or pyrolysis, and in investigating the structures of potential alkanol dehydration catalysts.

Acknowledgment. This work was supported in part by the National Science Foundation Solid-State Chemistry Program (Grant DMR 83-11339), by the Experimental and Theoretical Geochemistry Program (Grant EAR 84-08421), and by the Mobil Foundation.

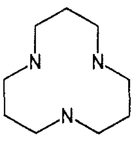
Unusually Basic, Rapidly Protonated Bicyclic Triamine: 11-Methylene-1,5,9-triazabicyclo[7.3.3]pentadecane

Thomas W. Bell,* Heung-Jin Choi, and William Harte

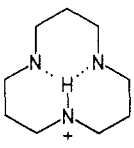
Department of Chemistry, State University of New York
Stony Brook, New York 11794-3400

Received July 21, 1986

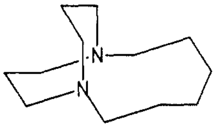
Macrocyclic polyamines have proven to be useful cation receptors in which multiple pairs of nonbonded electrons stabilize a charged guest.[1-5] The high basicity of 1,5,9-triazacyclododecane (**1**)[6] suggests that when three nitrogen atoms are linked in pairs by three-atom bridges the monocation may be stabilized by a hydrogen bonding network, as shown in **1**·H$^+$. Nitrogen lone pairs are even more rigidly organized in diazabicyclo[*n*.3.3]alkanes for which *n* > 4. For example, Alder et al. have shown that in 1,8-diazabicyclo[6.3.3]tetradecane (**2**) the internally protonated species is very stable, but it forms extremely slowly by an intramolecular redox process, apparently because the protonation site is shielded from external attack.[7] In this paper we describe a combination of the structural features of **1** and **2** that leads to a potent proton receptor in which an exposed basic site provides a pathway for rapid protonation.



1



1·H$^+$



2

The target system of this study, triamine **3**, contains a 2-methylene-1,3-propanediyl bridge, which serves as an easily introduced conformational marker and as a potential site for further functionalization. Thus, 1,5,9-triazacyclododecane[8] and 3-iodo-2-(iodomethyl)-1-propene[9] were added simultaneously to K_2CO_3 in isopropyl alcohol (Figure 1). The high basicity and lipophilicity of the product became apparent when the pH of the reaction mixture was adjusted to 10–11 by using aqueous NaOH and chloroform was used to extract the product. Hydriodic acid was sequestered from this basic, iodide-containing solution, for recrystallization of the chloroform extract afforded 83% of pure **3**·HI[10] as colorless prisms, mp 199–200 °C. Deprotonation may be accomplished by repeatedly washing a chloroform solution of **3**·HI with 2 N aqueous NaOH or by distillation of the salt from powdered KOH. For comparison purposes, the *N*-methyl derivative **4**[10] was prepared by Eschweiler–Clarke methylation of **3**.[10]

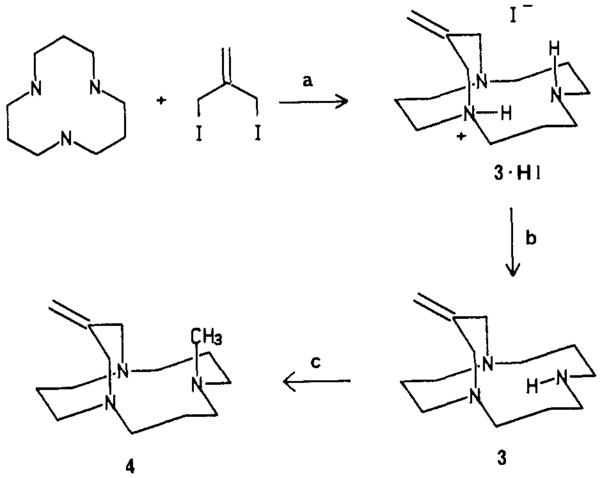


Figure 1. Synthesis of 11-methylene-1,5,9-triazabicyclo[7.3.3.]pentadecane (**3**) and *N*-methyl derivative **4**: (a) K_2CO_3, isopropyl alcohol, reflux (83%); (b) KOH, distillation at 110 °C, 1 mmHg (74% overall); (c) HCO_2H, CH_2O, H_2O, 120 °C, 6 h; distillation at 100–110 °C, 0.3 mmHg (60%).

Single-crystal X-ray diffraction[11] and solution NMR studies of **3**·HI confirm the presence of an internal hydrogen bonded network. In the crystal conformation of **3**·HI, the smaller bridges are oriented anti to the large bridge, which adopts a chairlike conformation. One N–H proton was located in an "axial" orientation, whereas the internal proton could not be located by difference Fourier maps. The nitrogen atoms form an approximate equilateral triangle with an average interatomic distance of 2.75 Å. The internal proton, which was fixed at a bridgehead nitrogen for calculation purposes, probably exchanges rapidly between the three sites. Proton NMR spectroscopy,[12] in combination with various two-dimensional NMR methods (COSY, CSCM, and NOESY), indicates that **3**·HI adopts a very similar conformation in $CDCl_3$ solution. As expected from the crystal conformation of **3**·HI, the exocyclic methylene protons (H_a, δ 5.00) are significantly coupled only to the out-of-plane allylic protons (H_b, δ 3.90, J_{ab} = 1.7 Hz). Their geminal partners (H_b', δ 3.05, $J_{bb'}$ = 13.5 Hz) are expectedly shielded by the anti-directed bridgehead lone-pair electrons.[13] A significant 2D NOE correlation is observed between H_a and H_c (Figure 2).

---

(1) Kimura, E. *Top. Curr. Chem.* **1985**, *128*, 113–141.

(2) Alder, R. W.; Sessions, R. B. In *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Part 2*; Patai, S., Ed.; Wiley: New York, 1982; pp 763–803.

(3) *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979.

(4) Riedo, T. J.; Kaden, T. A. *Chimia* **1977**, *31*, 220–222; *Helv. Chim. Acta* **1979**, *62*, 1089–1096.

(5) (a) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499–1502. (b) Zompa, L. J. *Ibid.* **1978**, *17*, 2531–2536.

(6) pK_{a_3} = 13.2, pK_{a_2} = 7.4;[4] pK_{a_3} = 12.6, pK_{a_2} = 7.6.[5b]

(7) Alder, R. W.; Sessions, R. B. *Tetrahedron Lett.* **1982**, *23*, 1121–1124. Alder, R. W.; Moss, R. E.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 997–998.

(8) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86–97.

(9) Schulze, v. K.; Winkler, G.; Dietrich, W.; Muhlstadt, M. *J. Prakt. Chem.* **1977**, *319*, 463–474.

(10) All new compounds gave ^1H NMR, ^{13}C NMR, IR, and microanalytical data (C, H, N: ±0.3%) consistent with the proposed structures.

(11) Space group *Cc*. Unit cell parameters: a = 13.487 (3) Å, b = 8.909 (2) Å, c = 13.797 (5) Å, β = 111.62°, V = 1541 (1) Å^3, Z = 4. Densities: D_c = 1.514 g/cm^3, D_m = 1.476 g/cm^3. Formula: $C_{13}H_{26}N_3I$ (351.28 amu). Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.71073 Å) in the $\omega - 2\theta$ mode. The structure was solved by the Patterson method using 659 of the 1514 reflections measured. Most hydrogen atom positions were calculated using standard geometries in the later stages of refinement. Refinement factors: R_{uw} = 0.057; R_w' = 0.062. Bond angles and lengths and positional and thermal parameters are included as supplementary material.

(12) At 300 MHz in $CDCl_3$ (20 °C) the NH protons of **3**·HI are *both* deshielded (10.5 and 11.5 ppm), indicating that the large bridge may undergo rapid inversion. At 40 °C these resonances are coalesced.

(13) Similar shielding effects are observed for protons α to nitrogen in six-membered rings. For example, see: Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192–4201. Weisman, G. R.; Johnson, V.; Fiala, R. E. *Tetrahedron Lett.* **1980**, *21*, 3635–3638 and references therein.

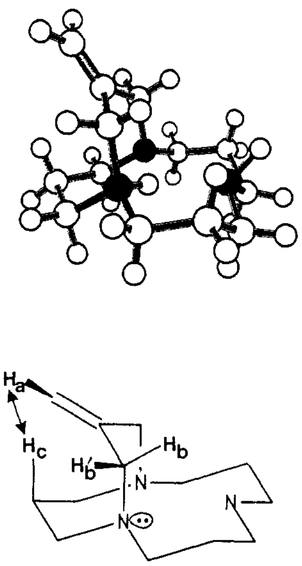


Figure 2. Crystal conformation (top) and ^1H NMR features of **3**·HI (bottom). Two-dimensional NOE correlation indicated by arrow.

We estimate that the acid dissociation constants for **3** and **4** correspond to pK_{a_3} > 13.5, since they cannot be measured by aqueous titration.[14] Moreover, **3**·H^+ and **4**·H^+ strongly resist protonation, as indicated by the low values of their second acid dissociation constants: pK_{a_2} = 4.4 and 4.9 for **3** and **4**, respectively. Thus, pK_{a_3} − pK_{a_2} is at least 8.6 pK_a units, whereas this value is only 5.0[5b] or 5.8[4] pK_a units for macrocycle **1**. This phenomenon has been observed for bridgehead diamines in which protonation relieves strain and indicates that **3**·H^+ and **4**·H^+ are stabilized species.[2] The exceptional stability of **3**·H^+ suggests that bicyclization could be a proton-templated process, as has been observed in cryptand synthesis.[15] Unlike many bridgehead bicyclic diamines,[7,16] **3** and **4** immediately form internally protonated salts when trifluoroacetic acid is added to the $CDCl_3$ solutions. Alder et al. have reported that 1,5-diazabicyclo[6.3.3]tetradecane must be heated overnight in trifluoroacetic acid to obtain the inside protonated species [δ(NH) = 17.25].[7]

In summary, we have found that bicyclization of a macrocyclic triamine can enhance the conformational organization of three basic sites. In contrast to bicyclic diamines that protonate slowly, bicyclic triamines in which a third site is positioned on a flexible bridge are protonated very rapidly. This "proton relay" concept should prove to be of considerable utility in the design of rapid-acting "proton sponges"[17] and receptors for other ions.

Acknowledgment. We gratefully thank Professor Joseph Lauher for his assistance with X-ray crystallographic and computer graphic techniques and Dr. Lisa Deuring for her aid with two-dimensional NMR experiments. Support by the New York Science and Technology foundation through the Center for Biotechnology is gratefully acknowledged.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, bond distances, and bond angles for **3**·HI (4 pages). Ordering information is given on any current masthead page.

---

(14) The pH of 0.1 M solutions of these bases are approximately 13. ^1H NMR experiments have established that in Me_2SO-d_6 **3** is slightly more basic than 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), which has an aqueous pK_a of approximately 13.5: Barton, D. H.; Eliot, J. D.; Gero, S. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2085-2090.

(15) Anelli, P. L.; Montanari, F.; Quici, S. *J. Org. Chem.* **1985**, *50*, 3453-3457.

(16) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321-327.

(17) For further recent examples of "proton sponges", see: Saupe, T.; Krieger, C.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 451-453. Werstiuk, N. H.; Butler, D. N.; Datta, S. *Can. J. Chem.* **1986**, *64*, 760-763.

Ferromagnetic Transition in a Bimetallic Molecular System

Yu Pei, Michel Verdaguer, and Olivier Kahn*

Laboratoire de Spectrochimie des Eléments de Transition
UA No. 420, Université de Paris-Sud, 91405 Orsay, France

Jorunn Sletten

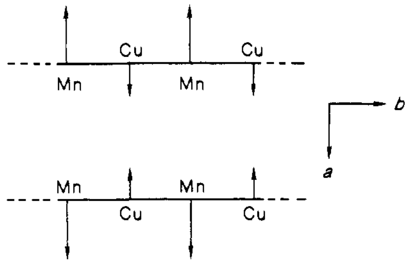
Department of Chemistry, University of Bergen
5000 Bergen, Norway

Jean-Pierre Renard

Institut d'Electronique Fondamentale, UA No. 022
Université de Paris-Sud, 91405 Orsay, France

Received August 1, 1986

For a few years, we have participated to the efforts to design molecular compounds ordering ferromagnetically.[1-5] Our first strategy has been to impose ferromagnetic interactions between nearest-neighbor metal centers owing to the orthogonality, strict (symmetry imposed) or accidental, of the magnetic orbitals. This approach allowed us to design ferromagnetically coupled dinuclear complexes[6] but we have not been able yet to extend it to three-dimensional lattices. Recently, we have proposed an alternative strategy[3] consisting to polarize local spins $^5/_2$ (Mn^{2+} or Fe^{3+}) along the same direction through antiferromagnetic interactions with local spins $^1/_2$ (Cu^{2+}). That approach already led us to a $Mn^{2+}Cu^{2+}Mn^{2+}$ trinuclear species with a spin $^9/_2$ ground state[7] and to $Mn^{2+}Cu^{2+}$ ordered bimetallic chains exhibiting one-dimensional ferromagnetic-like behaviors in the low-temperature range.[3,8] However, all those compounds display a three-dimensional antiferromagnetic ordering at very low temperature. $MnCu(pba)(H_2O)_3{\cdot}2H_2O$ (**1**) where pba denotes 1,3-propylenebis(oxamato) is a recently described chain compound of this kind.[3,9] The variation vs. the temperature T of the product $\chi_M T$, χ_M being the molar magnetic susceptibility per MnCu unit, increases upon cooling down below 115 K in a ferromagnetic-like fashion but exhibits a sharp maximum at 2.3 K due to the antiferromagnetic ordering of the ferrimagnetic chains.[9] In **1**, the chains run along the *b* axis of the orthorhombic system and are linked together through hydrogen bonding, which provides an interchain interaction pathway. The relative positions of two adjacent chains in the *a* direction are as shown in I with Cu···Cu = 6.545 Å and Mn···Mn = 6.997 Å as shortest interchain metal–metal separations in this direction. In the *c* direction, the shortest interchain separations are also Cu···Cu = Mn···Mn = 5.2105 Å. This



I

---

(1) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368-371.

(2) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147-2156.

(3) Pei, Y.; Kahn, O.; Sletten, J. *J. Am. Chem. Soc.* **1986**, *108*, 3143-3145.

(4) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Zhang, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1026.

(5) Bellito, C.; Day, P.; Wood, T. E. *J. Chem. Soc., Dalton Trans.* **1986**, 847.

(6) Kahn, O. *Angew. Chem.* **1985**, *97*, 837-853.

(7) Pei, Y.; Journaux, Y.; Dei, A.; Gatteschi, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1300-1301.

(8) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727-3737.

(9) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, J. P. *Inorg. Chem.*, in press.

0002-7863/86/1508-7428$01.50/0