

Stoichiometry and Conformation of the Azacrown Moiety in Sodium Complexes of Azacrown Ethers. A Raman/IR Spectroscopic Study. Part II: Complexes of 4,13-Diaza-15-crown-5

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Abstract. 4,13-Diaza-15-crown-5 and three of its sodium complexes (bromide, iodide and thiocyanate) were studied using Raman and IR spectroscopy and normal coordinate calculations, following the corresponding study on the sodium complexes of 4,13-diaza-18-crown-6 in the preceding paper. Complex formation was again accompanied by a characteristic shift of the bands, especially of those in the 800–900 cm^{-1} region. The complexes of 4-13-diaza-15-crown-5 were distinct from those of 4-13-diaza-18-crown-6, in that both of the bands at 830 and 890 cm^{-1} of the parent azacrown were affected on complex formation and in that only the 1:1 complex was formed. Normal mode calculations were made to predict conformations of the azacrown ring of the parent 4,13-diaza-15-crown-5 and its sodium complexes. Attention was paid to the different extent of mismatch in size of a sodium ion and azacrown cavities.

Key words: Azacrown ether, Sodium complex, Conformation, Raman/IR spectra, Normal mode calculations

1. Introduction

The preceding paper [1] presented a Raman/IR spectroscopic study on sodium complexes of 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (4,13-diaza-18-crown-6, abbreviated as A_218C6). This revealed a rather complex conformational change of the azacrown ring on complex formation, which has been attributed to the high degrees of motional freedom of the ring due to the 'mismatch' in size of a sodium ion and the azacrown ring. The companion azacrown, 1,7,10-trioxa-4,13-diazacyclopentadecane (4,13-diaza-15-crown-5, abbreviated as A_215C5) has a smaller cavity which fits a sodium ion much better than A_218C6 . In the present

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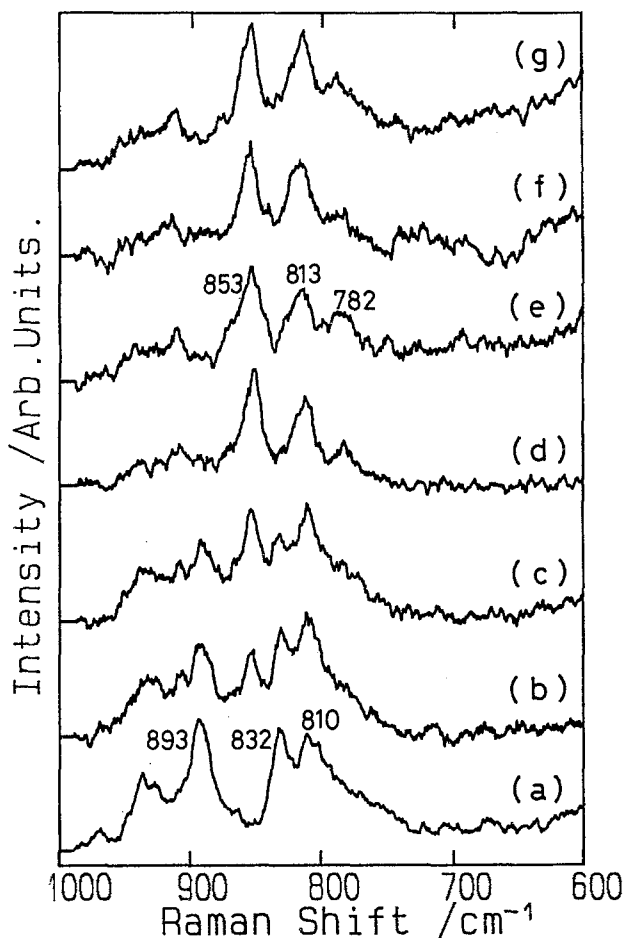


Fig. 1. Raman spectra of the NaBr-A₂15C₅ system for various [NaBr]/[A₂15C₅] ratios. (a) A₂15C₅, (b)–(g) [NaBr]/[A₂15C₅] = 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0, respectively.

paper we present a Raman/IR spectroscopic study on A₂15C₅ and its three sodium complexes (bromide, iodide and thiocyanate). In contrast to the case of A₂18C₆, no crystal structure has been reported for A₂15C₅. Normal mode calculations have therefore been performed to predict conformations of the azacrown ring in the parent azacrown and in the sodium complexes. A different approach from the case of A₂18C₆ was adopted in the calculations.

2. Experimental

A₂15C₅ from Merck was recrystallized from *n*-heptane. All other experimental procedures were essentially the same as those for the A₂18C₆ complexes, as reported in the preceding paper [1].

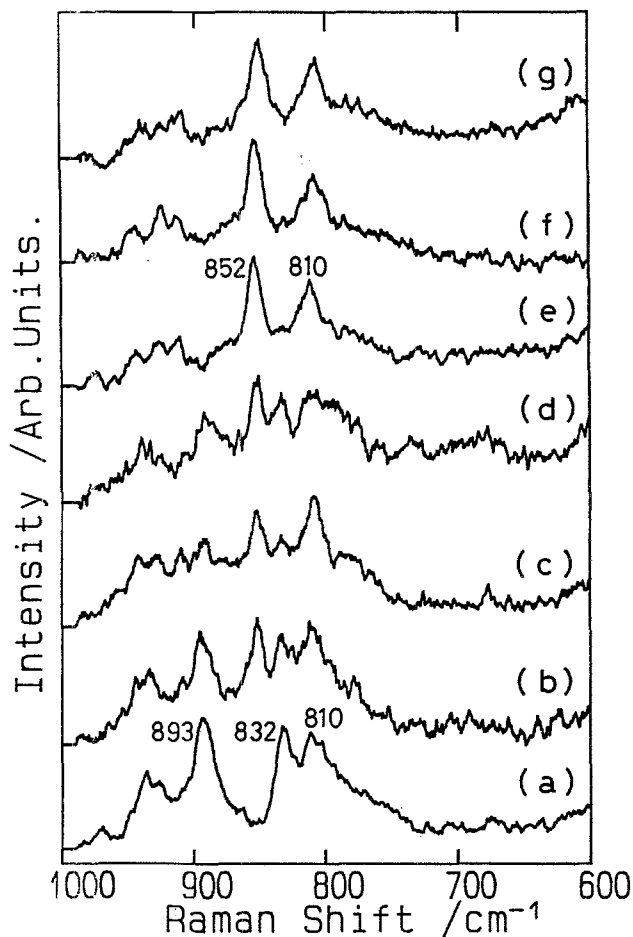


Fig. 2. Raman spectra of the NaI-A₂15C5 system for various [NaI]/[A₂15C5] ratios. (a) A₂15C5, (b)–(g) [NaI]/[A₂15C5] = 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0, respectively.

3. Experimental Results

The Raman spectra of the NaBr, NaI, and NaSCN complexes of A₂15C5 are shown in Figures 1, 2, and 3, respectively. The positions of the Raman and IR bands are given in Table I and Figure 4. The band positions are all similar in the three complexes, although the difference in relative band intensities and the presence of extra bands due to the SCN moiety in the NaSCN complex give a different-looking profile for the NaSCN complex in comparison with the other two. The most prominent feature among these spectra is the appearance of a sharp band near 850 cm⁻¹ on complex formation, at the expense of the bands of the parent azacrown near 890 and 830 cm⁻¹. This is distinct from the A₂18C6 cases reported in Part I [1], in which only the 890 cm⁻¹ band decreases in intensity. The spectral

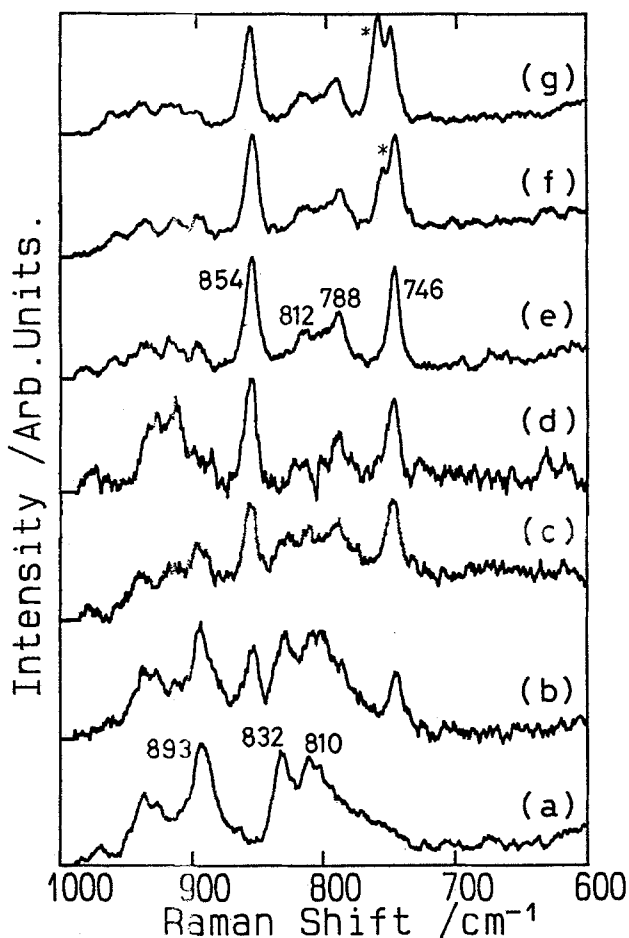


Fig. 3. Raman spectra of the NaSCN-A₂15C5 system for various [NaSCN]/[A₂15C5] ratios. (a) A₂15C5, (b)-(g) [NaSCN]/[A₂15C5] = 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0, respectively.

change levels off at a salt/azacrown ratio of unity, indicating the formation of 1 : 1 complexes.

3.1. NORMAL COORDINATE CALCULATIONS

Normal coordinate calculations were done using the MVIB program [2] to predict the conformations of parent and complexed A₂15C5. No crystal structure analyses have been reported for either of these compounds. We tried to deduce local conformations of the azacrown ring in the parent compound and the complexes from the distributions of vibrational bands. A different approach from the case of the A₂18C6 complexes was adopted here. Matsuura *et al.* [3] have used model compounds CH₃(OCH₂CH₂)_nOCH₃ ($n = 2, 3$ and 6) to establish such a relationship for oxyethylene chains. We used a model compound CH₃O—CH₂—

TABLE I. Observed wavenumbers (cm^{-1}) and vibrational assignments for parent $\text{A}_2\text{15C5}$ and its NaBr, NaI and NaSCN (1 : 1) complexes.

$\text{A}_2\text{15C5}$		NaBr		NaI		NaSCN ^a		Assignments
R	IR	R	IR	R	IR	R	IR	
1327 vw	1330 m		1332 s		1331 m	1332 m		CH_2 wag
					1315 w	1310 vw		CH_2 wag
1295 sh								CH_2 tw
1289 w		1301 vw		1296 sh		1294 w		CH_2 tw
	1270 w		1281 w		1275 m		1279 m	CH_2 tw
		1274 w		1276 sh		1271 s		CH_2 tw
		1268 w		1266 sh				CH_2 tw
		1264 w		1260 m	1260 m	1260 sh	1262 m	CH_2 tw
	1233 m	1256 w	1240 w		1233 m		1233 w	CH_2 tw
1236 m		1238 vw				1231 w		CH_2 tw
1216 w					1205 vw		1215 w	CH_2 tw
	1199 vw				1191 vw		1190 vw	CH_2 tw
		1172 w		1172 vw	1152 sh	1163 w		CC—NC str
1151 m							1153 m	CC—NC str
		1136 w		1136 m		1134 m		CH_2 rock
	1107 vs		1100 vs	1100 vw	1103 vs		1100 vs	CC—OC str
				1090 vw				CC—OC str
	1078 sh				1080 vs	1070 w	1084 vs	CH_2 rock
			1056 sh	1050 vw	1070 sh	1063 s	1074 vs	CC—OC str
	958 w			959 vw		959 vw		OC—CO str
940 m				943 vw		935 w		CH_2 rock
930 vw	930 w	942 vs	941 s	926 vw	935 s		948 s	CH_2 rock
925 vw								CH_2 rock
							910 m	OC—CO str
		911 w		909 w		918 w		CH_2 rock
893 s	900 vw			896 vw		896 w		CC—OC str
891 sh						875 vw	882 s	CC—OC str
832 m		853 s		852 s		854 s		CC—OC str
	828 s		845 w	850 sh	844 m		847 w	CC—OC str
818 w			815 w		806 m	816 sh	809 sh	CC—NC str
810 m		813 m		810 m		812 w	800 sh	CC—NC str
		782 w		794 vw		788 m	780 sh	NH <i>para</i> bend
			767 w		745 m			?
				579 vs		579 vw	570 w	CCO def
		555 vw				556 vw	545 w	CCO def
547 vw		551 vw			517 w			CCO def
352 vw						384 vw		CCN, CCO def
334 w				336 vw		358 vw		CCO def
329 sh		320 w						
310 w		308 m		308 w		309 s		OC—CO tors
288 w						304 sh		OC—CO tors

^a Bands of SCN appear at 746 s (R), 730 w and 460 w (IR) cm^{-1} .

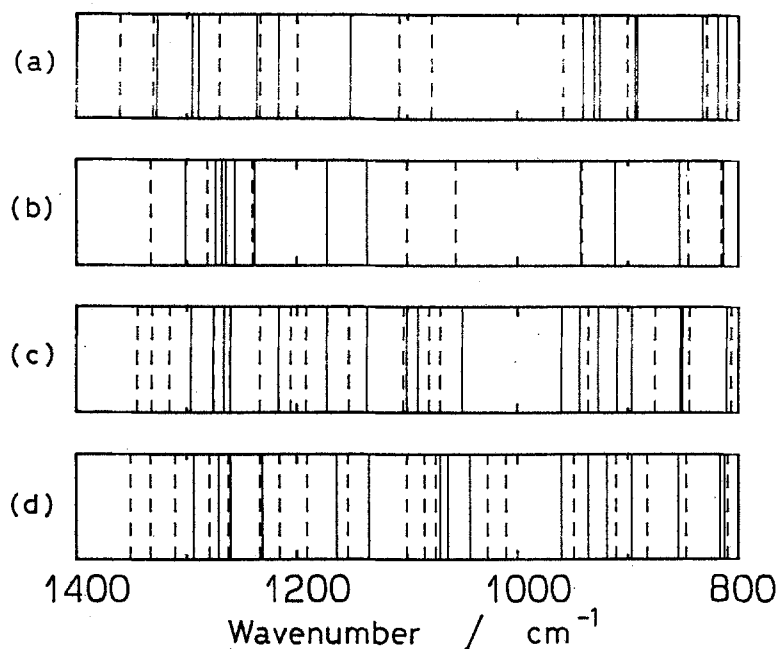


Fig. 4. Positions of the observed bands for A_215C_5 (a) and its NaBr(b), NaI(c) and NaSCN(d) complexes. Solid and broken lines show Raman and IR bands, respectively.

$CH_2-NH-CH_2-CH_2-O-CH_2-CH_2-OCH_3$ to perform a similar analysis of the aza-compound. Calculations were done for 214 conformations, 70 of which are shown in Figure 5, in which positions of vibrational bands are plotted for these conformations. A glance at the figure tells us that the distributions of bands in the $850-1050\text{ cm}^{-1}$ region, where C—C, C—O and C—N skeletal stretching vibrations occur, are very sensitive to local conformations. We can extract useful information on the relationship between local conformation and distribution of bands. Some of these interrelations are collected in Table II, in which characteristic wavenumbers of vibrational bands are given for various local conformations for the $CH_2-CH_2-NH-CH_2-CH_2$ and $O-CH_2-CH_2-O$ moieties. In the following, we discuss the conformation of the azacrown moiety on the basis of the derived interrelationships. One has to be careful in these analyses, since a variety of different local conformations can give vibrational bands in similar regions. The conformations predicted are subject to further examinations for the establishment.

a. Parent A_215C_5

The distribution of bands in the observed spectrum (see Figure 4(a)) is characterized by the presence of a group of bands near 940 cm^{-1} and open windows on both sides. On the higher wavenumber side, bands appear at 1216, 1330 and 1360

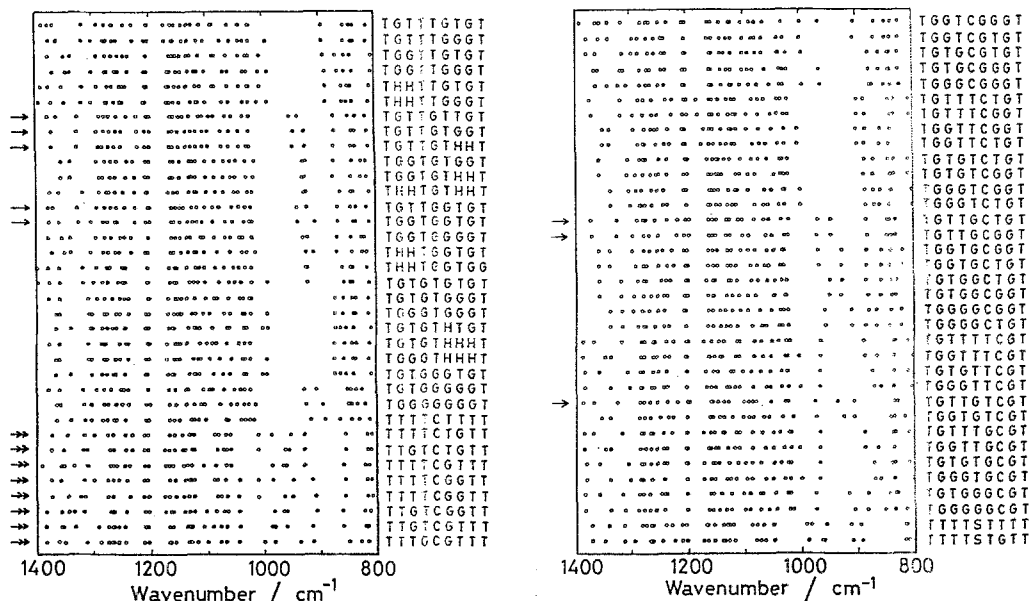
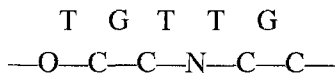
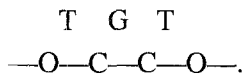


Fig. 5. Positions of the bands calculated for various conformations of the model compound $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$. T, G, H, S, K and C stand for *trans*, *gauche*⁺, *gauche*⁻, *skew*⁺, *skew*⁻ and *cis*, respectively. 70 of 214 calculated conformations are shown. For arrows and double arrows, see text.

cm^{-1} . Comparison with calculated distributions of the bands (Figure 5) tells us that these characteristics are realized, for example, by the conformations designated by arrows. When we extract features common to these, we obtain



and



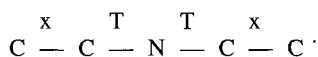
Consulting Table II and a similar table (Table I) in Ref. [3], we have additional, though less certain, relationships (G stands for either G or H, x either for T, G, or H):

- Gxxx (C—C—N—C—C) from 810(R) and 1216(R) cm^{-1} ,
- xTxx (C—C—N—C—C) from 1107(IR) cm^{-1} ,
- xGx (O—C—C—O) from 893(R) and 900(IR) cm^{-1} ,
- Txx (O—C—C—O) from 1289(R) and 1330(IR) cm^{-1} , and

TABLE II. Position of the bands characteristic to various local conformations of the A_215C5 ring.^a

Position of bands (cm^{-1})	Conformation	Position of bands (cm^{-1})	Conformation
1370–1360	xT—Tx	1040–1035	TG—Tx
1360–1345	xG—Tx	1030–1025	TG—Tx
~1325	GT—TG	1025–1020	TT—TT
1320–1310	xT—Tx	1020–1015	TT—GG
1310–1300	xG—Tx	1015–1010	TT—TT
1250–1245	xG—xx	1010–1000	Tx—Gx
1230–1220	Gx—xx	~995	GG—TT
~1180	TT—TT	990–980	TG—TT
~1180	TT—GT	~970	TG—GT
~1170	GG—GG	~960	TG—TT
1180–1150	Tx—xx	~945	TG—GT
~1150	GG—GG	~940	GT—TG
1150–1130	TT—xx	940–935	TG—TT
1140–1125	xG—TG	~935	TT—TT
~1120	xG—TG	930–925	GG—Tx
1120–1110	xT—xx	~920	GG—GG
~1105	xT—xx	~905	Gx—TT
~1100	TT—GG	900–885	Tx—xG
~1095	TG—GT	875–870	Tx—xG
~1085	GG—TG	870–855	TT—GG
~1085	TG—GT	~855	TG—GG
1100–1080	Tx—Tx	855–850	TT—TG
1065–1060	GT—xx	850–840	TG—TG
1055–1050	GG—TG	835–820	GG—xx
1050–1040	TT—Tx	~815	Gx—xx
~1040	GG—GG		

^a xT—Tx shows the conformation for

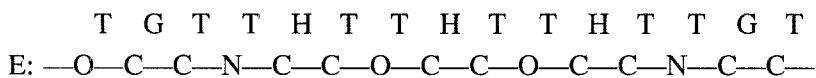


The symbol x stands for either T, G, or H.

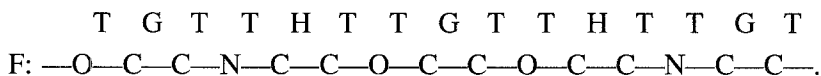
xGxxGx (O—C—C—N—C—C—O) from 832(R) and 828(IR) cm^{-1} .

Given the condition of ring closure and assuming the highest attainable symmetry (C_2), the following two conformations, E and F, are deduced as the most probable

candidates for the compound (note that G and H give equivalent *local* conformations in these cases):



and



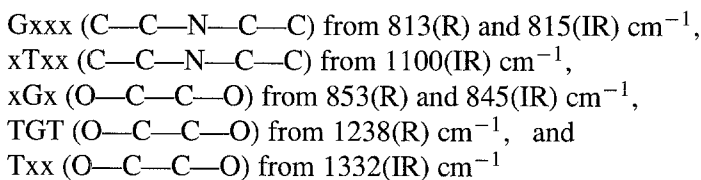
These conformations are shown in Figures 6(a) and (b). However, the present analysis does not permit us to tell which of these two is to be chosen for the structure of parent A_215C5 .

Intramolecular C—H ···O hydrogen bond formation is known to be present in free 18C6 [4]. Similar C—H ···O and/or N—H ···O interactions may be operative in the present case. Normal coordinate calculations in the present study, however, cannot determine the direction of N—H bonds. Examination of the hydrogen bond formation awaits future study.

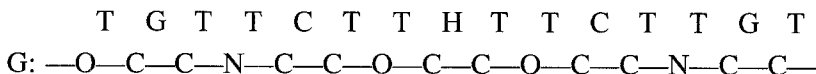
b. Sodium Complexes

The band positions of the azacrown moiety in the NaBr, NaI and NaSCN complexes are mutually similar (see Figures 4(b)–(d)). The most prominent feature in the observed spectra is the presence of bands near 850 cm^{-1} , in place of those near 830 and 890 cm^{-1} for the parent compound.

The distributions of bands featuring these characteristics are best reproduced by the conformations with double arrows in Figure 5. Conditions of ring closure and smooth transformation from the free azacrown, together with additional relationships from Table II and those from Table I in Ref. [3]:



lead to the C_2 structure



as shown in Figure 7, as the most probable candidate for the conformation of the azacrown ring in the three sodium complexes.

The conformational change of the azacrown ring on complex formation of A_215C5 seems to be much smaller compared to that in the A_218C6 case. It is a natural conjecture to regard such a trend as reflecting the smaller extent of

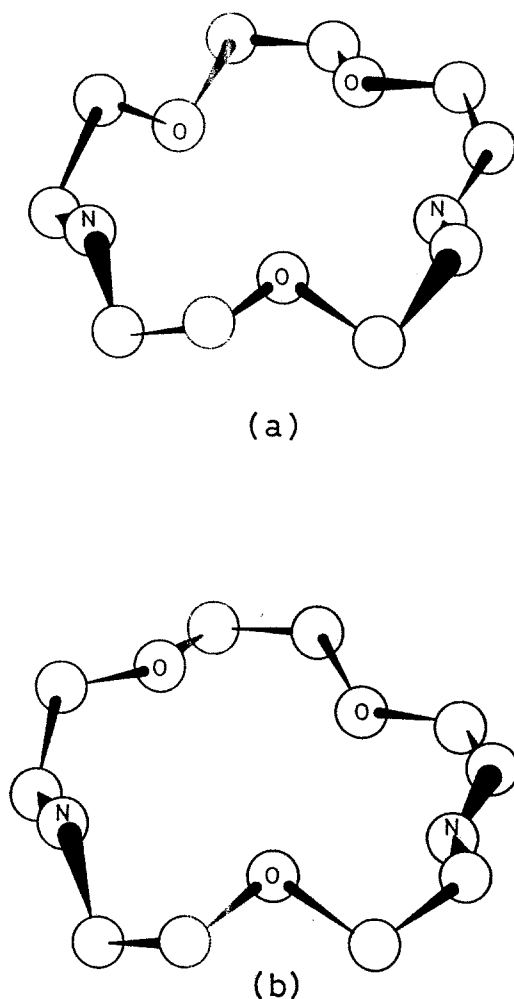


Fig. 6. Projected images of two predicted molecular conformations of 4,13-diaza-15-crown-5.

mismatch in the size of a sodium ion and the cavity of A_215C5 , compared to the case of A_218C6 .

4. Conclusions

The parent azacrown and three sodium complexes (bromide, iodide and thiocyanate) of 4,13-diaza-15-crown-5 (A_215C5) have been studied by Raman/IR spectroscopy and normal coordinate calculations. Only 1 : 1 stoichiometry of the complex was found, in contrast to the case of 4-13-diaza-18-crown-6 (A_218C6) where both 1 : 1 and 2 : 1 complexes were found. Normal coordinate calculations predict the conformations of the azacrown moiety in the parent compound and sodium complexes. The conformational change of the azacrown ring on complex

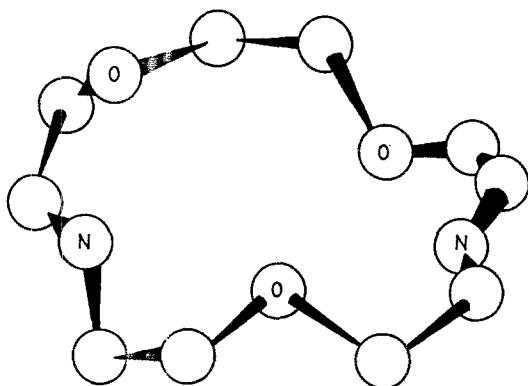


Fig. 7. Projected image of a predicted molecular conformation of the azacrown ring in the 1 : 1 complex of NaX/A₂15C₅, where X = Br, I, or SCN.

formation with a sodium ion seems to be smaller for A₂15C₅ as compared to A₂18C₆, reflecting the extent of mismatch in the size of the azacrown ring and a sodium ion.

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References

1. T. Chujo, I. Saraoka, S. Kato, H. Sato, K. Fukuhara, and H. Matsuura: *J. Incl. Phenom.* **22**, 41 (this issue).
2. H. Matsuura, K. Fukuhara, K. Kaneko, and H. Yoshida: *J. Mol. Struct.* **265**, 269 (1992).
3. H. Matsuura and K. Fukuhara: *J. Polymer Sci., Part B, Polym. Phys.* **24**, 1383 (1986).
4. I. Goldberg: in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.), *Complexes of Crown Ethers with Molecular Guests, Inclusion Compounds*, Vol. 2, Ch. 9, Academic Press (1984), p. 284.