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

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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·NO3)− [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 hexafluoroantiminate (Hy1NA·SbF6−); 2-tert-butyl-3-(2-naphthyl)-2,3-diazabicyclo[2.2.2]octane radical cation hexafluoroantiminate (Hy2NA·SbF6−); 1,5-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2][oct-3-yl]naphthalene dication bis(tetraphenylborate) (Hy23NA2−(Ph4B)2); and 2,7-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2][oct-3-yl]naphthalene dication bis(hexafluoroantiminate) (Hy27NA2−(SbF6−)2CH3CN) 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 (θ(0)) in the range 122–130°, are compared with those for tetraalkyldihydrazines that have θ(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 intercalation radical cations.

Charge-localized intercalation compounds (Robin-Day Class II systems)1 may be symbolized as IM−B−Mn+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, ∆G° for electron-transfer is zero. The intercalation 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 intercalation compounds to test the classical Marcus–Hush theory assumption that the electron-transfer barrier could be accurately predicted from the intercalation band of Class II compounds, using the energy of the band maximum as Marcus’s reorganization energy λ and the Hush eq 1 for evaluation of the off-diagonal matrix element, Hab, where μ12 is the transition dipole moment, usually evaluated using Hush’s Gaussian approximation,6,7 and ∆μ is the change in dipole moment, estimated as e dab, where dab 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 intercalation radical cations, although the range of rate constants that can be measured is rather narrow, about a factor of 10 centered at about 108 M−1 s−1, so most intercalation compounds have rate constants that are either too fast or too slow to measure.9 The parent Hy24PH+ 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 Hy23DU+; because Hab is, as expected, approximately proportional to cos φ. 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 intercalation 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 NCCH bond distances, the pyramidality at nitrogen, and the twist angles θ and φ at the hydrazine unit. Here we use Δαav, the difference of the average of the bond angles at nitrogen from the 120° for planarity as our measure

Hab = (μ12/Δμ)λ

(1)
of pyramidality because \( \Delta_{\alpha_{av}} \) is nearly linear with fractional s orbital character and hence lone pair ionization potential all the way from planarity to being bent past tetrahedral (\( \Delta_{\alpha_{av}} > 10.5^\circ \)). 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 \( \theta \) and \( \phi \) from the structural data.

\[
\begin{align*}
\alpha & = 124.1(7) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\beta & = 8.0(1) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\phi & = -37.5(2) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\theta & = 124.1(1) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\phi & = 32.6(3) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\theta & = 121.6(3) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu}) \\
\phi & = 107.3(3) \quad \Delta_{\alpha_{av}}(N_{tBu}) \quad \Delta_{\alpha_{av}}(N_{Bu})
\end{align*}
\]

In this work, we compare structural data for the neutral and radical cation oxidation levels of the \( \alpha \) (1) and \( \beta \) (2)-Hy-substituted naphthalenes, as well 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 anthracene 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 Hy\(_2\)D\(_U^0\), which results in poor quality for the structure (so it is not included in the discussion here). Although we had obtained a structure for Hy\(_2\)D\(_U^0\), it was too disordered to be useful here and is not reported. However, the structure of Hy\(_2\)D\(_U^+\) is reported because it gives a third oxidized Hy unit for comparison with that of Hy\(_2\)D\(_U^0\) (see Table 1).

The \( \text{Hy}^0 \) and \( \text{Hy}^+ \) units of HyPH systems are compared in Tables 2 and 3, respectively. The very short lifetime of \( \text{Hy}^\text{PH}^+ \) precludes obtaining data exactly analogous to that of Table 1 for Hy\(_2\)D\(_U^+\), but if we compare the available data it is clear that the methyls do indeed increase \( \phi \) for Hy\(_0^+\) by about 18°, which leads to the significant difference in \( H_{ab} \) that is observed (the \( \cos \phi_1 \) values are 0.67 for Hy\(_0^+\) and 0.40 for Hy\(_2\)D\(_U^0\)).

### Table 1. Hy\(_+^+\) Units of HyDU Systems

<table>
<thead>
<tr>
<th>HyDU(_+^+) Units of HyDU Systems</th>
<th>HyDU(_+^+) (1+ unit)</th>
<th>HyDU(_+^0) (1+ unit)</th>
<th>HyDU(_+^+) (1+ unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(NN), Å</td>
<td>1.354(12)</td>
<td>1.346(2)</td>
<td>1.356(3)</td>
</tr>
<tr>
<td>d(NC(_tBu)), Å</td>
<td>1.490(13)</td>
<td>1.455(3)</td>
<td>1.443(3)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{tBu}) ) °</td>
<td>1.53(8)</td>
<td>1.0(2)</td>
<td>1.5(3)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{Bu}) ) °</td>
<td>1.23(8)</td>
<td>1.4(2)</td>
<td>1.5(3)</td>
</tr>
<tr>
<td>( \phi ) °</td>
<td>63.8(4) (14)</td>
<td>(156.6(2)</td>
<td>156.1(3)</td>
</tr>
<tr>
<td>( \theta ) °</td>
<td>45.14(14)</td>
<td>(144.8(3)</td>
<td>(148.0(4)</td>
</tr>
</tbody>
</table>

Table 2. Hy\(_0^0\) Units of HyPH Systems

<table>
<thead>
<tr>
<th>HyPH(_0^0) Units of HyPH Systems</th>
<th>HyPH(_0^0) (1+ unit)</th>
<th>HyPH(_0^+) (1+ unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(NN), Å</td>
<td>1.355(2)</td>
<td>1.351(2)</td>
</tr>
<tr>
<td>d(NC(_tBu)), Å</td>
<td>1.440(2)</td>
<td>1.443(3)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{tBu}) ) °</td>
<td>0.9(1)</td>
<td>0.7(2)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{Bu}) ) °</td>
<td>3.0(1)</td>
<td>2.8(2)</td>
</tr>
<tr>
<td>( \phi ) °</td>
<td>(159.2(2)</td>
<td>53.1(3)</td>
</tr>
<tr>
<td>( \theta ) °</td>
<td>(114.6(2)</td>
<td>152.8(3)</td>
</tr>
<tr>
<td>( \phi ) °</td>
<td>(153.6(2)</td>
<td>57.5(3)</td>
</tr>
</tbody>
</table>

Table 3. Hy\(_+^+\) Units of HyPH Systems

<table>
<thead>
<tr>
<th>HyPH(_+^+) Units of HyPH Systems</th>
<th>HyPH(_+^+) (1+ unit)</th>
<th>HyPH(_+^0) (1+ unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(NN), Å</td>
<td>1.461(2)</td>
<td>1.454(3)</td>
</tr>
<tr>
<td>d(NC(_tBu)), Å</td>
<td>1.440(2)</td>
<td>1.426(3)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{tBu}) ) °</td>
<td>6.9(1)</td>
<td>6.4(2)</td>
</tr>
<tr>
<td>( \Delta_{\alpha_{av}}(N_{Bu}) ) °</td>
<td>8.0(1)</td>
<td>7.3(2)</td>
</tr>
<tr>
<td>( \phi ) °</td>
<td>-37.5(2)</td>
<td>-32.6(3)</td>
</tr>
<tr>
<td>( \theta ) °</td>
<td>124.1(1) (13)</td>
<td>121.6(3)</td>
</tr>
<tr>
<td>( \phi ) °</td>
<td>-105.8(1)</td>
<td>-107.3(3)</td>
</tr>
</tbody>
</table>

* Ref 10. 

Figure 1. Molecular drawing (50% probability ellipsoids) of Hy\(_NA^+\) (SbF\(_6^-\)) (30% probability ellipsoids).

Because we have obtained crystal structures for both 0 and +1 oxidation states of Hy\(_NA^+\) and Hy\(_NA^0\) (for molecular drawings of the radical cations, see Figures 1 and 2) as well as Hy\(_NA^0\), 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 \( \theta(0) \) in a
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 \( \text{Hy}^+ \) groups arises from the 2+ oxidation level of disubstituted compounds, which contain two \( \text{Hy}^+ \) groups. Crystal structures are only available for the 1,5-bridged \( \alpha \)-substituted (Figure 3) and 2,7-bridged \( \alpha \)-substituted naphthalene-bridged monohydrazine radical cations with those of the dihydrazine. 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 \( \text{Hy}^2 \)−Ar−\( \text{Hy}^0 \) in the dication, and the dicaticonic oxidation state of \( \text{Hy}^+ \) is extremely unstable, resulting in de-tert-butylation.14 Two nonidentical \( \text{Hy}^+ \) units are present in the crystal of \( \text{Hy}^2 \)−\( \text{Hy}^0 \)−\( \text{Ph}_4 \text{B} \)−(SbF$_6$)$_2$·CH$_3$CN, leading to the two sets of parameters in Table 6. The structure of \( \text{Hy}^2 \)−\( \text{Hy}^0 \)−\( \text{Ph}_4 \text{B} \)−(SbF$_6$)$_2$·CH$_3$CN 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 oxidation level crystal structures are available, which were all tetraalkylhydrazines.
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 tBu, making $\theta(0)$ near 126°, and $\theta(+) = 149\text{°}-157\text{°}$, corresponding to pyramidalities at N between 14 and 30% of the way from planar to tetrahedral. The $\Delta \theta(\text{NN})$ values for these compounds of intermediate $\theta$ value are 7.2 $\pm$ 0.6°, clearly intermediate between the 10.2 $\pm$ 0.4° range found for $\theta(0) = 180\text{°}$ hydrazines and 10.9 $\pm$ 1.0 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 $\theta(0)$ $\sim 90\text{°}$ acyclic compounds that have the smallest (under 0.6 eV)$^{\text{(8)}}$ $\theta(0)$ is the most important factor in determining the size of the Marcus reorganization energy $\lambda$, 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.$^{\text{(8)}}$

Conclusions

The changes in NN distance and the pyramidality 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 $\pm$ 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$_3^-$, Hy$_4$NA$^+$SbF$_6^-$, Hy$_4$NA$^+$SbF$_6^-$, Hy$_4$NA$^+$SbF$_6^-$, Hy$_4$NA$^+$SbF$_6^-$, and Hy$_4$NA$^+$SbF$_6^-$, CH$_3$CN. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(8) For discussion of other ways of getting $\Delta \theta(\text{NN})$, see Nelsen, S. F.; Newton, M. D. J. Phys. Chem. A 2000, 104, 10023–10031.