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Small aza cages as "fast proton sponges" and strong lithium binders

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CONTENTS

A. INTRODUCTION

The design and synthesis of new compounds in order to achieve expected or new chemical properties is one of the most fascinating aspects of modern synthetic chemistry. Among the many thousands of new compounds synthesized each year, macrocyclic compounds play an important role. The ever growing interest in this very active field stems from different points of view, including selective ion recognition, transport processes, reaction catalysis, industrial applications, model systems, and others [1–17]. Numerous books on macrocyclic chemistry have been published in the last few years [18–27].

Molecular topology and the nature of donor atoms are the two most important parameters influencing the chemical properties of macrocyclic compounds. Different classes of synthetic macrocyclic compounds have been developed and, in addition to the most studied crown-ether family, the aza-crowns are the next most studied class of synthetic macrocycles [19,25]. These compounds could be considered to be derived from crown ethers by replacing the oxygen donor atoms with softer nitrogen donor atoms. The presence of this kind of donor atom makes these compounds water soluble bases and very prone to bind transition metal ions [28,29].

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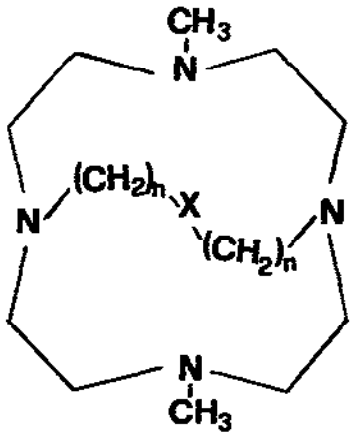
B. AZA CAGES

In the last few years, we have been interested in the chemistry of a series of small aza cages of the general formula reported in Fig. 1 [30]. These macrocycles are built upon a basal twelve-membered tetraazamacrocycle [31] in which two trans nitrogen atoms are connected through either two propylenic or ethylenic chains disposed around the "apical" X group (see Fig. 1). These are highly pre-organized molecules in which a three-dimensional cavity is present. The chemistry of these compounds can be better understood by taking into account the following main characteristics: (i) the size of the cavity; (ii) the rigidity and molecular pre-organization; and (iii) the nature of the donor atoms [32–35]. The average cavity size is rather small and only metal ions of appropriate size can be encapsulated with a high degree of selectivity ("metal ion recognition") i.e. most of these compounds are able to bind Li^+ strongly but none show an appreciable interaction with Na^+. If we consider that Cu^{2+} is also encapsulated by all members of the series, it can be roughly said that, on pure reciprocal dimensional bases, metal ions with ionic radii of at most 0.85–0.9 Å can be encapsulated, it being impossible for larger metal ions to get into the cage cavity. The size of the cavity is also influenced by the length of the



C1(NH,3): X=NH, n=3 **C2(S, 3): X=S, n=3**

C3(O, 3): X=O, n=3 **C4(CH_2, 3): X=CH_2, n=3**

C5(N-CH_3, 3): X=N-CH_3, n=3 **C6(NH, 2): X=NH, n=2**

C7(N-CH_3, 2): X=N-CH_3, n=2 **C8(N-Bz, 2): X=N-Bz, n=2**

Fig. 1. General drawing and abbreviations of the macrobicyclic cages. The apical group and the number of hydrocarbon atoms present in the bridging chains are given in parentheses.

hydrocarbon chains disposed around the X apical group and by the bulkiness of the group X itself. So far, the following atoms/groups have been studied: CH_2 [39], S [34], O [36], NH [32,33,40,41], N–CH_3 [37,38,42,43], N–benzyl [44]. Rigidity is another important characteristic of these compounds. The presence of short ethylenic chains on the twelve-membered macrocycle makes this part of the overall molecular framework rather rigid. The two methyl groups in the trans position further contribute to the molecular crowding. The constraint imposed by the connecting bridge (X-$[(CH_2)_n]_2$–; $n=2,3$) forces the nitrogen donor atoms in the tetraazamacrocycle to stay in an endo configuration and to create a high molecular pre-organization. The last important parameter which influences the chemical properties of these compounds is the nature of the apical group X. When the apical group is NH or O, we obtain extremely strong bases: i.e. stronger than OH^- in aqueous solution, which have been termed: *fast proton sponges* [45–47].

C. SYNTHETIC PROCEDURE

All cages of the series so far synthesized have been obtained by a non-template procedure with the general strategy reported in Fig. 2. The preparation of a *trans*-dimethylated twelve-membered tetraazamacrocycle Me_2[12]aneN_4 as starting material is the first step of the synthetic route for all cages of the series [31]. The formation of the three-dimensional cavity, by connecting the two secondary nitrogens with the appropriate unit, is the second step of the synthesis. Different overall yields have been obtained depending upon the length of the bridging chains and the nature of the leaving group: OTs, OMs, Cl. When the acid dichlorides are employed, the resulting amides are reduced by diborane. Since all the syntheses are non-template, free or, at most, protonated cages are obtained.

(i) Protonation

All cages are polybases in aqueous solution. The equilibrium constants for the stepwise equilibria (1) are reported in Table 1.

$$[H_{i-1}C]^{(i-1)+} + H^+ = [H_iC]^{i+} \quad (1)$$

The compounds are all rather strong bases with the first protonation step having $\log K_1 > 11.5$. Two of them, C1(NH,3) and C3(O,3) behave as extremely strong bases: the first proton not being removed even in strong alkaline solution [32,36]. NMR experiments indicate that, in the monoprotonated species $[HL]^+$, the proton is rapidly exchanged with acidic hydrogens, on the NMR time scale. For this reason, these cages have been termed *fast proton sponges*. The X-ray crystal structure determination of the monoprotonated $[HC1]^+$ cation showed that protonation occurs on the secondary apical amino group (see Fig. 3) with the two hydrogen atoms of the protonated nitrogen forming hydrogen bonds with N7 and N1, respectively [33].

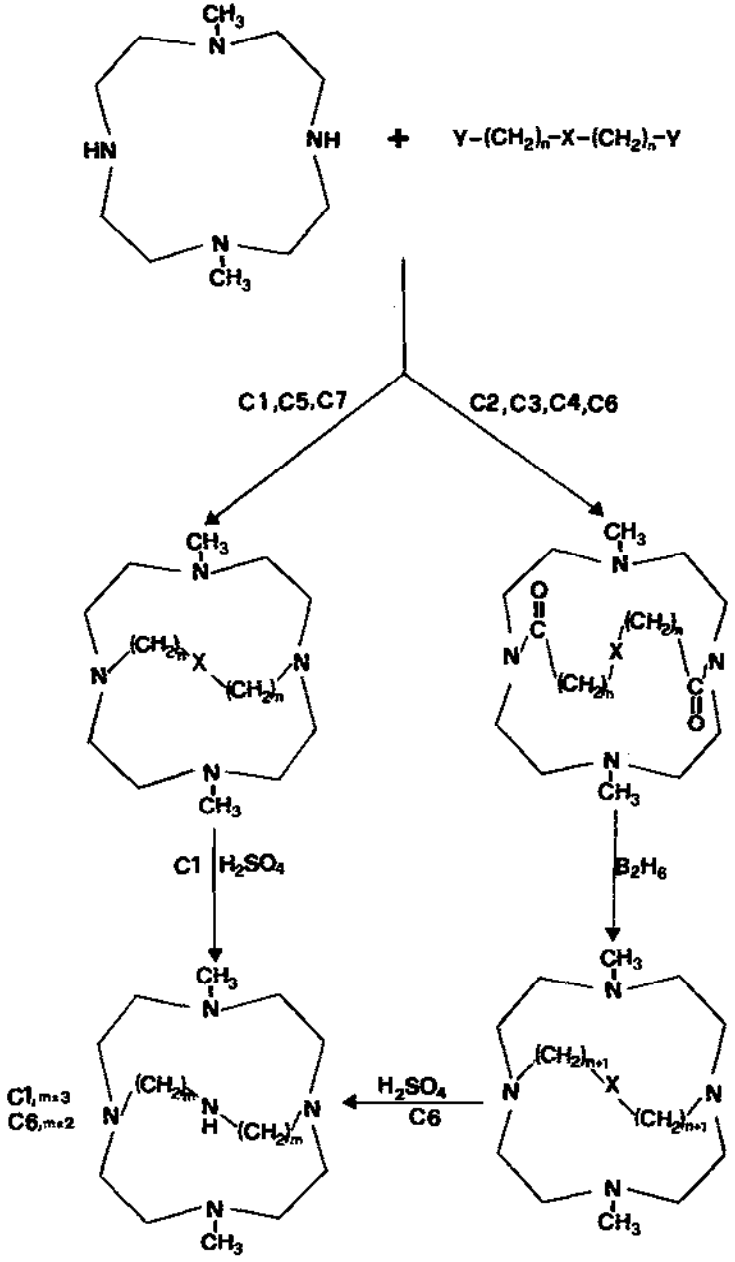


Fig. 2. Reaction pathway for the synthesis of macrobicyclic aza cages.

TABLE 1

Logarithms of the basicity constants of cages (C) in aqueous solution ($pK_w = 13.73$) and in water–DMSO mixture (50:50, mol:mol, $pK_w = 17.6$)
Measurements were carried out at 25°C and ionic strength (I) = 0.15 (NaCl)

Step	Cage							
	C1	C2	C3	C4	C5	C6	C7	C8
Aqueous solution								
1	>14[a]	11.91[b]	>14[c]	12.00[d]	11.83[e]	12.48[f]	11.8[g]	11.8[h]
2	8.41	8.78	11.21	7.86	9.53	9.05	10.0	8.3
3					3.43			
Water–DMSO								
1	14.8[c]	12.7[c]	14.0[c]	<13[d]	n.m.[i]			
2	5.6	5.5	8.2	4.1				

[a] Ref. 32. [b] Ref. 34. [c] Ref. 36. [d] Ref. 39. [e] Ref. 38. [f] Ref. 41. [g] Ref. 43. [h] Ref. 44. [i] n.m. = not measurable. Ref. 36, the low solubility of C5 prevented the determination of the basicity constants.

The H···N distances of 2.28 and 2.04 Å indicate rather weak hydrogen bonds, but each hydrogen of the NH_2^+ group further interact with both bridgehead nitrogen atoms. Thus an array of six hydrogen bonds, ranging from 2.44 to 2.76 Å, is formed which makes the structure particularly stable from the thermodynamic point of view, albeit that no single hydrogen bond is particularly strong [33]. We can say that it is a special molecular pre-organization which makes these structural features of the

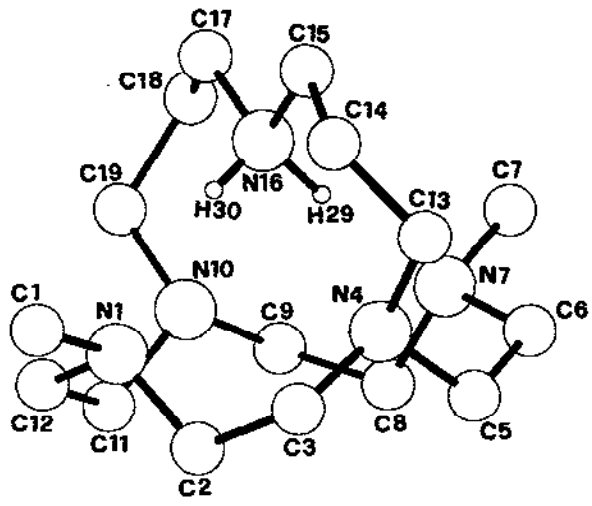


Fig. 3. Drawing of the $[HC1]^+$ cation. Atomic coordinates taken from ref. 33.

monoprotonated species of C1(NH,3), which are also in agreement with the fast protonation/deprotonation kinetic. Similar basicity behaviour is found for the monoprotonated species of the C3(O,3) cage [36].

Replacing the N–H apical group with a bulkier N–CH_3 produces a cage C5(N–CH_3,3) which is a much weaker base (log $K_1 = 11.83$) [37,38] than C1(NH,3). The crystal structure of the monoprotonated species of C5(N–CH_3,3) (see Fig. 4) shows [37,38] that the macrocycle is protonated at the methylated "apical" N5 and displays an overall conformation similar to that of the related cage C1(NH,3) [33]. Repulsions between the methyl group attached to the apical nitrogen atom N5 and the methyl group on one nitrogen atom of the basal plane force the N5–H10 bond to bend and point perpendicularly toward the basal plane. As a consequence of this imposed conformation, the average value of the hydrogen bond H10···N distances (2.54 Å) is considerably longer than that found for the H···N distances (2.38 Å) of the analogous species of C1(NH,3) [33]. The lower thermodynamic stability of the monoprotonated species $[HC5]^+$ with respect to $[HC1]^+$ is due to a weaker hydrogen bond network, present in the former species [38].

Another clear indication of the key role played by molecular topology in determining the proton-binding characteristics of these compounds is the log $K_1 =$ 12.00 of C4(CH_2,3) (see Table 1), where no donor atoms are present in the bridging unit [39]. C4(CH_2,3) is significantly more basic than the monocyclic 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (log $K_1 = 9.70$), where only tertiary nitrogen atoms are present [29]. Furthermore, the very favourable enthalpic term ($\Delta H_1^\circ = -54.0$ kJ mol^{-1}) for the first protonation step of C4(CH_2,3) indicates a strong interaction between proton and nitrogen atoms [39]. A similar high basicity in the first protonation step is found for the sulphur derivative C2(S,3) [34]; also, in this

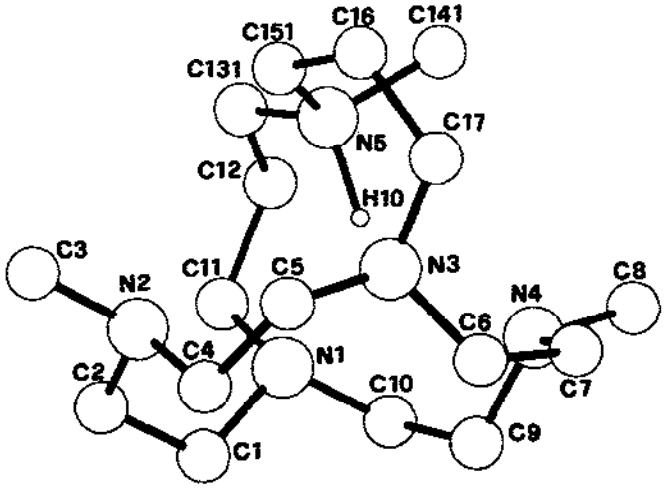


Fig. 4. Drawing of the $[HC5]^+$ cation. Atomic coordinates taken from ref. 38.

case, the strong proton–nitrogen interaction is demonstrated by the high enthalpy of protonation ($\Delta H_1^\circ = -55.6$ kJ mol^{-1}).

As far as the second protonation step is concerned, the following general consideration could be made: because of molecular rigidity, two positive charges are brought close to each other and thus the system is destabilized. In the case of the proton sponge C1(NH,3), the addition of the second proton destroys the hydrogen-bond framework of the monoprotonated species and the difference between log K_1(>14) and log K_2(8.41) is particularly large [32]. Only in the case of the oxo-cage C3(O,3) is the basicity still high even in the second protonation step (log K = 11.21), the highest basicity among the cages so far investigated [36]. An X-ray crystal structure study carried out on the picrate salt of the diprotonated derivative of C3(O,3) has shown that the cage is protonated on the methylated tertiary nitrogens (see Fig. 5) and displays a conformation similar to that of the monoprotonated cage C1(NH,3) (see Fig. 3) [36]. The four nitrogen atoms are almost coplanar, and form the basal plane of a slightly distorted square pyramid with the oxygen atom at the apex. The hydrogens bonded to N(1) and N(7) form hydrogen bonds with the apical oxygen (mean N–H···) distances 3.13 Å). The two hydrogen bonds are nearly linear. Each hydrogen atom of the CH_3NH^+ group can further interact electrostatically with both bridgehead nitrogen atoms N(4) and N(10), (see Fig. 5), these distances ranging from 2.32 to 2.54 Å [36]. Such additional interactions have been invoked to explain the high basicity of C3(O,3) [36]. In the case of cages C4(CH_2,3) and C5(N–CH_3,3) the crystal structures of the diprotonated species have been carried out. The structure of $[H_2C4]^{2+}$ shows the four nitrogen atoms to be in the endo conformation [39]. The two hydrogen atoms are bound to the methylated nitrogen atoms and are encapsulated within the cavity. The electrostatic repulsion between

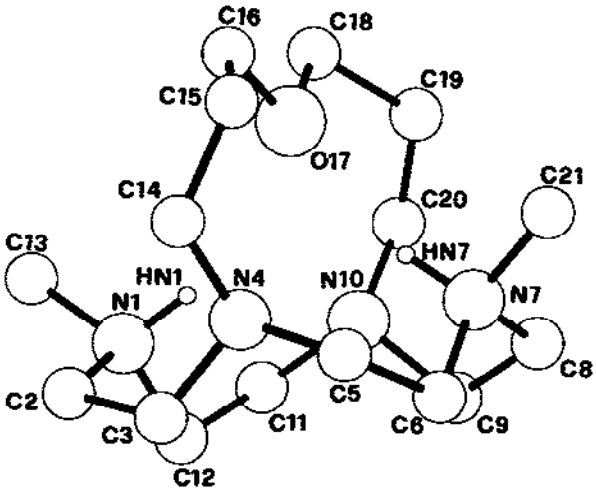


Fig. 5. Drawing of the $[H_2C3]^{2+}$ cation. Atomic coordinates taken from ref. 36.

them is overwhelmed by the electrostatic attractions between each proton and the bridgehead nitrogens. A similar situation was found for the diprotonated species $[H_2C3]^{2+}$. However, such a conformation is not the only one possible, as demonstrated by the structure of the $[H_2C5]^{2+}$ species [38] (see Fig. 6). In this case, the two acidic hydrogens have not been located but it is evident that the cage conformation is different from that of $[H_2C4]^{2+}$ and $[H_2C3]^{2+}$. The very short distance between the methylated nitrogen of the base (2.88 Å) suggested the protonation of one of these nitrogen atoms and the occurrence of a strong linear hydrogen bond between them [38]. Other structural considerations suggested that the other protonation occurs at the apical nitrogen in order to minimize the electrostatic repulsions between the protons. In conclusion, the conformation of the diprotonated cages is dependent upon the molecular geometry and from a delicate balance between electrostatic attractions and repulsions [38].

The third protonation constant was determined under the experimental conditions employed for the cage C5(N–CH_3,3). Its value, log $K = 3.43$, (see Table 1) is six log units smaller than the second protonation constant, indicating that the three positive charges experience electrostatic repulsion since they are close to each other.

In many cases, basicity constants have been determined in mixed water–DMSO (50% mol:mol) solvent (see Table 1). In the last solvent there is no more proton sponge behaviour and, as already found in aqueous solution, all equilibria are fast on the potentiometric time scale.

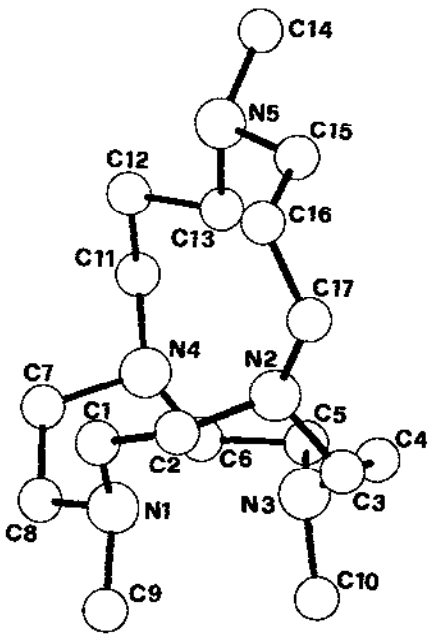


Fig. 6. Drawing of the $[H_2C5]^{2+}$ cation. Atomic coordinates taken from ref. 39.

(ii) Lithium complexes

Selective lithium encapsulation in aqueous solution is the most fascinating ligational property of these compounds. The lithium ion reacts with the monoprotonated species of the precursor of the series C1(NH,3) at very high pH [32]. Only in 1 mol dm^{-3} KOH did the formation of a lithium complex appear to be complete. It is interesting to note that only when a nitrogen donor atom is present in the apical position is the Li^+ encapsulated and the complex formed. The methylated derivative C5(N–CH_3,3) forms a stable lithium complex ($\log K = 3.2$, see Table 2). The Li^+ encapsulation has been followed by ^{13}C and ^{7}Li NMR techniques [37,38]. The ^{13}C NMR spectrum of a solution containing the preformed [LiC5][Cl] salt in alkaline solution consists of ten sharp signals at room temperature, independent of the solvent, typical of a time-averaged C_s symmetry, with the lithium atom and the nitrogen atoms of the three N–CH_3 groups lying in the symmetry plane. The ^{7}Li spectrum of the complex shows two sharp signals, one for the complexed (+0.88 ppm) and one for the free lithium, indicating a slow exchange between the two species on the NMR time scale. Direct measurement, by microcalorimetry, of the enthalpy of the reaction

$$Li^+_{(aq)} + L_{(aq)} = [LiL]^+_{(aq)} \quad (2)$$

has shown that the driving force for this reaction is the entropy ($\Delta S^\circ = 54.2$ J mol^{-1} K^{-1}), the enthalpy of reaction being only very slightly favourable ($-\Delta H^\circ = 2.1$ kJ mol^{-1}) [38]. The insertion of the metal ion into the small hydrophobic cavity requires removal of all the water molecules that surround the free Li^+ in aqueous solution, thus raising the translational entropy change.

The crystal structure of the [LiC5][BPh_4] salt showed that the compound consisted of discrete $[LiC5]^+$ cations and $[BPh_4]^-$ anions, (Fig. 7). The Li^+ is enclosed in the cage cavity and adopts a five-coordinate geometry, which is best

TABLE 2

Stability constants (logarithms) of lithium complexes of cages in aqueous solution

Cages	log*K*	Ref.
C1(NH,3)	n.m.[a]	32
C2(S,3)	n.s.[b]	34
C3(O,3)	n.s.[b]	36
C4(CH_2,3)	n.s.[b]	39
C5(N–CH_3,3)	3.2	37,38
C6(NH, 2)	4.8	40,41
C7(N–CH_3,2)	5.5	43
C8(N–Bz, 2)	3.0	44

[a]Not measurable. [b]Not studied.

described as a distorted square pyramid. The Li^+ ion is located 0.85 Å above the average plane of the basal nitrogen atoms.

The shortening of the hydrocarbon chains disposed around the apical group produces a smaller cavity which fits the lithium ion better. Indeed, the cage C6(NH,2) and even better its methylated derivative C7(N–CH_3,2) form very stable inclusion Li^+ complexes, log $K = 4.8$ and log $K = 5.2$ for reaction (2), respectively [40,41,43]. In Fig. 8 the ^{13}C and ^7Li NMR spectra of $[LiC6]^+$ complex are reported. The ^{13}C spectrum is consistent with a time-averaged C_S symmetry, while the ^7Li spectrum exhibits two sharp peaks (see Fig. 8), one for free lithium and one for the complexed, highly deshielded lithium (2.85 ppm) [41]. Furthermore, the chemical shift of the complexed lithium is essentially independent of the solvent, in agreement with the tight encapsulation of the metal ion and the absence of coordinated solvent molecules. The crystal structure of $[LiC6][ClO_4]$ reflects the great ability of C6 to bind Li^+. The lithium ion is wholly wrapped by the cage (see Fig. 9) and located at the centre of a fairly regular trigonal-bipyramidal arrangement of the five nitrogen atoms [41]. Indeed, the bond angles N–Li–N were 117.1, 120.7, and 122.1°, whereas the bond angles N_{apex}–Li–N varied from 88.5 to 91.0°. The Li–N mean distance was 2.04 Å, indicating rather strong Li–N interactions for the $[LiC6][ClO_4]$ complex, in agreement with its high thermodynamic stability. The methylation of the apical group of the cage C6(NH,2) yields the C7(N–CH_3,2) cage, which forms the most stable lithium complex (log $K = 5.2$) so far obtained [43]. The ^7Li NMR has the same two-peak pattern as the other lithium cage complexes, with $\delta = 2.88$ ppm. Apparently the methylation of the apical group increases the lithium binding capability of these cages. The crystal structure of the $[LiC7][BPh_4]$ salt showed that lithium

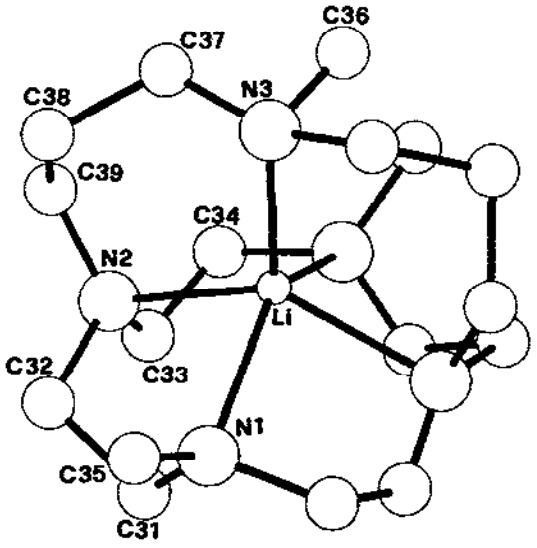


Fig. 7. Drawing of the complex cation $[LiC5]^+$. Atomic coordinates taken from ref. 38.

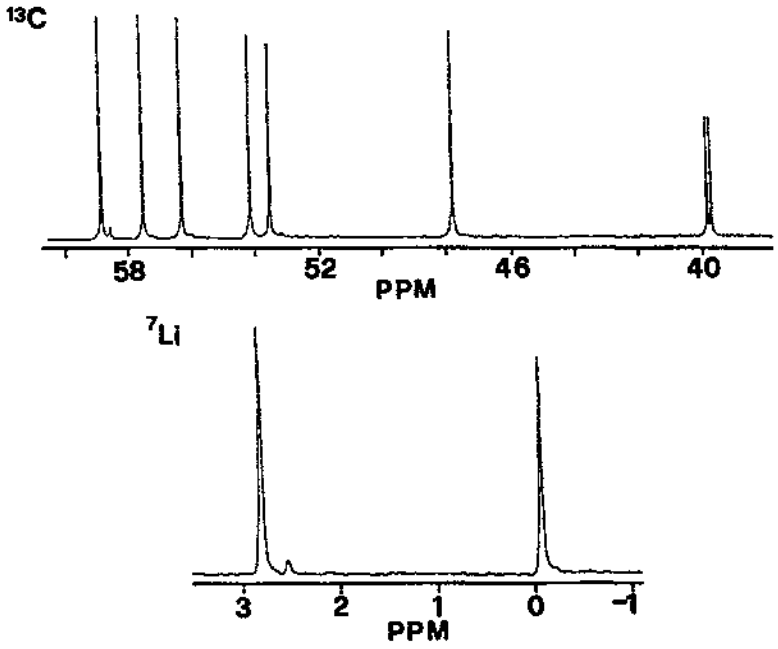


Fig. 8. ^{13}C (top) and ^{7}Li (bottom) NMR spectra of $[LiC6]^+$ complex in aqueous solution.

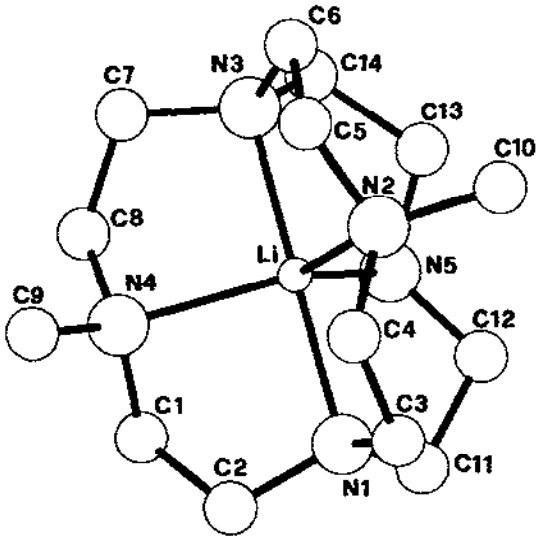


Fig. 9. Drawing of the complex cation $[LiC6]^+$. Atomic coordinates taken from ref. 41.

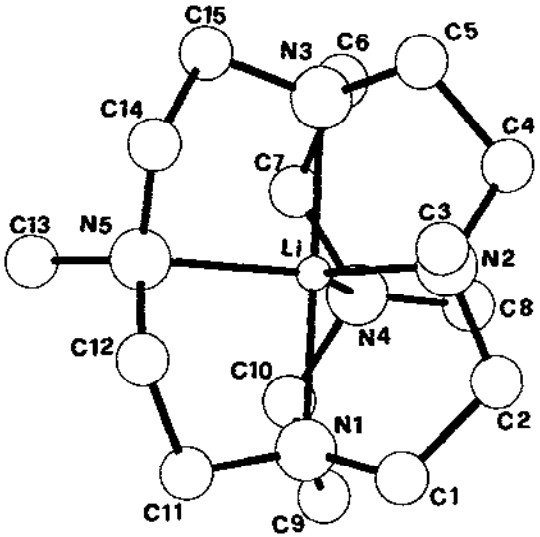


Fig. 10. Drawing of the complex cation $[LiC7]^+$. Atomic coordinates taken from ref. 43.

is complexed by the cage C7(N–CH_3,2) (see Fig. 10) in much the same way as by the cage C6(NH,2). The lithium atom adopts a rather regular bipyramidal geometry with the Li–N shortest distance of 2.01 Å [43]. The bond angles N–Li–N were 119.9, 121.0, 119.1, 89.9, and 90.1°. The more regular complexation in the solid state is coupled with a greater stability in aqueous solution.

D. CONCLUSIONS

The ability to discriminate between alkaline ions, the formation of exceptionally stable lithium complexes, as well as the remarkable proton transfer properties make this family of small aza-cages interesting compounds from both the theoretical and practical point of view.

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