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# Novel Macrocycles. Part 6. Synthesis, Structures and Cation Binding from Optical Spectroscopy of 9,10-Anthraquinone-crown Ethers ⋆

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**Abstract.** The 9,10-anthraquinone-[12]crown-4, [15]crown-5 and [18]crown-6 derivatives were synthesized from 1,2-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone which were condensed with dihalides or ditosylates of polyethylene glycols in alkali carbonate/DMSO. The 9,10-anthraquinone derived polyoxacyclo-alkanes were characterized with IR, mass spectrometry, $^{1}$H, $^{13}$C spectroscopy and elemental analysis. The cation binding properties were studied with UV-vis spectroscopy. The association constants found in acetonitrile were selectively dependent on the cation radius and macrocycle size as well as the molecular structures. The observed results from UV-vis studies, however, showed the stronger complexing role of 1,2-derived macrocycles compared to those of 1,8-derivatives. The theoretical conformational analysis and the energy optimisations of the 9,10-anthraquinone-macrocycles carried out with MM+ method explained the binding results.

**Key words:** macrocycles, 9,10-anthraquinones, optical UV-vis and fluorescence spectroscopy, ion binding

## 1. Introduction

Several types of macrocyclic ethers have been designed and characterised since their discovery by Pedersen [1]. The chromogenic macrocycles designed have been used for analytical applications since the chromo- and fluoroionophore type of macrocycles have been found to be sensitive sensors for ion binding [2–5]. We have reported the synthesis and cationic recognition of some fluorogenic crown ethers during our work on macrocycles [6]. 6,7- and 7,8-Dioxabenzo-$\alpha$-pyrone derived macrocycles synthesized have exhibited cation dependent fluorescence spectral alterations in acetonitrile due to complex formation [7–9].

We now extend our study on novel macrocycle structures with chromo- and fluorogenic moieties in order to investigate the macrocycle-ion binding properties with optical sensors. We have studied 9,10-anthraquinone derivatives of well known chromophores which are quite stable in strong acids and at elevated temper-

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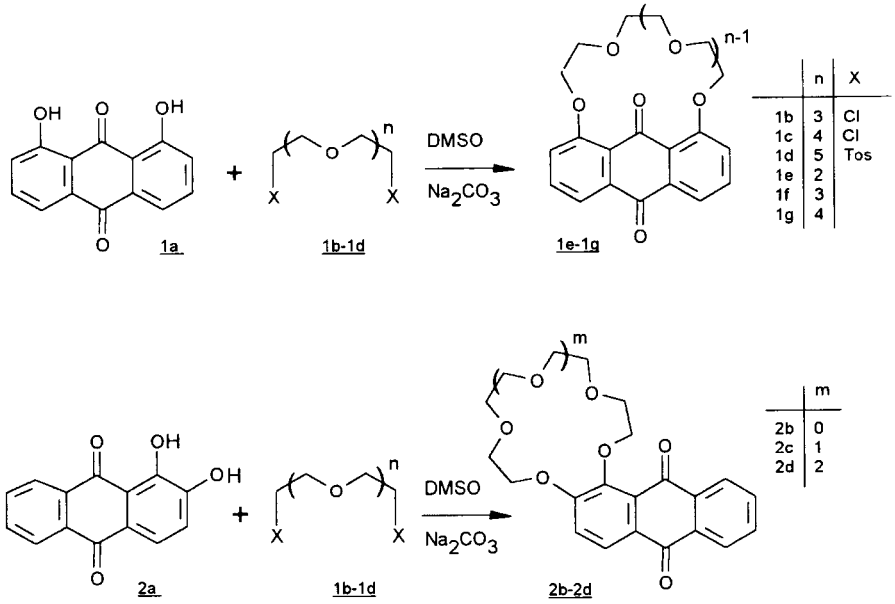



*Scheme 1.*

atures as the dyes which exhibit the visible absorptions due to $n \rightarrow \Pi^*$ transitions [10].

The present work deals with the synthesis, spectral characterisation, molecular mechanics calculations and optical studies of the complex formation of 9,10-anthraquinone derivatives of [12]crown-4, [15]crown-5 and [18]-crown-6. The two sets of macrocycles were obtained from 1,8-dihydroxy-9,10-anthraquinone and 1,2-dihydroxy-9,10-anthraquinone, Scheme 1.

In fact, both series of anthraquinone macrocycles exhibited interesting optical responses upon cation binding in solution. The electronic absorption spectra of 1,2-macrocycle-anthraquinones have shown a blue shift of the absorption maxima due to complex formation in the presence of alkali cations while the 1,8-macrocycle derivatives have given a small red shift with a peak broadening upon cation complexation.

The fluorescence spectra of 1,2-macrocycle-9,10-anthraquinones are influenced by the cation binding as well as the 1,8-derivatives, however, the roles found are not satisfactory. We also studied the geometry optimisation of the conformational sequences of the polyoxaethylene backbone of the macrocycles and estimated the relative torsional barriers with the MM+ force field method using commercial software.

## 2. Experimental

### 2.1. SYNTHESIS, STRUCTURE AND SPECTRAL DATA

Chemicals were from Fluka unless otherwise cited. The mps are uncorrected. IR spectra were recorded as KBr pellets with a Jasco FT-IR spectrometer, model 5300. El mass spectra were obtained with a Fisons instrument, model ZapSpec with a direct inlet probe. $^{13}C$, $^{1}H$ and 2D HETCORR and COSY NMR spectra were recorded with a Bruker instrument model Avance 400 in $CDCl_3$ and TMS was the internal reference.

Dihydroxy-9,10-anthraquinones and pentaethyleneglycol ditosylate were from Fluka and used without further purification. DMSO was from Merck. The dichlorides of polyglycols were available to us from an earlier study [8, 9]. 1,2- or 1,8-Dihydroxy-9,10-anthraquinone (4.80 g, 20 mmol), DMSO (50 mL), alkali carbonate ($Li^+$, $Na^+$ or $K^+$) (40 mmol) and 1,8-dichloro-3,6-dioxaoctane (20 mmol) (or 1,11-dichloro-3,6,9-trioxaundecane or penta-ethyleneglycol ditosylate) were stirred in a 100 mL flask whilst heating at 80–90 °C for 80–90 h. The mixture was acidified with dilute HCI (2M, 40–50 mL) and the raw product extracted with $CHCl_3$ ($3 \times 50$ mL) was dried with dry alumina, (Merck) filtered and concentrated. The raw material was chromatographed with basic alumina, (Merck) with $CHCl_3$ or $CH_2Cl_2$ and recrystallised mostly from THF. Data of compounds **1e**–**2d** are given in Table 1.

Accordingly, 1,8-dihydroxy-9,10-anthraquinone, **1a**, reacted with 1,8-dichloro-3,6-dioxaoctane, **1b**, and 1,11-dichloro-3,6,9-trioxaundecane, **1c**, and pentaethyleneglycol ditosylate, **1d**, afforded **1e, 1f** and **1g** respectively**.** 1,2-dihydroxy-9, 10-anthraquinone, **2a**, reacted with **1b**, **1c** and **1d** and afforded **2b, 2c** and **2d.** The yields and the spectral data of the products are shown in Tables 1–3. The NMR spectral results for the structural identification of the compounds **1e–2d** are separately given in Tables 2 and 3 (see Scheme 1). However, no first order homonuclear coupling constants were observed [13].

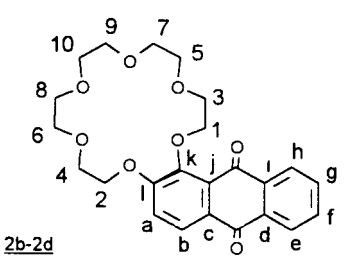
### 2.2. OPTICAL SPECTROSCOPY MEASUREMENTS

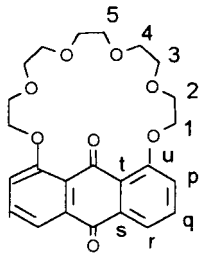
Optical spectra were obtained with a Philips UV-vis spectrophotometer, model Lambda 2 in 10 mm silica cells in dry acetonitrile ($H_2O\% \ll 0.05$) at room temperature. The absorbance of the 9,10-anthraquinone macrocycles were determined in the presence of various salt concentrations, $[A_0^+]$, dissolved in acetonitrile and the mole fraction of complexed macrocycle, $P_L$, were estimated. The inverse of initial cation concentrations, $1/[A_0^+]$ were plotted versus experimentally found $(1 - P_A)(1 - P_L)/(P_L)$ values and the inverse of the slope of the line gave the, $K_a$ value ($\ln K_a$; $\pm 0.02$) according to Equations (1) and (2), Table 4, Figures 2 and 3. The geometry optimization studies were performed on a PC with MM+ force field calculations using HyperChem®, Ver 4.0, see Table 5 [14].

*Table I.* The structural and spectroscopic data of the 9, 10-anthraquinone macrocycles.

| Comp. | Yield | mp | IR ($cm^{-1}$) | Calcd % C | Found C % | Calcd % H | Found H % | Mass (m/z) |
|---|---|---|---|---|---|---|---|---|
| **1e** | 20 | 149 | 2940, 1680, 1130, 1080, 760 | 67.80 | 67.71 | 5.12 | 5.02 | 354, 311, 266 |
| **1f** | 28 | 128 | 2920, 1675, 1120, 1070, 780 | 66.33 | 66.30 | 5.57 | 5.60 | 398, 355, 266 |
| **1g** | 18 | 75 | 2960, 1680, 1130, 1080, 785 | 65.15 | 65.08 | 5.95 | 5.99 | 442, 399, 266 |
| **2b** | 22 | 175 | 2950, 1690, 1280, 1050, 740 | 67.80 | 67.84 | 5.12 | 5.15 | 354, 266, 240 |
| **2c** | 30 | 161 | 2940, 1670, 1270, 1070, 900 | 66.33 | 66.35 | 5.57 | 5.55 | 398, 266, 240 |
| **2d** | 25 | 107 | 2960, 1680, 1270, 1120, 870 | 65.15 | 65.19 | 5.93 | 5.97 | 442, 266, 240 |

*Table II.* 100 MHz $^{13}C$ NMR data of 9,10-anthraquinone macrocycles in $CDCl_3$, referenced to TMS [a]




| Comp. | v-1 | v-2 | v-3 | v-4 | v-5 | p | q | r | s | t | u | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1e** | 70.99 | 69.24 | 70.21 | – | – | 133.3 | 120.4 | 119.4 | 135.0 | 127.6 | 157.8 | | | | | | | | | | | |
| **1f** | 71.00 | 69.25 | 70.25 | 70.80 | – | 134.7 | 120.1 | 119.7 | 136.7 | 127.0 | 159.5 | | | | | | | | | | | |
| **1g** | 71.15 | 69.29 | 70.37 | 70.83 | 72.90 | 134.1 | 123.9 | 121.0 | 135.5 | 127.4 | 159.0 | | | | | | | | | | | |
| Comp. | v-1 | v-2 | v-3 | v-4 | v-5 | v-6 | v-7 | v-8 | v-9 | v-10 | a | b | c | d | e, h | f | g | i | j | k | l | |
| **2b** | 76.91 | 71.09 | 72.52 | 71.62 | 74.20 | 73.10 | – | – | – | – | | | | | | | | | | | | |
| **2c** | 73.32 | 61.58 | 72.78 | 71.10 | 72.56 | 72.45 | 73.02 | 75.57 | – | – | 117.7 | 125.2 | 128.5 | 127.7 | 126.7 | 133.5 | 133.8 | 133.0 | 135.2 | 150.2 | 160.0 | |
| **2d**[b] | 73.02 | 63.82 | 70.46 | 69.39 | 70.83 | 70.52 | 70.85 | 70.09 | 71.23 | 71.6 | 117.1 | 125.2 | 127.2 | 127.5 | 127.1 | 133.5 | 133.9 | 133.1 | 135.5 | 150.1 | 159.9 | |

[a] 2D HETCOR and COSY spectra of the compounds were evaluated.
[b] 500 MHz in $CDCl_3$.

*Table III.* 400 MHz [1]H NMR data of 9,10-anthraquinone macrocycles in $CDCl_3$, referenced to TMS [b].

| Comp. | v-1 | v-2 | v-3 | v-4 | v-5 | p | q | r | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1e** | 4.24, 4H, m | 3.92, 4H, m | 3.76 4H, s | – | – | 7.20, 2H, d | 7.57, 2H, t | 7.74, 2H, d | | | |
| **1f** | 4.18, 4H, t | 3.93, 4H, t | 3.81 4H, t | 3.74 4H, t | – | 7.20, 2H, d | 7.50, 2H, t | 7.79, 2H, d | | | |
| **1g** | 4.18, 4H, t | 3.98, 4H, t | 3.86 4H, t | 3.72 4H, t | 3.66 4H, s | 7.22, 2H, d | 7.55, 2H, t | 7.80, 2H, d | | | |
| Comp. | v-1 | v-2 | v-3 | v-4 | v-5 | v-6 or 6, 7, 8 | v-8, 9, 10 | a | b | g, f | e, h |
| **2b** | 4.35, 2H, t | 4.24, 2H, t | 4.04, 2H, m | 3.96, 2H, m | 3.89, 2H, m | 3.86, 2H, m | – | 7.24, 1H, d | 8.15, 1H, d | 7.76, 2H, p | 8.25, 2H, q |
| **2c** | 4.33, 2H, t | 4.27, 2H, t | 4.11, 2H, t | 4.01, 2H, t | 3.84, 2H, m | 3.77, 6H, m | – | 7.24, 1H, d | 8.15, 1H, d | 7.76, 2H, p | 8.25, 2H, q |
| **2d**[b] | 4.35, 2H, t | 4.29, 2H, t | 4.08, 2H, t | 4.05, 2H, t | – | 3.79, 6H, m | 3.67, 6H, m | 7.24, 1H, d | 8.15, 1H, d | 7.76, 2H, p | 8.25, 2H, q |

[a] See Table 2 for the molecule assignments.
[b] 500 MHz in $CDCl_3$.

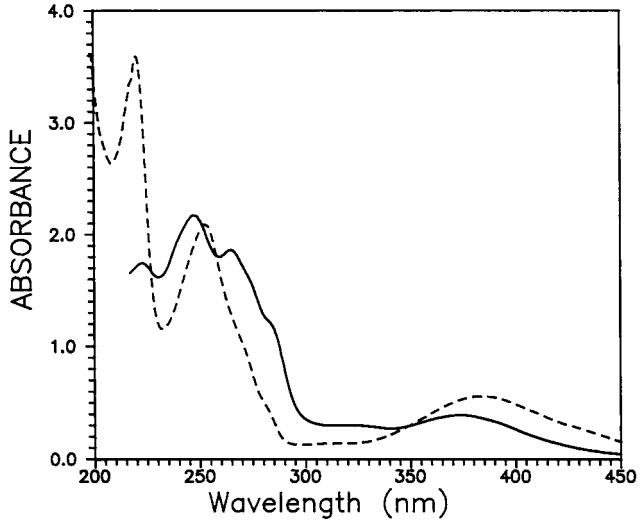



*Figure 1.* The UV-vis spectra of compounds **2c**, (——) and **1f**, (. . . ) in acetonitrile, ($7.50 \times 10^{-5}$ mol $L^{-1}$).

## 3. Results and Discussions

### 3.1. Optical Spectroscopy of Cation Complexing

Optical sensors for ions and molecules are of growing interest due to the increasing demand for optical monitors particularly for chemical and environmental problems and for biological systems [10]. On the other hand, the photochemistry of anthracene has been interesting for the design of the chromophores while the 9,10-anthraquinone derivatives were recently studied [10–12].

In this work we originally reported two new recognition aspects in macrocyclic chemistry. Primarily, the use of nonionic chromogenic macrocycles without hetero atoms exhibiting an isosbestic point on the UV-vis spectra upon complex formation is less known in macrocyclic chemistry as discussed by Vögtle [3]. Next is the linear regressions for estimation of the association constants of 1 : 1 complexing which is used for the first time in the presence of the non-equivalent initial concentrations of the cation and the ligand in solution, Equations (1) and (2) [7].

A highly conjugated 9,10-anthraquinone group attached to a macrocycle, particularly the 1,2-macrocycle-anthraquinones, were found to be good probes for cation binding studies using UV-vis spectroscopy in solution. The $\Pi \rightarrow \Pi^*$ transitions of 9,10-anthraquinone macrocycles observed around 270 nm as well as the $n \rightarrow \Pi^*$ transitions observed at 370 nm are clearly influenced upon cation complexing in acetonitrile. This is observed only in some nonhydroxylic polar solvents, Figure 1. However, the electron withdrawing effect of such conjugation on macrocycle backbone diminished the cation binding power of the macrocycles.

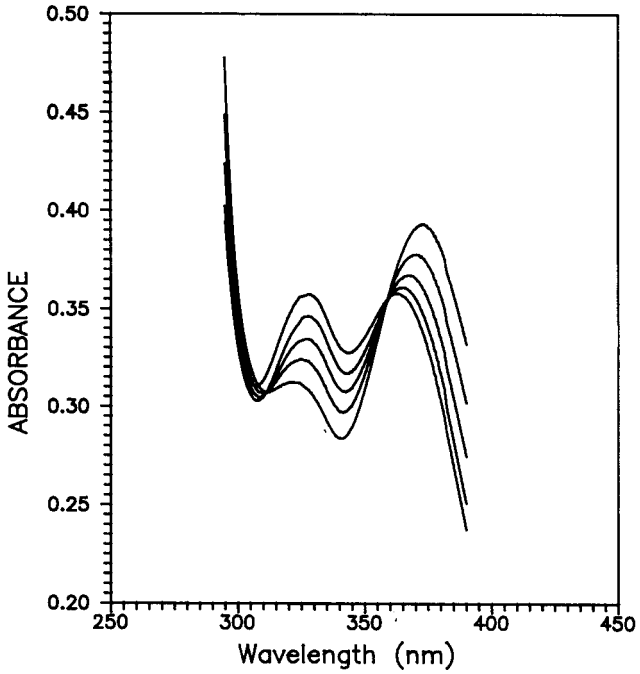



*Figure 2.* The $NaClO_4$ titration of compound **2c** ($7.50 \times 10^{-5}$ mol $L^{-1}$) observed with UV-vis spectra in acetonitrile with various salt concentrations (0.22, 1.13, 2.40, 5.06 and 11.06 $\times 10^{-5}$ mol $L^{-1}$).

The cation binding study of compounds **2b–2d** were conducted with UV-vis spectroscopy in acetonitrile. The complexing macrocycle solutions in acetonitrile exhibited two maxima at $\lambda_{max}$ = 373 nm for the free macrocycle and at $\lambda_{max}$ = 333 nm due to a cationic complex. The equilibrium of the free and cation complexing species allowed us to estimate the binding powers, see Figures 2 and 3. The association constants, $K_a$, were calculated using the absorbance measurements of free and complexed ligands as in Equations (1) and (2). $[A_0^+]$ and $[L_0]$ are the initial concentration of a cation and a ligand respectively, $P_L = [A^+L]/[L_0]$ is the mole fraction of complexed ligand and, $P_A = [A^+L]/[A_0^+]$ is complexed cation and $[L_0] \neq [A_0^+]$, see Figure 2 and Table 4 [6, 7].

$$K_a = [A^+L]/[A^+][L], \tag{1}$$

$$1/\{K_a[A_0^+]\} = (1 - P_L)(1 - P_A)/P_L. \tag{2}$$

In this work, the binding powers of cations, $Li^+$, $Na^+$, $K^+$ and $Mg^{2+}$ obtained by optical spectroscopy were consistent with the 1,2-anthraquinone-macrocycle sizes. The large macrocycles better complexed with large radii ions and small macrocycles with small radii cations. However, $Li^+$ showed a higher effect for 15-crown-5 derivatives that is not uncommon for the cation, Table 4. On the other

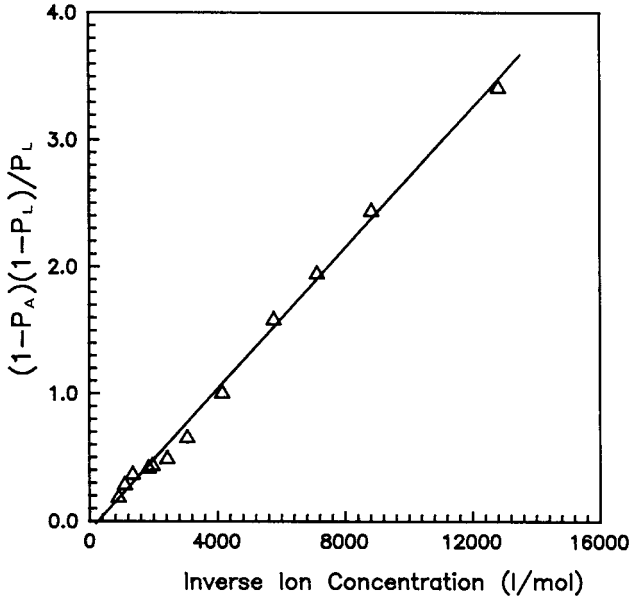



*Figure 3.* The plot of inverse concentration, $1/[L_O]$ of $NaClO_4$ versus $(1-P_L)(1-P_A)/P_L$ for compound **2c** ($7.5 \times 10^{-5}$ mol $L^{-1}$) for the estimation of (1 : 1) association constant, $\ln K_a$, of the complex.

*Table IV.* The 1 : 1 binding data from UV-vis spectra for 9,10-anthraquinone-1,2-crowns at 298 K in $CH_3CN$.

| Cation | Macrocycle | $\lambda_{max}$ (nm) | $\xi_{\lambda_{max}}$ | $\ln K_a$ | $-\Delta G$ (kJ/mol) |
|---|---|---|---|---|---|
| Free | Compound **2c** | 373 | 2477 | – | – |
| $NaClO_4$ | Compound **2c** | 333 | 1723 | 8.19 | 20.02 |
| KSCN | Compound **2c** | 333 | 1732 | 6.31 | 15.56 |
| $LiClO_4$ | Compound **2c** | 333 | 2007 | 9.73 | 23.99 |
| $MgClO_4$ | Compound **2c** | 333 | 1606 | 6.24 | 15.39 |
| Free | Compound **2d** | 373 | 2802 | – | – |
| KSCN | Compound **2d** | 332 | 1520 | 8.11 | 20.00 |
| NaSCN | Compound **2d** | 332 | 1502 | 7.50 | 18.50 |

hand, 1,8-macrocycle-1,9-anthraquinone derivatives showed a small complexing effect using the UV-vis spectra absorption at 383 nm, probably due to the hindering role of the carbonyl groups.

Steady-state fluorescence spectra of the free and cationic solutions of the compounds were examined. Strong quenching effects were observed on the fluorescence spectra of both 1,8- and 1,2-macrocycles due to concentration limits, over

$10^{-5}$ mol $L^{-1}$. We were, therefore, not able to report any binding effect using fluorescence spectroscopy.

The 9,10-anthraquinone end groups of some podand molecules and some similar macrocycles with 9,10-anthraquinone groups have been investigated by Gokel *et al*. They have, however, followed a different route for the synthesis working on redox switched-cation binding properties [11].

### 3.2. Conformational Geometry Optimisations

The encapsulation role of the macrocycles is a function of the conformation of the —$CH_2CH_2O$— backbone where the oxygen atoms are expected to be oriented to bind the central cation. However, the size of the macrocycle is important for the minimum energy of the ensemble conformation performing maximum enthalpy of ion binding [1–3]. Computational methods have been recently increasingly used for molecular mechanics or semi-empirical calculations of macrocycles and detailed descriptions have been provided for the important conformations in gas or condensed phases, in particular for cation binding [14–16].

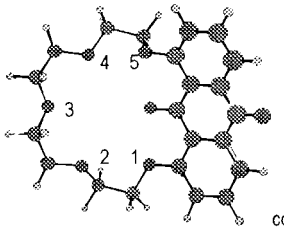
The structures of macrocycles obtained from dihydroxy-9,10-anthraquinones were interesting since the cyclic backbone motions are restricted due to the aromatic carbonyls. We investigated the macrocyclic backbone geometry optimizations with theoretical molecular mechanics, MM+ force field calculations using steepest descent supplied by HyperChem® [13–15].

We examined the barrier energy of the dihedral angles of a unit conformation of the macrocycle backbone with the geometry optimization method using commercial software. The optimised diamond lattice structure energies of such compounds estimated with steepest descent gave the best values although, other force field methods were tried. We surveyed all probable conformational sequences of the macrocycle backbones and the O—$CH_2CH_2$ unit groups were observed to possess *anti*, ±*gauche*, *anti* ($a$, $\pm g$, $a$) conformational unit sequences with a minimum barrier energy. The dihedral torsional energies for 4 and 5 oxygen member macrocycles were the lowest whilst the six oxygen members of the *all* $a$, $\pm g$, $a$ sequences interestingly exhibited higher energies as displayed in Tables 5 and 6 [13, 14].

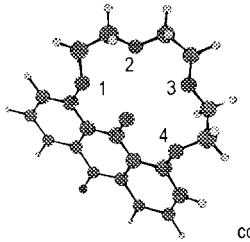
The results of such estimations, however, explained the preferential complex formation role of the compounds. Namely, the 1,2-anthraquinone macrocycles showed the usual binding effect similar to that for 1,2-benzocrown ethers while the 1,8-anthraquinone macrocycles showed poor ion binding effect due to the steric role of the aromatic carbonyl which is almost coplanar with the ring oxygen atoms especially for the larger rings, as displayed in Table 5.

The geometry optimization results are interesting since both the aliphatic and aromatic parts of the molecules are coplanar in most of the structures, as given in Table 6. The 1,2-macrocycle chains, though, not completely free from the effect of the carbonyl groups of 9,10-anthraquinone are better cation binding systems. However, 9,10-anthraquinone macrocycles are more rigid and the torsional energies are

*Table V.* The MM+, geometry optimizations of Compounds **1e**–**1g**, energies are kJ $Mol^{-1}$ (±0.1).*




compound 1f

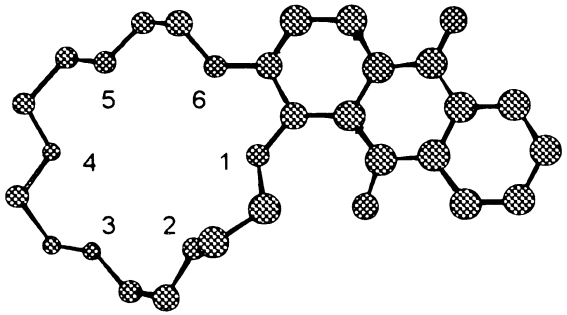



compound 1e

| Compound | 1,2-angle | Energy | 2,3-angle | Energy | 3,4-angle | Energy | 4,5-angle | Energy | 5,6-angle | Energy |
|---|---|---|---|---|---|---|---|---|---|---|
| **1e** | 63.78 | 38.0 | −66.11 | 17.4 | 58.65 | 40.3 | – | – | – | – |
| **1f** | −56.34 | 28.9 | 69.65 | 17.6 | −59.83 | 17.3 | −49.39 | 29.6 | – | – |
| **1g** | 68.22 | 41.8 | 52.43 | 26.3 | −62.40 | 13.5 | −57.15 | 22.1 | −77.92 | 49.6 |

* The charge densities were not included in the geometry optimisation calculations.

*Table VI.* The MM+, geometry optimizations of Compounds **2b**–**2d**, no hydrogens are shown, energies are kJ $Mol^{-1}$.*




| Compound | 1,2-angle | Energy | 2,3-angle | Energy | 3,4-angle | Energy | 4,5-angle | Energy | 5,6-angle | Energy |
|---|---|---|---|---|---|---|---|---|---|---|
| **2b** | −69.41 | 43.3 | 62.15 | 32.4 | −52.33 | 26.4 | – | – | – | – |
| **2c** | −55.99 | 28.8 | 55.71 | 17.5 | −55.78 | 14.6 | 52.83 | 16.8 | – | – |
| **2d** | 72.57 | 31.4 | 47.12 | 22.1 | 63.64 | 20.4 | −56.26 | 25.1 | 42.28 | 28.1 |

* The charge densities were not included in the geometry optimization calculations.

higher compared to those found for 1,2-benzocrown ethers estimated with similar methods [14]. The minimum energy of conformational sequences are the *all* $a$, $\pm g$, $a$ form which is a requirement for a macrocycle to form a stable complex.

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