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(16) The ligand field bands for Ru(II) pyridine- and pyrazine-type complexes are obscured by the intense MLCT bands. In terms of σ basicity, py-X is more similar to NH_3 than to the nitriles.
(17) Confirming work on Ru(II)–Rh(III) dimers with other bridging ligands is currently under study both by photochemistry and cyclic voltammetry.
(18) Since calculations of the excited states give only estimated energies, we cannot eliminate the possibility of the energy transfer reaction occurring between MLCT(Ru(II)) and ^{3}LF(Rh(III)). We are currently studying bridging ligands where the MLCT maximum is at higher energy (like 4-CNpy) but the bridge is symmetrical (like pyz) to try and clarify this interpretation.

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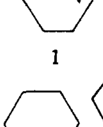
1,6-Diazabicyclo[4.4.4]tetradecane and Its Oxidized Ions

Sir:

The chemistry of medium-ring bridged bicyclic compounds is largely unexplored. While these molecules may possess many interesting properties, their uniqueness lies in the opportunities for intrabridgehead interactions. Repulsive as well as attractive interactions can be studied in these triple constrained[1] systems. In complementary fashion, the unique structural feature of propellanes is the bond common to all three rings. In particular, cleavage of this bond is an advantageous strategy for the synthesis of bridged medium-ring bicyclic compounds.[2] We have made 1,6-diazabicyclo[4.4.4]tetradecane[3] (**1**) by this route and report on its properties and those of the oxidized ions derived from it. Its protonated ions are discussed in the following communication.[4]

Reaction of 1,6-diazabicyclo[4.4.0]decane[5] with excess 1,4-dibromobutane at 100 °C furnishes the salt **4**.[6] Cyclization occurs on treatment with $AgBF_4$ in 40% aqueous HBF_4 and **3**, mp 221–225 °C dec,[6] is precipitated by the addition of EtOH. Reduction of **3** to **1** is conveniently accomplished by addition of **3** to Na/NH_3 solution, quenching with MeOH, evaporation of solvents and sublimation of **1**, mp 170–175 °C (sealed tube),[6] from the residue (84% yield). The diamine **1** and dication salt **3** react stoichiometrically in CH_3CN to give **2**, isolated by evaporation as a dark red crystalline solid.[6] This simple electron-transfer reaction is remarkably slow (k_2 = 0.2 L mol^{-1} s^{-1} at 25 °C); the rate is not much changed by the addition of 10% H_2O, but is accelerated by I^-. Study of the $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3}$ system by cyclic voltammetry[7] is complicated by distended waves due to slow electron transfers especially for the $\mathbf{2} \rightleftharpoons \mathbf{3}$ couple. $E°$ for the $\mathbf{1} \rightleftharpoons \mathbf{2}$ couple is −0.1 V vs. SCE, which demonstrates the extreme ease of oxidation of **1**. These slow electron transfers may in part reflect poor overlap of the donor and acceptor orbitals.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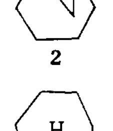
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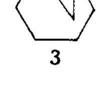
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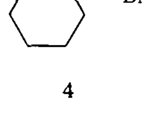
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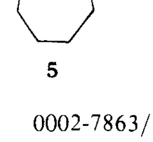
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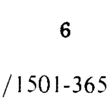
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It is helpful to discuss the structures of **1**, **2**, and **3** in reverse order. The dication **3** is quite clearly a [4.4.4]propellane, with an all-chair, D_3, structure. The ^{1}H NMR spectrum at room temperature shows nonequivalent α-CH protons, equatorial δ 3.86 and axial δ 5.02. Coalescence occurs at +90 °C, so that the ring-flipping barrier is similar to that of the parent hydrocarbon.[8] The ^{13}C spectrum shows two resonances at −60.7 and −15.8 ppm at all temperatures. The dication salt **3** is indefinitely stable in acidic aqueous solution.

Treatment of **3** with 1 equv of aqueous K_2CO_3 gives a salt $C_{12}H_{23}N_2BF_4$, which is reducible by $LiAlH_4$ in THF to form **1**. This salt shows 11 ^{13}C NMR signals (one coincidence) with a unique CH group absorbing at −100.5 ppm and δ 5.42 in ^{1}H NMR. On the basis of the position of these signals we assign the tricyclic structure **5** to this salt, rather than the bicyclic immonium structure.

The radical cation salt, **2**, *is indefinitely stable as a solid and is stable for months in organic or aqueous solution in the absence of base.* In butyronitrile solution the ESR spectrum is a simple 15-line multiplet, unchanged between −100 and +100 °C. The intensities fit a pattern derived from hyperfine coupling to two equivalent nitrogens (a_N = 34.4 G) and six equivalent protons (a_H = 17.2 G), with a line width of 2 G. The ENDOR spectrum in CH_2Cl_2[9] shows four hydrogen hyperfine couplings of 17.8, 0.79, 0.29, and 0.08 G. Thus real or time-averaged D_3 or C_{3h} symmetry is indicated. The nitrogen hyperfine coupling is remarkably large, much bigger than in the 1,5-diazabicyclo[3.3.3]undecane radical cation **6** (14.7 G).[2b] We believe this indicates strong inward pyramidalization of the nitrogens in **2** and feel that a D_3 structure with chair-like C_4N_2 rings is probable, but with a stretched N–N distance relative to **3**.[10] The single large hydrogen splitting would then be due to the α proton equatorial to the C_4N_2 ring. The differences in nitrogen geometry between **2** and its bicyclo[3.3.3]undecane analogues[2b,11] are those which might be anticipated from the structural constraints of the hydrocarbon bridges and suggest a remarkable flexibility for the N–N interaction ("3-electron σ bond"). Despite these differences the electronic spectrum of **2** is very similar to the of **6**, consisting of one strong (oscillator strength, 0.1) and extremely broad absorption, λ_{max} 480 nm, presumably due to an $n_+(\uparrow\downarrow)$-$n_-(\uparrow) \rightarrow n_+(\uparrow)$-$n_-(\uparrow)$ transition.

Diamine **1** is a volatile waxy solid, notably insoluble in water and forming only weak hydrogen bonds (IR in $CDCl_3$).[12] It shows unusually strong UV absorption at λ_{max} 233 nm (ϵ 8100) with a shoulder at 261 nm (ϵ 3800) in isooctane, which either indicates flattened nitrogens, cf. manxine,[13] or some N–N interaction, or both. Out,out- or out,in-pyramidalization of the nitrogens in **1** seems improbable on this evidence. The ^{13}C NMR spectrum shows only two resonances down to −140 °C at −55.0 and −30.9 ppm, but in ^{1}H NMR nonequivalent hydrogens on the α-CH_2 groups are seen below −50 °C, indicating interconversion of D_3 or C_{3h} structures. A D_3 structure with slightly inwardly pyramidalized nitrogens and a longer N–N distance than **2** (or **3**) seems most likely. After exposure to air for 1–2 h, **1** forms an amorphous white material, insoluble in all solvents, even acids.

The isolation of all three oxidation states **1**, **2**, and **3** of the 1,6-diazabicyclo[4.4.4]tetradecane system as stable materials demonstrates the potentialities of these triply constrained

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medium-ring systems for the creation of simple but unusual bonding situations.

References and Notes

(1) A chemical reaction or structural interaction (e.g., hydrogen bonding) may be studied in unconstrained (intermolecular, i) or singly (intramolecular, ii), doubly (transannular, iii,) or triply constrained (intrabridgehead, iv) systems.

$Me_2N^{+}—H:NMe_2$

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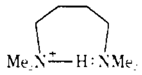

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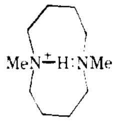

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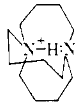

iv

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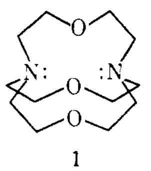
Inside- and Outside-Protonated Ions from 1,6-Diazabicyclo[4.4.4]tetradecane

Sir:

Inside, outside isomerism[1] and encapsulation[2] are two interesting features of the chemistry of macrobicyclic compounds, and it is important to establish size limitations for these phenomena. In particular, what is the smallest system which can encapsulate the smallest ion, the proton? The smallest known cryptand, **1**, can encapsulate two protons or one lithium ion.[4] We report that 1,6-diazabicyclo[4.4.4]tetradecane (**2**)[3] can form an inside-monoprotonated ion, but that the proton can neither be inserted nor removed by simple proton-transfer reactions.



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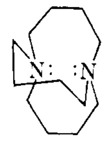

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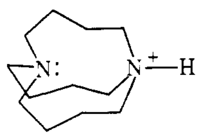

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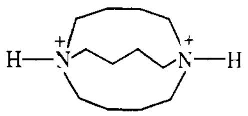

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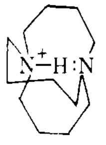

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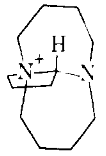

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Outside protonation of **2** is characterized by $pK_{a1} = 6.5 \pm 0.5$,[5] $pK_{a2} = -3.25$.[6] These values are about 4 and 10 log units lower respectively than those for normal diamines with comparable N–N distances, and surely reflect the strain introduced by outward pyramidalization of the nitrogens of **2**.[7] 1,5-Diazabicyclo[3.3.3]undecane has pK_a values of 10.3 and 6.5,[8] while those for 1,4-diazabicyclo[2.2.2]octane are 8.82 and 2.97.[9] The salt **3**·BF_4[10] has ^{13}C resonances at −58.0, −51.4, −27.3, and −23.5 ppm (D_2O solution) and ^1H absorption ($CDCl_3$ solution) at δ 7.9 (NH), 3.54 (CH_2-N^+H, $J_{HCNH} = 5$ Hz), 2.62 (CH_2-N), and 2.00 and 1.85 (β-CH_2 groups). Slow proton transfer between equivalent nitrogens of a monoprotonated diamine is unusual, but reflects the large ΔpK_a for **2**. The ion **4** in HSO_3F solution has ^{13}C resonances at −52.2 and −20.3 ppm (unchanged at −90 °C) and ^1H absorption at δ 7.15 (NH), 3.58, and 2.43. Methylene group protons become nonequivalent below −70 °C. A C_{3h} or, more likely, D_3 structure for **4** is suggested.

Inside protonation of **2** might be thermodynamically favorable but kinetically difficult, based on analogy with **1**[3] and with 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene.[11] In practice we cannot *insert* a solvent proton into **2** at all. Thus heating **2** with an equivalent of *p*-toluenesulfonic acid in H_2O at 200 °C does not lead to **5**. However, when solutions of **2** in moderately strongly acidic media (40–70% H_2SO_4, CF_3SO_3H in CH_3CN, $Et_2OH^+BF_4^-$ in CH_2Cl_2) are left for a week or more, the NMR spectrum due to the $\mathbf{3} \rightleftharpoons \mathbf{4}$ equilibrium is replaced by that of **5**, accompanied by variable amounts of **6**.[4] The inside protonated ion, isolated as **5** BF_4,[10] was recognized from the extremely deshielded NH proton at δ 17.4 and the inertness of this proton to exchange, even after 3 h at 100 °C in 1 M NaOD/D_2O. Ion **5** shows ^{13}C absorption at −52.0 and −26.2 ppm (unchanged at −30 °C) and ^1H absorption at δ 2.70 and 1.92 for α- and β-CH_2. The protons of these CH_2 groups are nonequivalent at −30 °C, and a D_3 conformation for **5** seems likely. IR absorption for N—H···N is at 1400 cm^{-1} (broad).

The inside protonated ion is extraordinarily inert to deprotonation or further protonation. Deprotonation does not occur under conditions where n-Bu_4N^+ undergoes Hoffmann elimination, e.g., 2 h in $NaNH_2/NH_3$ at −33 °C or dry thermolysis of hydroxide salts at 160° for 0.5 h. Formation of an inside, outside diprotonated ion occurs in 1:1 HSO_3F/SbF_5 but not in HSO_3F alone. This dication has ^1H NMR absorptions at δ 7.30 (N-H), 3.9 and 3.60 (α-CH_2), and 2.45 (β-CH_2). Only one NH is observed, but there are no absorptions at very low field, indicating disruption of the N—H···N bond.

The reactions which produce **5** are most unusual and are not simple proton transfers. We have made the following observations for reactions in 40–70% aqueous H_2SO_4. (i) In 60–70% H_2SO_4, **5** is the only product, but in more dilute acid it is accompanied by irreproducibly variable amounts of **6** (up to ~1:1 **5**:**6** ratio). Reaction rates are generally fastest at ~50% acid but are also quite irreproducible. (ii) Reactions are dramati-

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