^{-1} s^{-1})]; 269.7, 3.1, 1117; 277.7, 5.8, 2089; 282.3, 7.5, 2702; 288.0, 10.7, 3855; 292.7, 14.2, 5116; 293.7, 14.4, 5118; 297.8, 19.0, 6845; 303.2, 23.9, 8611; 308.1, 29.0, 10448; (run 2) [**nPh-1**]^0 = 0.177 M, [**nPh-1**]$^+$ = 7.60 mM; 268.1, 2.6, 1075; 276.4, 4.8, 1984; 280.8, 6.3, 2604; 284.4, 7.9, 3266; 288.0, 9.3, 3844; 292.7, 11.3, 4671; 294.0, 12.0, 4960; 296.0, 13.2, 5456; 299.1, 15.9, 6573. These data give k_{ex} (25 °C) = 6.56 × 10^3 (M^{-1} s^{-1}); $\Delta G^{\ddagger} = 12.2_5 \pm 0.0_2$ (kcal/mol); $\Delta H^{\ddagger} = 8.8 \pm 0.4$ (kcal/mol); $\Delta S^{\ddagger} = -11.6 \pm 1.2$ (eu). **For xPh-1$^{0/+}$**: (run 1) [**xPh-1**]^0 = 0.112 M, [**xPh-1**]$^+$ = 5.4 mM; 276.9, 6.3, 3665; 280.4, 7.6, 4422; 284.3, 9.7, 5643; 287.7, 11.5, 6690; 292.0, 14.5, 8436; 292.5, 14.7, 8552; 295.8, 19.0, 11054; 299.5, 21.6, 12566; (run 2) [**xPh-1**]^0 = 0.220 M, [**xPh-1**]$^+$ = 11.4 mM; 274.8, 13.1, 3610; 279.1, 15.4, 4244; 284.2, 21.3, 5870; 290.0, 28.6, 7882; 293.2, 31.5, 8681; 294.9, 34.8, 9590; 298.6, 40.1, 11051. These data give k_{ex} (25 °C) = 11.4 × 10^3 (M^{-1} s^{-1}); $\Delta G^{\ddagger} = 11.9 \pm 0.02$ (kcal/mol); $\Delta H^{\ddagger} = 7.3 \pm 0.5$ (kcal/mol); $\Delta S^{\ddagger} = -13.6 \pm 1.2$ (eu).

Calculations. Molecular mechanics calculations used Allinger's MM2 method,[18] and minima on the energy surface were located using Saunders's VAXMOL5 search program,[19] modified by Peter A. Petillo to allow use of a VAX 8650 to run the calculations employing initial structures generated[20] from AM1 calculations.[21] The lower steric energy MM2 structures were used as input for AM1 calculations, which used Clark's VAMP programs on a Stardent 3000 or VAX 8650 computer.[22]

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Supplementary Material Available: Copies of ^{1}H NMR spectra of **nPh-3**, **xPh-3**, **nPh-1**, **xPh-1**, **nPh-2**, **xPh-2**, and **nCy-2** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and may be ordered from the ACS; see any current masthead page for ordering information.

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(20) We used program NEWSEL, supplied by Peter A. Petillo.

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

(22) VAMP 5.0, modified for use on a Stardent computer was supplied by Timothy Clark: Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. *VAMP 5.0*, Oxford Molecular: Oxford, 1994.