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A Thermodynamic and Structural Study of the Interactions
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Some Primary Organic Ammonium Cations

by

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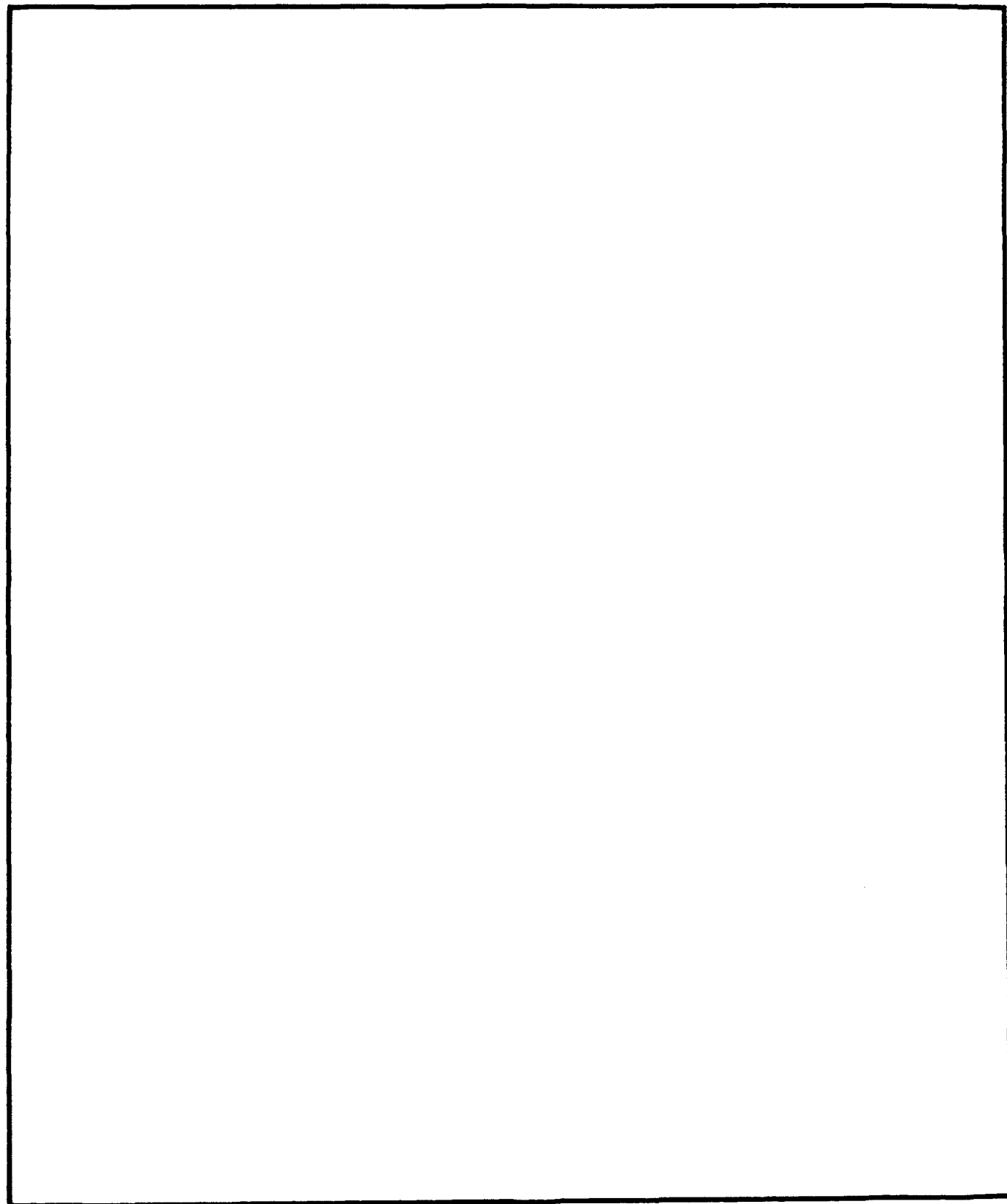


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A Thermodynamic and Structural Study of the Interactions of Pyridino- and Diketopyridino-18-Crown-6 Ligands with Some Primary Organic Ammonium Cations

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Abstract. Equilibrium constant (K), enthalpy change (ΔH), and entropy change (ΔS) values have been determined calorimetrically at 25°C in 90% MeOH–10% H₂O (v/v) for the interactions of pyridino-18-crown-6 (P18C6) and diketopyridino-18-crown-6 (K₂P18C6) with perchlorate salts of ammonium, benzylammonium, α -phenylethylammonium, β -phenylethylammonium, and α -(1-naphthyl)ethylammonium cations. The crystal structure of the complex of P18C6 with benzylammonium perchlorate was determined by X-ray crystallography. The ¹H 1D and 2D NMR spectra of some of these complexes were used to elucidate their structural features in solution. The log K values for the interaction of the ammonium cations with P18C6 are larger than those with K₂P18C6, probably due to the higher degree of structural flexibility of P18C6. Ligand K₂P18C6 displays appreciable π – π interaction with α -(1-naphthyl)ethylammonium cation, but not with α -phenylethylammonium cation.

Key words. Crown ether–primary ammonium cation complexation, formation constants (K), enthalpy changes (ΔH), entropy changes (ΔS), titration calorimetry, π – π interaction between ligand and cation.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 00000 (22 pages)

1. Introduction

Macrocycles of the 18-crown-6 (18C6) type are recognized as good receptors of primary ammonium cations through tripod hydrogen bonding (Figure 1) [1–3]. Therefore, the study of the enantiomeric recognition of chiral primary ammonium cations and amino acids by chiral 18C6 type macrocyclic ligands and their derivatives has been of much interest [4–7]. Earlier, it was found in our laboratory that chiral macrocycle (*S,S*)-dimethyldiketopyridino-18-crown-6 (M₂K₂P18C6) displayed significant enantiomeric recognition for the (*R*)- α -(1-naphthyl)ethylammonium cation (NapCH(CH₃)NH₃⁺) over the (*S*) counterpart in methanol [4]. Later, it was found that two analogous macrocycles (*S,S*)-diphenyldiketopyridino-18-crown-6 (Ph₂K₂P18C6) and (*R,R*)-di(tert-butyl)-pyridino-18-crown-6 (tBu₂P18C6) (see structures) exhibited even greater enantiomeric recognition for NapCH(CH₃)NH₃⁺ [7]. An important reason for chiral recognition in the chiral (*S,S*)-M₂K₂P18C6 system was that the steric repulsion between the methyl group

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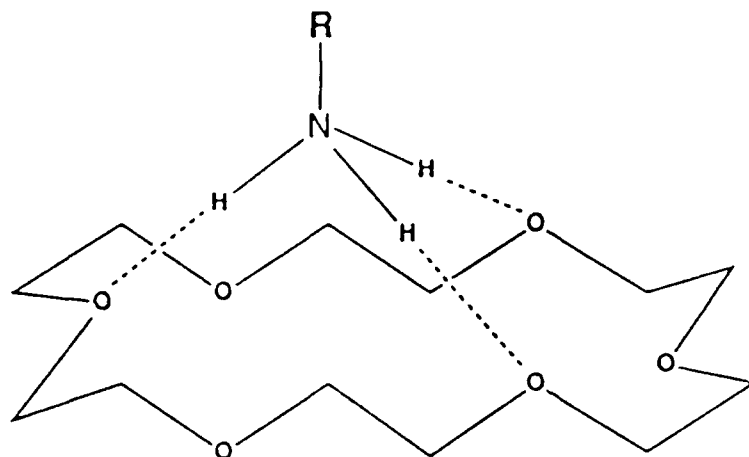
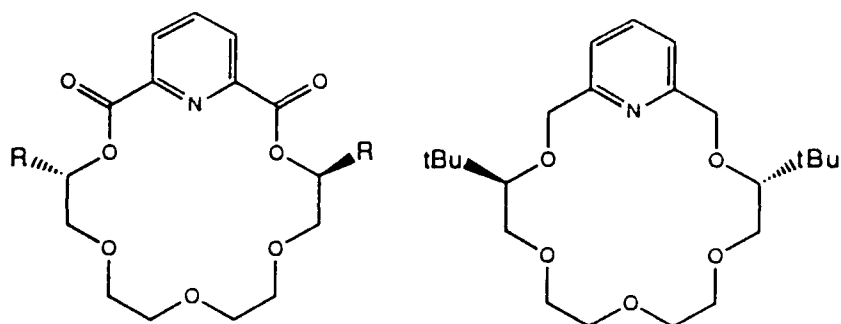
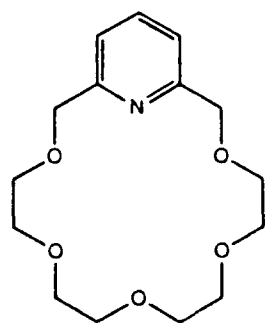


Fig. 1. Binding of ammonium cation to 18-crown-6 through a tripod hydrogen bond.

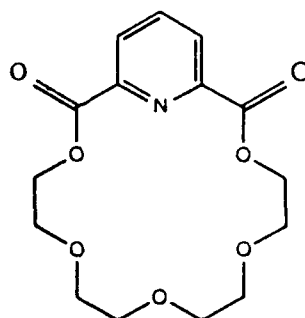


R = Me: (S,S)-M₂K₂P18C6
 R = Ph: (S,S)-Ph₂K₂P18C6

(R,R)-(tBu)₂P18C6



P18C6



K₂P18C6

of the ligand and the naphthyl group of the ammonium cation in the (SS)-(R) complex was significantly less than that in the (DD)-(S) complex, as implied from X-ray crystallographic data [5]. However, this difference in steric repulsion was possible only because the naphthyl group of the cation and the pyridine group of the ligand were overlapping in both the (SS)-(R) and (SS)-(S) complexes. Therefore, the π - π interaction that brought the two aromatic groups into an overlapping conformation was expected to be an important contributor to chiral recognition.

In the present work, an effort was made to investigate the π - π interaction through a comparative study of the interactions of a series of primary ammonium cations with P18C6 and K₂P18C6 (see structures), the achiral analogues of M₂K₂P18C6. Macrocycles P18C6 and K₂P18C6 both have a pyridine subring which is capable of π - π interaction, but K₂P18C6 differs from P18C6 by having two ester carbonyl (keto) groups. The ester carbonyl groups in K₂P18C6 will enlarge the π area, but reduce the basicity of the pyridine nitrogen and the flexibility of the ligand molecule. Thus, it is of interest to compare the two ligands in their associations with primary ammonium cations each of which contains an aromatic side group.

2. Experimental Section

2.1. MATERIALS

Macrocycle P18C6 was prepared as reported [8]. Macrocycle K₂P18C6 was recrystallized from the product of Parish Chemical Company (Orem, UT). The perchlorate salts of ammonium, benzylammonium, α -phenylethylammonium, β -phenylethylammonium, and α -(1-naphthyl)ethylammonium cations were prepared by treating the free amines (Aldrich) with diluted aqueous perchloric acid (Aldrich). The salts were crystallized from the resulting aqueous solution followed by recrystallization from a chloroform/acetonitrile mixture. The perchlorate salts of all of the amines thus prepared were needle shaped white crystals.

2.2. DETERMINATION OF LOG K AND ΔH VALUES

Equilibrium constant (K) and enthalpy change (ΔH) values for the macrocycle-ammonium cation interactions were determined in 90% MeOH–10% H₂O (v/v) at 25°C by an isoperibol titration calorimetry procedure, which has been described [9–11]. In each calorimetric measurement, a dewar, initially containing 25 ml of solution, was used. The titrate was always the ligand solution. The raw data were analyzed on a VAX 11/780 computer using computer program EQDH which was developed earlier in our laboratory [12]. The entropy change (ΔS) values were calculated according to the equation: $-2.303 RT \log K = \Delta H - T\Delta S$.

2.3. ¹H NMR EXPERIMENTS

The ^1H NMR spectra of the free ligands in CDCl_3 , the free ammonium salts in CD_3OD , and the complexes in CDCl_3 were taken on a Varian Gemini 200 MHz NMR spectrometer. 2D NOESY spectra of the $\text{K}_2\text{P18C6}$ complexes with $\text{PhCH}(\text{CH}_3)\text{NH}_3^+$ and $\text{NapCH}(\text{CH}_3)\text{NH}_3^+$ were taken on the same spectrometer.

2.4. X-RAY STRUCTURE DETERMINATION

Single crystals of the complex of P18C6 with benzylammonium perchlorate were grown from a methanol solution. A suitable crystal was mounted on a Nicolet R3 automated diffractometer which used graphite monochromated Mo- K_{α} radiation



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Table I. Crystal data and refinement data for the complex $[(\text{PhCH}_2\text{NH}_3)(\text{P18C6})]^+ \text{ClO}_4^-$.

Formula	$[(\text{C}_{15}\text{H}_{23}\text{NO}_3)(\text{C}_7\text{H}_{10}\text{N})]^+ \text{ClO}_4^-$
Formula weight	504.95
$F(000)$	1072
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$
μ (cm^{-1})	1.98
Space group	$P2_1/c$
a ($\text{\AA}$)	11.605(3)
b ($\text{\AA}$)	25.750(12)
c ($\text{\AA}$)	8.538(4)
β (deg)	98.73(2)
V ($\text{\AA}^3$)	2522(1)
Z	4
d_x (g cm^{-3})	1.33
$\sin \theta/\lambda$	0.54
Scan speed range (deg. min^{-1})	3.0 – 30.0
Total data	3717
Unique observed data	2035
Unobserved data ($F < 3\sigma(F)$)	1287
R_{in}	0.026(6)
R	0.075
R_w	0.056
G value for weighting scheme	1.9×10^{-4}
Goodness of fit	1.6
largest peaks in difference map ($e \text{\AA}^{-3}$)	0.35, –0.26

($\lambda = 0.70173 \text{\AA}$). The orientation matrix and lattice parameters were calculated using a least-squares procedure involving 20 carefully centered data ($7.2 < 2\theta < 21.0^\circ$). The crystal data and experimental parameters are summarized in Table I. Single crystal intensity data were collected using a θ - 2θ variable speed scan data collection mode to a 2θ limit of 45° ($\sin \theta/\lambda = 0.54$). Weights of the form $1/(\sigma^2(F) + G \cdot F^2)$ were applied to the data and the G value was refined in order to bring the goodness of the fit term to approximately one.

The trial model was obtained using direct methods. All of the non-hydrogen atoms were located in the E map. It became evident in the early stages of the refinement that the oxygens of the ClO_4^- were disordered. This disorder was resolved by describing the ion as having two different oxygen atom orientations about the Cl atom. Both orientations were refined with restrained Cl—O and O—O interatomic distances and with the occupancy factor of Cl being 1.0. The occupancy factors of the oxygens of the more populated sites were set at 0.80 and those of the oxygens at the less populated sites were set at 0.20. Positions for all hydrogens bonded to carbons were calculated based on known atom geometry with C—H distances of 0.96 $\text{\AA}$. These hydrogens were allowed to ride on their neighboring carbons during the refinement. Their thermal parameters were assigned the value of 1.2 times the initial equivalent isotropic thermal parameters of their neighboring carbons and were not refined. Positions for the hydrogens bonded to the nitrogen of the cation were taken from a difference map. During the refinement, these hydrogens were fixed to ride on the nitrogen and their isotropic thermal parameters were refined. All non-hydrogens except the perchlorate oxygens in the less populated sites were refined

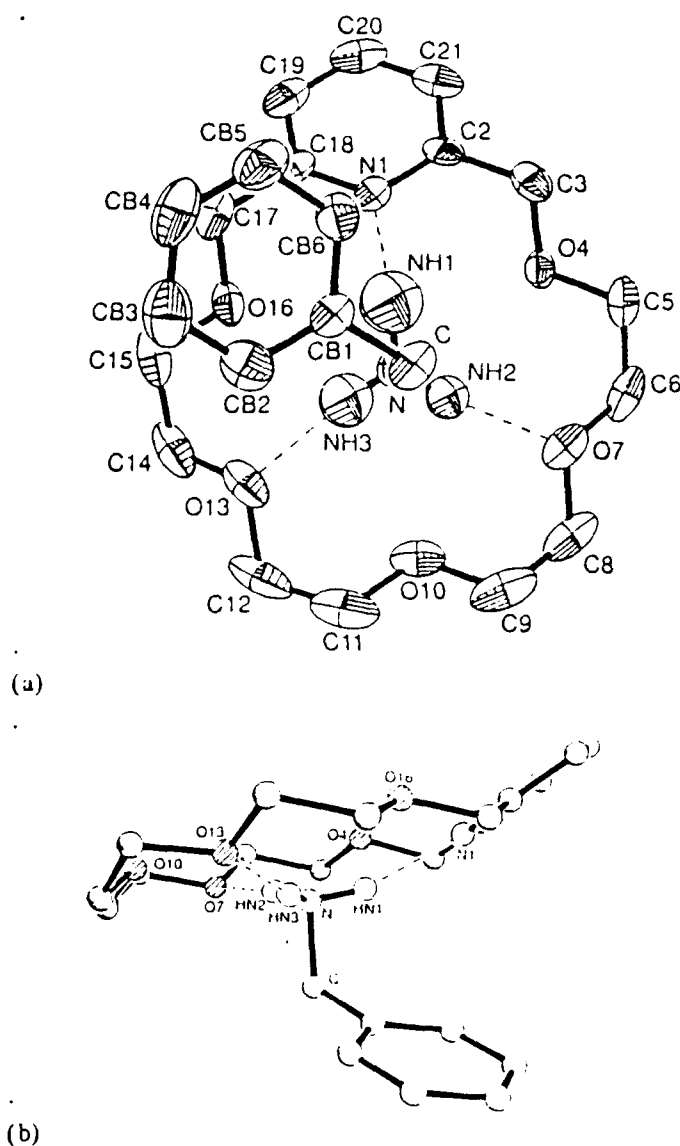


Fig. 2. Computer drawings of the crystal structure of the P18C6-PhCH₂NH₃⁺ complex with hydrogens of the ligand and the pyridine of the cation and the ClO₄⁻ omitted for clarity: (a) View perpendicular to the plane of the ligand with the thermal ellipsoids drawn at the 30% probability level to aid in the resolution of the atoms. (b) View from the side of the complex.

anisotropically. The final values for R and R_w were 0.075 and 0.056, respectively. Atomic scattering factors were taken from the literature [13]. Programs used in the solution and refining of this structure are contained in the SHELXTL [14] program package.

Ph₂ → This view of the complex perpendicular to the plane of crown which is shown in Figure 2a presents the atom labels, the thermal ellipsoids of the atoms, and the conformation of the molecule. A side view of the molecule using a ball and stick representation is shown in Figure 2b. These drawings were made using the program package SHELXTL PLUS [15]. Both drawings clearly show that there is no π - π interaction between the cation and the ligand. Positional parameters for the atoms and bond lengths and angles are included in Tables 1S and 2S of the supplementary material. The bond lengths have expected values. The average bond lengths in the

ligand are: $C_{\text{aliphatic}}-C_{\text{aliphatic}}$, 1.490(7) Å; $C_{\text{aliphatic}}-O$, 1.424(6) Å; $C-N$, 1.334(8) Å; $C_{\text{pyridine}}-C_{\text{pyridine}}$, 1.379(7) Å. Observed and calculated structure factors are contained in Table 3S of the supplementary material.

The attempt to describe the disorder in the ClO_4^- as discussed above was not completely successful as the four largest peaks in the final difference map were close to the Cl atom and the thermal parameters of the oxygen atoms of the anion varied greatly (see Table 1S). In addition, conformational disorder of atoms in the crown ligand is suggested by the large thermal parameters of C8, C9, C11, and C12 (see Table 1S and Figure 2a). Such disorder is likely caused by the presence of the rigid pyridine in the crown ring. It was not possible to resolve the disorder using room temperature data. Inasmuch as the purpose of the structural study was to determine if there was $\pi-\pi$ interaction between the ligand and the cation, there was no further attempt to improve the model of ClO_4^- or to resolve the disorder in the ring using low temperature data.

3. Results and Discussion

The $\log K$, ΔH , and ΔS values for the interactions of P18C6 and $\text{K}_2\text{P18C6}$ with a series of primary ammonium cations are listed in Table II. For each of the crown ether-ammonium cation complexes, a 1:1 ligand to cation stoichiometric ratio is assumed since the calorimetric data for each system were fitted well using the program EQDH [10] which assumes 1:1 complexation.

Two trends in the thermodynamic values listed in Table II deserve attention. First, P18C6 forms more stable complexes with the ammonium cations studied than $\text{K}_2\text{P18C6}$ by approximately one $\log K$ unit. The lower stabilities of the $\text{K}_2\text{P18C6}$ complexes result primarily from much less favorable entropy changes. The ΔH values for the interactions of P18C6 with the ammonium cations are close to those for the interactions of $\text{K}_2\text{P18C6}$ with the same cations, while the ΔS values for the two series are quite different (except for the interaction with $\text{PhCH}_2\text{NH}_3^+$). Second, P18C6 and $\text{K}_2\text{P18C6}$ form more stable complexes with $\text{NapCH}(\text{CH}_3)\text{NH}_3^+$ (by 0.15 and 0.22 $\log K$ unit, respectively) than with $\text{PhCH}(\text{CH}_3)\text{NH}_3^+$. Again, the difference in ΔS is more important than that in ΔH in determining the magnitude of $\log K$. - ΔS

A possible explanation for the first observation involves the presence of the ester carbonyl groups in $\text{K}_2\text{P18C6}$. This presence results in two negative effects on the interaction of the ligand with ammonium cations. First, the basicity of the ligand's pyridine nitrogen is reduced due to the electronic withdrawing effect of the two carbonyl groups, and second, the molecular flexibility of the ligand is reduced significantly compared to that of P18C6 due to the $\pi-\pi$ conjugation of the two keto groups with the pyridine ring. The decrease in the basicity of the ligand pyridine nitrogen should decrease the strength of the $\text{N}\cdots\text{H}-\text{N}^+$ hydrogen bond, and hence decrease the stability of complexes of $\text{K}_2\text{P18C6}$ with ammonium cations. The decrease in the ligand's molecular flexibility will reduce the amount of ligand conformational adjustment which is possible during complexation leading to unfavorable complex conformations with high strain energies. The resulting less stable complex requires less desolvation. Since fewer solvent molecules are involved in the desolvation process, the entropy change associated with the desolvation is less - N^+

Table II. Log K , ΔH and ΔS values* for the 1:1 interactions of P18C6 and K_3P18C6 with various ammonium cations (perchlorate salts) in 10% H_2O -90% $MeOH$ (v/v) at 25°C.

Ligand	Value	NH_4^+	$PhCH_2-$ NH_3^+	$PhCH(CH_3)-$ NH_3^+	$NapCH(CH_3)-$ NH_3^+	$PhCH_2CH_2-$ NH_3^+
P18C6	Log K	3.35(4)	3.78(5)	3.46(4)	3.61(4)	3.32(4)
	ΔH	-24.2(5)	-33.9(6)	-28.9(5)	-24.4(5)	-27.1(5)
	ΔS	-17.0	-41.3	-30.8	-12.6	-27.4
K_3P18C6	Log K	2.60(5)	2.68(5)	2.18(6)	2.40(5)	
	ΔH	-22.7(5)	-28.1(6)	-29.5(6)	-27.3(5)	
	ΔS	-26.3	-42.8	-57.3	-45.6	

*The average of three independent measurements. Uncertainties in last decimal place are given in parentheses. Units for ΔH and ΔS are kJ/mole and J/K · mole, respectively.

positive. Consequently, the entropy loss due to the ligand-cation association is less compensated by the entropy gain from desolvation. A more negative net entropy change is partly responsible for the destabilization of the K_2P18C6 complexes compared to the $P18C6$ complexes.

In order to understand the second observation, it is necessary to examine the structural difference between the $NapCH(CH_3)NH_3^+$ and $PhCH(CH_3)NH_3^+$ complexes of either $P18C6$ or K_2P18C6 . Comparison of the 1H NMR spectra of the $K_2P18C6-NapCH(CH_3)NH_3^+$ and $K_2P18C6-PhCH(CH_3)NH_3^+$ complexes to that of the free ligand showed that the pyridine signal of the ligand underwent a significant upfield shift (up to 30 Hz) upon complexation with $NapCH(CH_3)NH_3^+$, but a significant downfield shift (up to 17 Hz) upon complexation with $PhCH(CH_3)NH_3^+$. The upfield shift suggests the presence of a $\pi-\pi$ overlap between the naphthyl group of $NapCH(CH_3)NH_3^+$ and the pyridine group of the ligand, while the downfield shift suggests the separation of the phenyl group of $PhCH(CH_3)NH_3^+$ from the pyridine group of the ligand. The 1H NMR 2D-NOE (NOESY) spectra of the $K_2P18C6-NapCH(CH_3)NH_3^+$ and $K_2P18C6-PhCH(CH_3)NH_3^+$ complexes provide information which also supports the above suggestion. The NOESY spectrum of the $K_2P18C6-PhCH(CH_3)NH_3^+$ complex (Figure 3) showed two pairs of strong off-diagonal signals, one correlating the chemical shift of the pyridine protons of K_2P18C6 (centered at 8.30 ppm) with the chemical shift of the methyl group of the ammonium cation (1.60 ppm), and the other correlating the chemical shift of the protons on the 9,11 carbon atoms of K_2P18C6 (3.65 ppm) with the chemical shift of the α -phenyl group of the ammonium cation (7.28 ppm). The groups that are correlated in the NOESY spectrum are close together in the complex. Thus, the information in Figure 3 is consistent with the $K_2P18C6-PhCH(CH_3)NH_3^+$ structure shown in Figure 4a in which the α -phenyl group of the ammonium cation is in the opposite direction and far from the pyridine ring of K_2P18C6 . In this case, no $\pi-\pi$ interaction between the two aromatic groups is possible. In the NOESY spectrum of the $K_2P18C6-NapCH(CH_3)NH_3^+$ complex (Figure 5), the observation of a sole pair of off-diagonal signals which correlates the chemical shifts of the naphthylene protons of the ammonium cation (7.73 ppm) and those of the pyridine protons of the ligand (8.00 ppm) confirmed the existence of the $\pi-\pi$ overlap between the two aromatic groups (Figure 4b). In this case, the presence of a moderate or stronger $\pi-\pi$ overlap was found in an X-ray crystallographic study of the $NapCH(CH_3)NH_3^+-(S,S)-M_2K_2P18C6$ complex [5].

In the case of $NapCH(CH_3)NH_3^+$ and $PhCH(CH_3)NH_3^+$ complexes with $P18C6$, the 1H NMR spectra showed an upfield shift for the pyridine signal of $P18C6$ upon formation of either a $NapCH(CH_3)NH_3^+$ or a $PhCH(CH_3)NH_3^+$ or a complex with the ligand. This indicates that the $\pi-\pi$ overlap between the aromatic group of the cation and the pyridine group of the ligand may be present in both $NapCH(CH_3)NH_3^+$ and $PhCH(CH_3)NH_3^+$ complexes with $P18C6$. However, since the naphthyl group has a larger π area than the phenyl group, the extent of the $\pi-\pi$ overlap, and hence the $\pi-\pi$ interaction in the $NapCH(CH_3)NH_3^+-P18C6$ complex should be greater than that in the $PhCH(CH_3)NH_3^+-P18C6$ complex.

The effect of a stronger $\pi-\pi$ interaction in the $NapCH(CH_3)NH_3^+$ complexes than in the $PhCH(CH_3)NH_3^+$ complexes with either $P18C6$ or K_2P18C6 on the ΔH

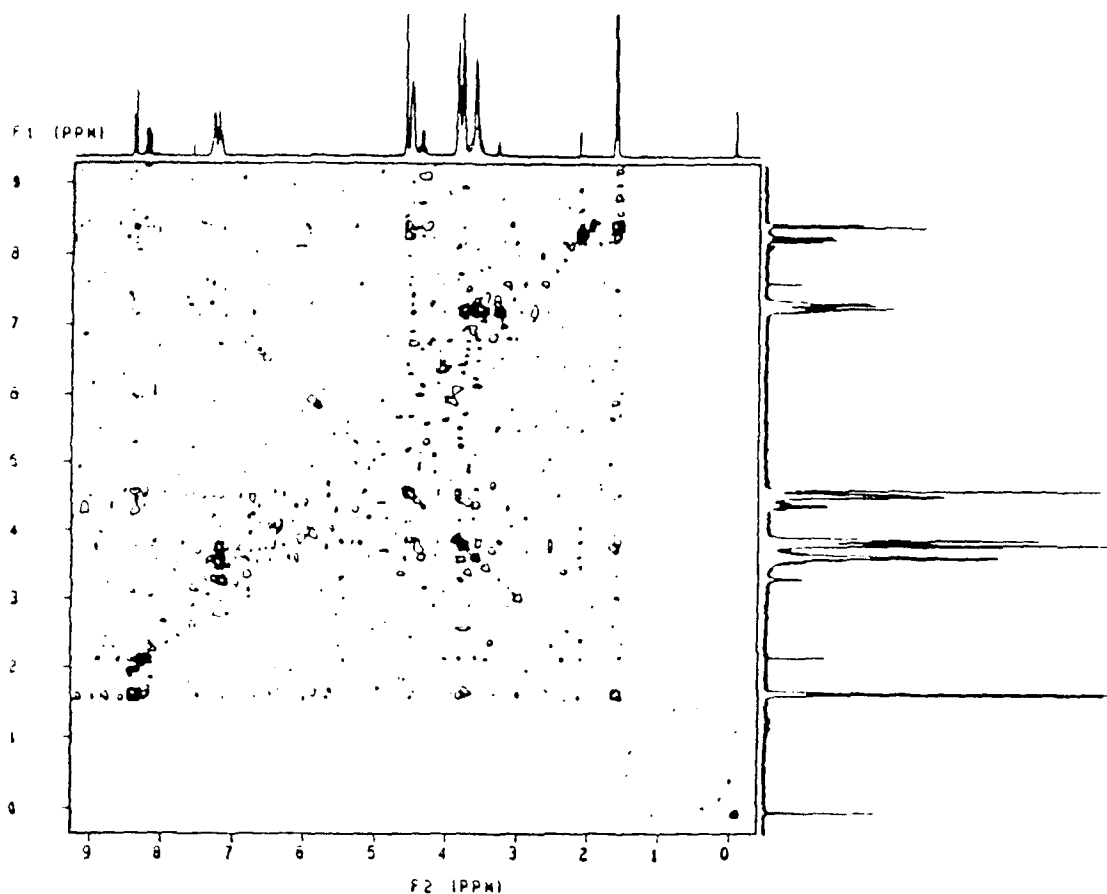


Fig. 3. 2D NOESY NMR spectrum of the $K_2P18C6-PhCH(CH_3)NH_3^+$ complex. The 1D spectra on the top and right are identical, and are the regular 1H NMR spectra of the complex. The ammonium cation peaks are located at 1.60, 4.35, and 7.28 ppm. The ligand peaks are at 3.65, 3.80, 4.35, 8.23, and 8.45 ppm.

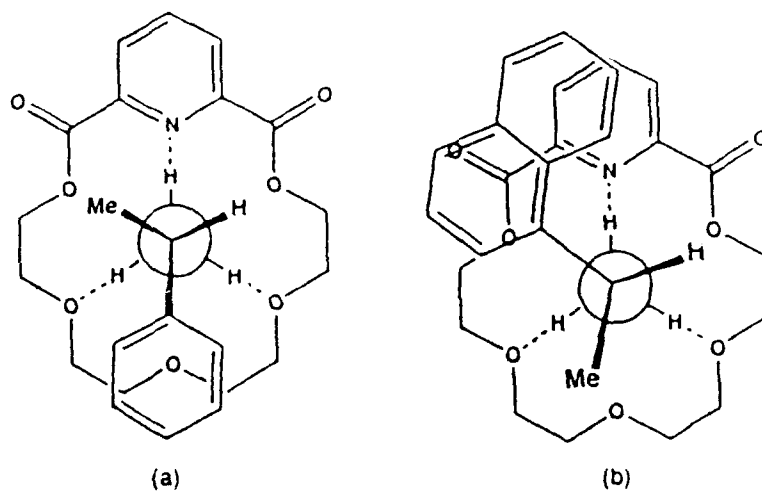


Fig. 4. Schematic representation of the molecular structures of the K_2P18C6 complexes with (a) $PhCH(CH_3)NH_3^+$ and (b) $NapCH(CH_3)NH_3^+$.

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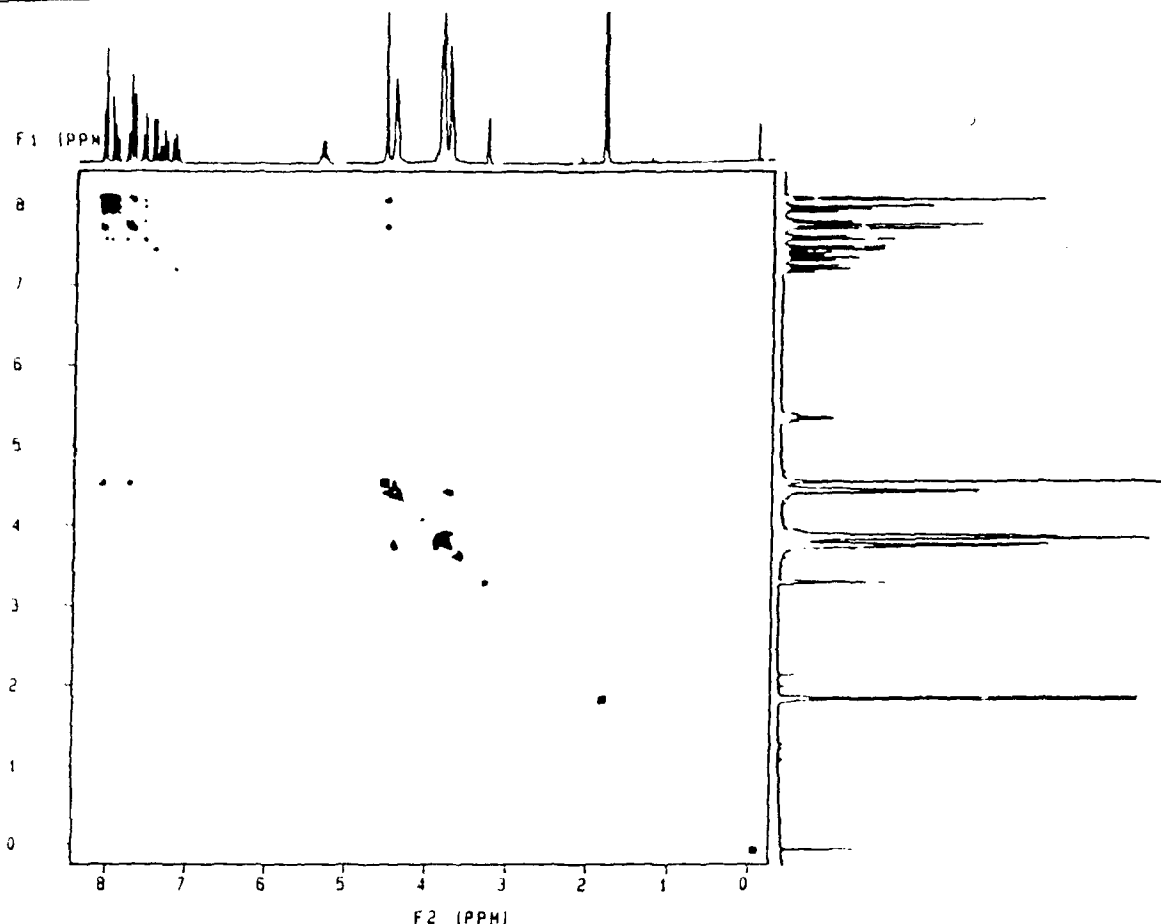


Fig. 5. 2D NOSEY NMR spectrum of the $K_2P18C6-NapCH(CH_3)NH_3^+$ complex. The 1D spectra on the top and right are identical, and are the regular 1H NMR spectra of the complex. The ammonium cation peaks are located at 1.83, 5.35, and 7.20–7.73 ppm. The ligand peaks are at 3.70, 3.85, 4.45, 7.90, and 8.10 ppm.

and ΔS values for the formation of these complexes may be explained as follows. Since the complex with stronger $\pi-\pi$ interaction is less exposed to the solvent than the one with weaker $\pi-\pi$ interaction, the former complex is less solvated than the latter. Desolvation is an entropy increasing and endothermic process. Therefore, the less negative ΔS and ΔH values for the formation of the $NapCH(CH_3)NH_3^+$ complexes with either P18C6 or K_2P18C6 are consistent with the greater extent of desolvation in the formation of these complexes.

Another unexpected fact which deserves attention is that the cation $PhCH_2NH_3^+$ forms a more stable complex than either NH_4^+ or $PhCH_2CH_2NH_3^+$ with P18C6, although the latter two cations are considered to be less sterically crowded than the former one. The crystal structure of the $PhCH_2NH_3^+-P18C6$ complex (Figure 2) showed the expected tripod hydrogen bond between the ligand and the cation. The hydrogen bond data are included in Table III. The crystal structure also established that the $\pi-\pi$ overlap between the phenyl group of the cation and the pyridine ring of the ligand was not present. Although the solution structure of the complex may differ from that in the solid state, the presence of the $\pi-\pi$ overlap is still unlikely

Table III. Data for hydrogen bonds linking the cation to the ligand.

D	H	A	H...A(Å)*	D...A(Å)	D—H...A(deg.)*
N	NH(1)	N(1)	1.92	2.886(6)	162
N	NH(2)	O(7)	2.00	2.935(6)	170
N	NH(3)	O(13)	2.01	2.843(5)	166

*The hydrogen positional parameters were not refined so e.s.d. values for the H...A distances and D—H...A angles were estimated at 0.02 Å and 2°, respectively.

due to the obviously unfavorable conformation which would result if the unparenthesized $N^+-C(-Ph)$ and $N^+-H(\cdots N)$ bonds were to overlap. Therefore, it is possible that the particularly high stability of the complex is not caused by $\pi-\pi$ interaction. The actual cause is not understood at this point.

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