

SELF-CONSISTENT CHARGE AND CONFIGURATION (SCCC) CALCULATIONS ON CROWN ETHERS

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Abstract : The bonding in 12-crown-4 [I], 1, 7-diaza-12-crown-4 [II] tetraaza-12-crown-4 [III] and [12-crown-4] Na⁺ complex was investigated by performing self consistent charge and configuration [SCCC] calculations. These calculations on crown ethers [I] - [III] indicate that the ionic character of bonds between neighbouring pairs of atoms decreases when the oxygen atoms in 12-crown-4 [I] are replaced by nitrogen atoms. They also indicate that the negative gross atomic charges on the oxygen atoms in 12-crown-4 [I] are greater than those on nitrogen atoms in tetraaza-12-crown-4 [III] and this may be the reason why macrocycles and cryptands containing oxygen as the donor atom form more stable complexes with alkali metals than their nitrogen analogues. SCCC calculations on [12-crown-4] Na⁺ complex indicate that 12-crown-4 will form a stable complex with Na⁺ ion at a distance 0.150 nm above the centre of the plane constructed by the four oxygen atoms in the crown ether. This calculation also shows that the bonding between 12-crown-4 and Na⁺ ion has both electro-static and covalent contributions and that a part of the positive charge on Na⁺ ion is neutralised by pulling the electron density all the way from hydrogen atoms through orbital interactions.

1. Introduction

The crown ethers are cyclic compounds essentially made up of $[-CH_2-X-CH_2-]$ -repeating units where X = O, N or S. They have an interesting chemistry and one of their important properties is their ability to selectively take metal cations into their cavities to form stable complexes. They are also important with respect to metal ion transport. Hence the synthesis and characterisation of crown ethers and the study of their interaction with metal ions and ammonium guest molecules have been of interest to many chemists. Crown ethers are also of great interest to the theoretical chemists because they represent the simplest model system which might contain some of the features of enzyme specificity. The crown ethers can usually adopt more than one conformation. The actual conformation adopted depends on the nature of the guest molecule and this conformation may be different from the stable conformation of the uncomplexed crown ether. For example, 1, 4, 7, 10-tetraoxacyclododecane [12-crown-4] [I] can adopt^{4,7,16,17,20} three different conformations. Out of these, the $ag^+g^+ag^+g^+ag^+g^+$ confor-

mation [IV] of C_4 symmetry is observed^{3,4,5} in alkali metal complexes whereas the more stable conformation of uncomplexed 12-crown-4 is⁷ $ag^-g^+ag^+g^+ag^+g^-ag^-g^-$ conformation [V]. We present our results on the self-consistent charge and configuration [SCCC] calculations performed¹ on 12-crown-4 [I] 1,7-diaza-12-crown-4 [II] tetraza-12-crown-4 [III] and [12-crown-4] Na^+ complex [VI] in order to study the bonding in these molecules. The $ag^+g^+ag^+g^+ag^+g^+ag^+g^+$ conformation of 12-crown-4 was taken as the model for our calculations.

2. Computational Method

The method used was the FORTICON⁸ programme of Hoffmann and co-workers.^{1,2,3,5,8} This is an all valence electron calculation [3s and 3p atomic orbitals of sodium atom, 2s and 2p orbitals on second row atoms and 1s on hydrogen atom are used] and was used in its charge iteration mode. Iterations were continued until successive ones produced a change less than $10^{-4}e$ [e = electronic charge] in the charge on any atom. The geometry of 12-crown-4 used was taken from reported X-ray crystallographic data.¹⁶ The same geometry was used for diaza-12-crown-4 [IV], tetraaza-12-crown-4 [V] and [12-crown-4] Na^+ complex. C-H, C-C, C-O, C-N and N-H bond lengths of 0.1091, 0.1536, 0.1430, 0.1472 and 0.1008 nm respectively were used.

3. Results and Discussion

Self-consistent charge and configuration calculation provides four pieces of information, namely the gross atomic charges, the overlap populations, the molecular orbital energy levels and the LCAO expansion of molecular orbitals which could be used to compare the electronic structures of crown ethers and their complexes.

3.1 Gross Atomic Charges

The gross atomic charges are given in Table 1. The negative charges on oxygen atoms and positive charges on carbon atoms in 12-crown-4 and 1,7-diaza-12-crown-4 are in agreement with the more electronegative character of oxygen compared with carbon. The hydrogen atoms attached to carbon are also positively charged. Thus the oxygen atoms withdraw electrons not only from carbon but also from hydrogen through the orbital interaction. Table 1 also shows that the negative charges on oxygen atoms in 12-crown-4 [$-0.305e$] and 1,7-diaza-12-crown-4 [$-0.318e$] are very much greater than those on nitrogen atoms in 1,7-diaza-12-crown-4 [$-0.144e$] and tetraaza-12-crown-4 [$-0.155e$] and this difference in gross atomic charges is also in

Table 1. Gross Atomic Charges in Molecule I – IV

Atom	Gross Atomic Charges (in electron unit)			
	12-crown-4	Diaza-12-crown-4	Tetraaza-12-crown-4	(12-crown-4) Na ⁺ complex
O	-0.305	-0.318	—	-0.375
1 ^C	0.110	0.074	0.062	0.118
2 ^C	0.110	0.097	0.062	0.118
H	—	-0.144	-0.155	—
H(1 ^C)	0.021	0.007	0.003	0.077
H(2 ^C)	0.021	0.016	0.003	0.077
H(N)	—	0.026	0.022	—
Na ⁺	—	—	—	0.328

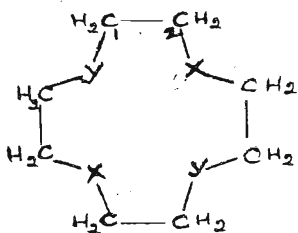
agreement with the electronegativities of oxygen and nitrogen atoms. For the same reason the positive charges on carbon atoms of 1,7-diaza-12-crown-4 and tetraaza-12-crown-4 (Table 1). The positive charges on hydrogen atoms attached to carbon are also very small [almost negligible] in the case of tetraaza-12-crown-4. In other words, overall charge separation in tetraaza-12-crown-4 is very much less when compared with those in 12-crown-4. This explains the observed^{12,13,15,18} marked decrease in stability of the alkali cation complexes with macrocycles and cryptands when oxygen binding sites are replaced by nitrogens.

3.2 The overlap population

Table 2. Overlap populations in molecules I – IV

Bond	Overlap Populations			
	12-crown-4	Diaza-12-crown-4	Tetraaza-12-crown-4	(12-crown-4) Na ⁺ complex
C–O	0.675	0.680	—	0.669
C–H	0.818	0.822	0.824	0.803
C–C	0.831	0.825	0.816	0.823
N–H	—	0.790	0.790	—
C–N	—	0.730	0.739	—
C–Na ⁺	—	—	—	0.124

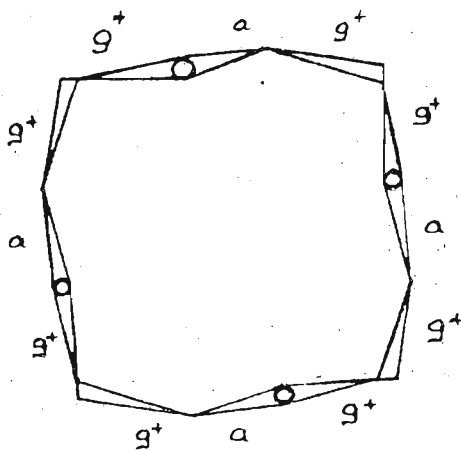
Further insight into the bonding is obtained from the overlap populations. The overlap populations between neighbouring pairs of atoms are given in Table 2. It shows that the overlap populations between carbon atoms and nitrogen atoms in diaza-12-crown-4 [0.730] and tetraaza-12-crown-4 [0.739]



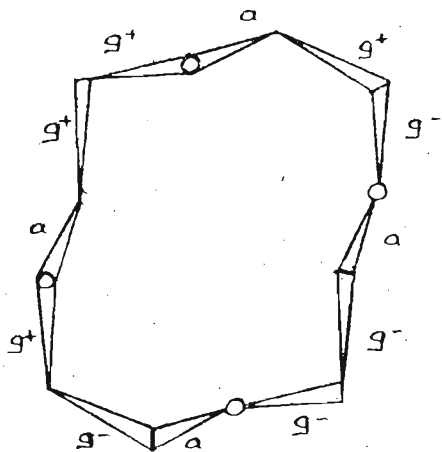
(I) X = Y = O

(II) X = O; Y = NH

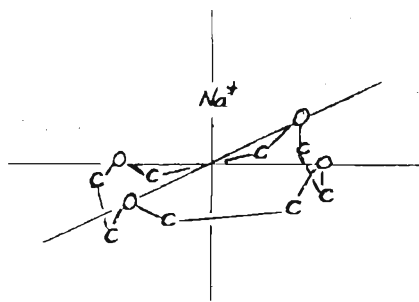
(III) X = Y = NH



(IV)



(V)



(VI)

are greater than those between carbon atoms and oxygen atoms in 12-crown-4 [0.675] and diaza-12-crown-4 [0.680]. This again reflects the more covalent character of C–N bond when compared with C–O bond. Table 2 also shows that the overlap populations between carbon atoms and hydrogen atoms increase when the heteroatoms in 12-crown-4 are changed from oxygen to nitrogen and this is in agreement with the observed decrease in positive charges on carbon and hydrogen atoms.

Table 3. Total Energy of Valence Electrons and Energies of first ten HOMO's and LUMO

Orbital	Energy/eV		
	12-crown-4	Diazo-12-crown-4	Tetraaza-12-crown-4
HOMO	-10.10 (9e)	- 9.90 (5e)	- 9.74(5b ₂)
	-10.12(7b ₁)	-10.40 (4e)	-10.25(12e)
	-10.15(6a ₁)	-10.80(14b)	-10.90(5a ₁)
	-10.81(6b ₁)	-10.95(12a)	-12.40(11e)
	-10.98 (8e)	-12.24(11a)	-12.58(10e)
	-11.19(5a ₁)	-12.43(13b)	-13.59(4b ₂)
	-12.53(5b ₂)	-12.63(12b)	-13.73 (9e)
	-12.58(4b ₂)	-12.92(11b)	-
	LUMO	-0.504(8b ₁)	0.675(13a)
Total Energy of Valence Electrons	-1260.13	-1247.8	-1237.6

3.3 Molecular Orbitals and the Energies of Valence Electrons

The calculated molecular orbital energies of the first ten highest occupied molecular orbitals (HOMO.s) and the total energy of valence electrons of 12-crown-4, diaza-12-crown-4 and tetraaza-12-crown-4 are given in Table 3. It is interesting to note that these calculated molecular orbital energies of 12-crown-4 agrees well with the reported⁹ binding energy values by photoelectron spectra. The LCAO expansion of these molecular orbitals show that, in 12-crown-4, the first eight HOMO.s have contributions from oxygen atoms only and hence could be considered as lone pair molecular orbitals. The ninth and tenth molecular orbitals [$E = -12.53\text{eV}$ and -12.58eV] have contributions from all oxygen atoms and carbon atoms and could be assigned to σ molecular orbitals. Similarly, in diaza-12-crown-4, the first six HOMO.s are found to have the lone pair nature [contributions from oxygen and nitrogen atoms only] whereas in tetraaza-12-crown-4, the first four HOMO.s have the lone pair nature [contributions from nitrogen atoms only]. Table 3 also gives the molecular orbital energies of LUMO of crown ethers.

The LCAO expansion of LUMO.s of crown ethers have contributions from the heteroatoms [oxygen atoms and/or nitrogen atoms] and carbon atoms. Table 3 further shows that the replacement of oxygen atoms by nitrogen atoms in crown ethers decreases the binding energies of valence electrons and increases the molecular orbital energy of LUMO slightly. In other words, the energy difference between HOMO and LUMO increases slightly from 12-crown-4 to tetraaza-12-crown-4.

3.4 [12-crown-4] Na⁺ Complex

SCCC calculations on [12-crown-4]Na⁺ complex were performed by changing the distance of Na⁺ from the centre of the plane constructed by the four oxygen atoms in 12-crown-4 in a direction perpendicular to the plane away from the carbon atoms. The plot of total energy of valence electrons vs the distance is shown in Figure 1. From this plot it is evident that Na⁺ ion is too large an ion to be at the centre of the cavity of 12-crown-4 and that the stable complex is formed when the Na⁺ ion is at a distance 0.150 nm out of plane. This is in agreement with the reported^{1,6} X-ray crystallographic data for bis[12-crown-4]Na⁺ complex. The bonding between the crown ether and Na⁺ ion could be considered to have both electrostatic and covalent contributions. The electrostatic contribution is mainly from the ion-dipole interaction between Na⁺ ion and negatively charged oxygen atoms. The gross atomic charges (Table 1) and the overlap populations (Table 2) of [12-crown-4] Na⁺ complex indicate that there is a reasonable amount of covalent contribution to bonding between Na⁺ ion and 12-crown-4. This is mainly due to charge transfer interaction. Table 1 shows that in [12-crown-4] Na⁺ complex, the negative charges on all oxygen atoms have been increased by 0.070e, the positive charges on carbon atoms have been increased only by a small amount [0.010e] and the positive charges on hydrogen atoms have been increased by 0.056e. This indicates that a part of the positive charge on Na⁺ ion is neutralised by pulling the electron density all the way from hydrogen atoms through orbital interaction. This is also indicated by reduction in the overlap populations between carbon and hydrogen atoms and carbon and oxygen atoms (Table 2).

4. Conclusion

SCCC calculations on crown ethers I – III indicate that the negative gross atomic charges on the heteroatoms decrease when the oxygen atoms in 12-crown-4 [I] are replaced by nitrogen atoms. This explains the observed^{12,13,15,18} marked decrease in stability constants of the alkali cation complexes of crown ethers and cryptands when oxygen binding sites are replaced by nitrogen atoms as the metal ion-oxygen bond in alkali metal complexes could be predominantly ionic. SCCC calculations on [12-crown-4] Na⁺ complex indicate that the arrangement for a stable complex is that with Na⁺ ion at a distance 0.150 nm above the centre of the plane

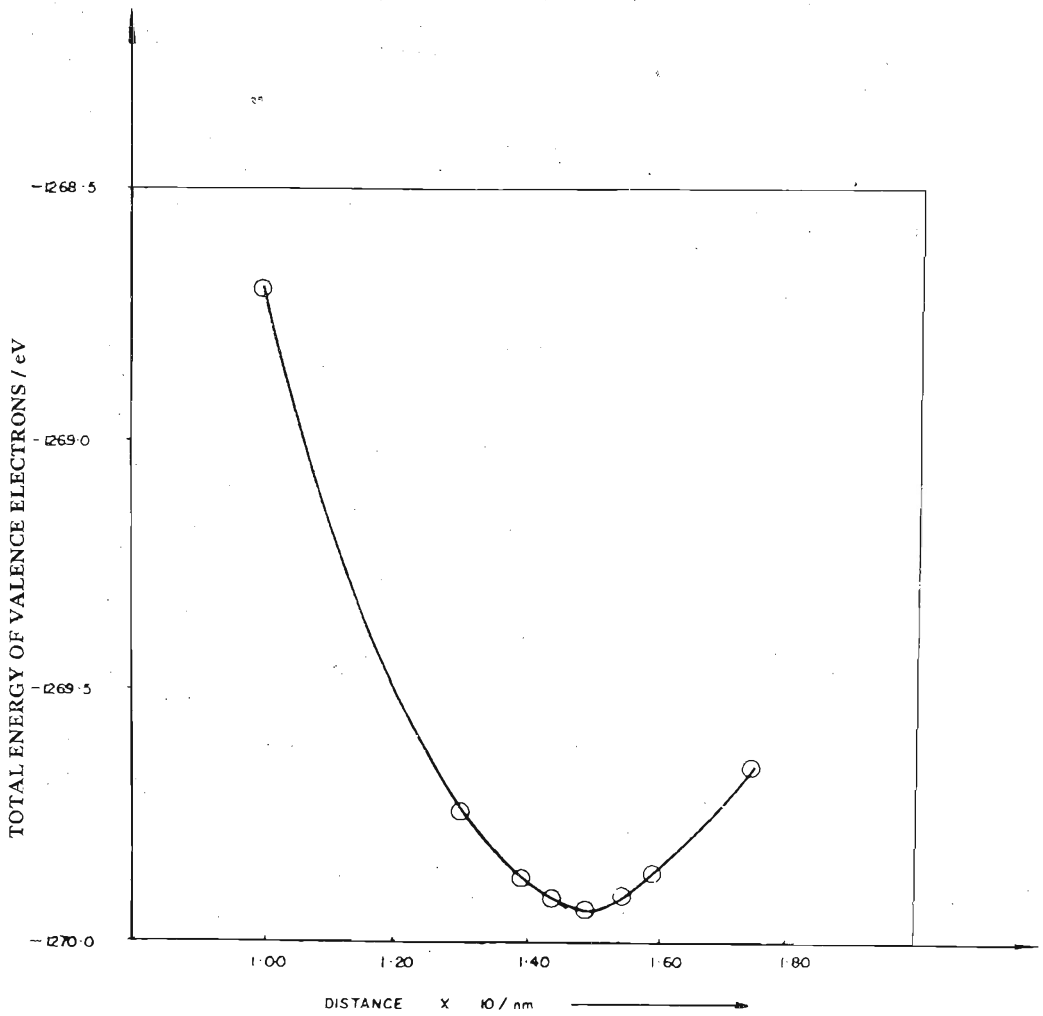


Figure 1. The plot of total energy of valence electrons of (12-crown-4) Na⁺ complex vs the distance of Na⁺ from the centre of the plane constructed by the four oxygen atoms in 12-crown-4.

constructed by the four oxygen atoms in the crown ether. This calculation also shows that the bonding between 12-crown-4 and Na^+ ion has both electrostatic and covalent contributions and a part of the positive charge on Na^+ ion is neutralised by pulling the electron density all the way from hydrogen atoms through orbital interactions. The observation that the aza crown ethers form stable complexes^{10,11,14,19} with transition metal ions than with alkali metal ion is consistent with the lower charge and higher overlap populations of carbon and nitrogen in crown ethers.

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