Pergamon

Tetrahedron 55 (1999) 14459–14466

TETRAHEDRON

Complexation of Crown and Diamond Conformers of Octamethoxyresorc[4]arene with Strong Electron Acceptors

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Received 15 July 1999; revised 17 September 1999; accepted 1 October 1999

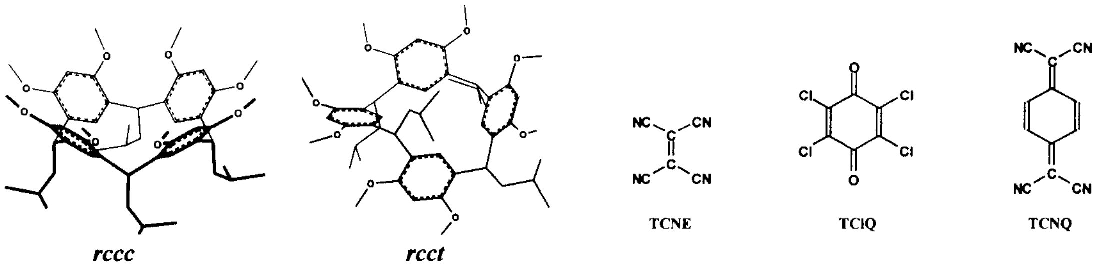
Abstract: Complexation of octamethoxyresorc[4]arene with strong electron acceptors was investigated. The compositions of complexes were determined using the Job method. The formation constants for these complexes were evaluated by the nonlinear least-squares regression analysis method. The structures of the complexes with TCNE are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: *octamethoxyresorc[4]arenes, CT complexes, structure*

Introduction

The synthesis of calixarenes and their use in physicochemical studies is one of most vigorously developing areas of supramolecular chemistry[1]. While the complexation properties of calixresorc[4]arenes are already well documented[2], the complexation properties of octamethoxyresorc[4]arenes are still relatively unknown. The Lewis acid-catalyzed synthesis of these compounds[3] leads to formation of three conformers, of which only the crown and diamond (*rccc* and *rcct*, respectively) conformers are formed in satisfactory yield.

The work presented here is part of our current studies of the complexation properties of calixresorc[4]arenes[4]. This paper deals with complexation of crown (rccc) and diamond (rcct) conformers of octamethoxyresorc[4]arene (OMRA) with tetracyanoethylene (TCNE), tetrachlorobenzoquinone (TClQ), and tetracyanoquinodimethane (TCNQ) – see Scheme 1.



Scheme 1

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PII: S0040-4020(99)00891-1

Results and Discussion

The investigated conformers of OMRA form complexes with the above-mentioned electron acceptors. New absorption bands appear in the UV-VIS spectrum of the chloroform solution of TCNE after addition of the crown conformer of OMRA (Fig. 1).

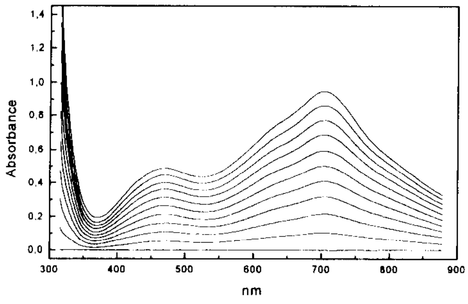


Fig. 1. Changes in the absorption spectrum of the TCNE solution in chloroform resulting from addition of the crown conformer of OMRA. Concentration of TCNE is $5\cdot10^{-2}$ M, concentration of OMRA varies from $3.8\cdot10^{-3}$ to $1.1\cdot10^{-2}$ M.

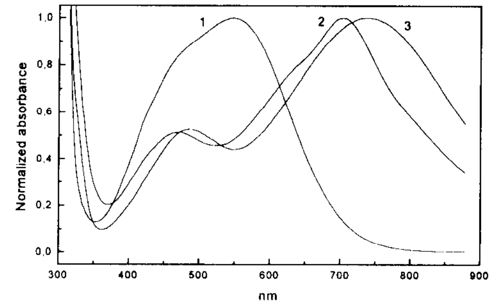


Fig. 2. A comparison of standardized absorption spectra in chloroform, of TCNE complexes with: 1) 1,3-DMB; 2) OMRA crown conformer; 3) OMRA diamond conformer.

Similar absorption bands appear after addition of the diamond conformer of OMRA to the chloroform solution of TCNE. The slight differences between the absorption spectra of these complexes with TCNE can be seen in Fig. 2. These spectra are compared to the absorption spectrum of the complex of 1,3-dimethoxybenzene (1,3-DMB) with TCNE in chloroform. The CT bands of the TCNE - OMRA conformers differ both in the peak wavelength and shape. The CT band for the complex of TCNE with the diamond conformer of OMRA has the greatest bathochromic shift (λ_{max} = 738 nm). Next, the maximum of the CT band for the complex of TCNE with the crown conformer of OMRA appears at λ_{max} = 705 nm. The different shapes of the absorption bands indicate that the geometry of the OMRA conformers plays a role in the interactions with TCNE in chloroform. This affects the appearance of the absorption band of the complex formed. Using the Job method[5], the complexes of OMRA conformers with TCNE in chloroform were found to have 1:1 stoichiometry (Fig. 3).

The formation constants of the discussed complexes were evaluated by nonlinear least-squares regresion analysis[6]. The results are given in Table 1. These calculations confirm the 1:1 stoichiometry of the complexes.

The investigated conformers of OMRA also form complexes with TClQ in chloroform which result in new absorption bands in the UV-VIS spectra (Fig. 4). However, the changes in absorption spectra resulting from complexation are not as distinct as in the case of TCNE complexes. The long-wave absorption band of the OMRA - TClQ complexes is only slightly shifted compared to that of the 1,3-DMB - TClQ complex. Accordingly, the formation constants of these complexes are much lower than the formation constants for

OMRA - TCNE complexes (Table 1). The calculation testifies to the 1:1 stoichiometry of both the OMRA complexes and the 1,3-DMB complexes.

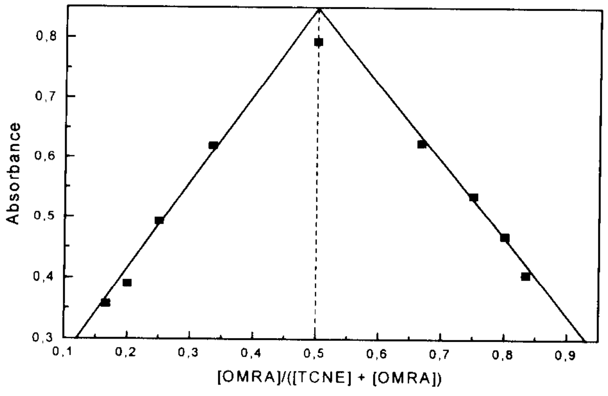


Fig. 3. Determination of the composition of TCNE – OMRA crown conformer complex by the Job method. Total concentration of OMRA and TCNE is 5·10^{-2} M.

Table 1. Formation constants (K [M^{-1}]) of the OMRA complexes and the 1,3-dimethoxybenzene complexes with: TCNE, TClQ and TCNQ at 25°C.

Electron Acceptors	Crown Conformer K [M^{-1}]	Diamond Conformer K [M^{-1}]	1,3-Dimethoxybenzene K [M^{-1}]
TCNE	4.00 ± 0.04	2.92 ± 0.01	1.49 ± 0.01
TClQ	0.68 ± 0.02	0.49 ± 0.03	1.00 ± 0.07
TCNQ	0.50 ± 0.02	-	0.38 ± 0.02

Still weaker complexes are formed when the electron acceptor is TCNQ. Only 1,3-DMB and OMRA crown conformer complex TCNQ in chloroform. This results in very weak absorption bands (Fig. 5). The calculation based on nonlinear least-squares regression analysis indicates the 1:1 stoichiometry of these complexes.

The results presented here indicate formation of 1:1 complexes between the OMRA conformers and the electron acceptors studied. ^{1}H-NMR spectra and quantum-mechanical calculations were performed for the OMRA-TCNE complex in order to propose a structure for these complexes.

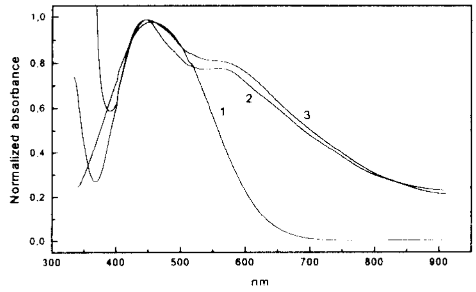


Fig. 4. A comparison of standardized absorption spectra in chloroform, of TCIQ complexes with: 1) 1,3-DMB; 2) OMRA crown conformer; 3) OMRA diamond conformer.

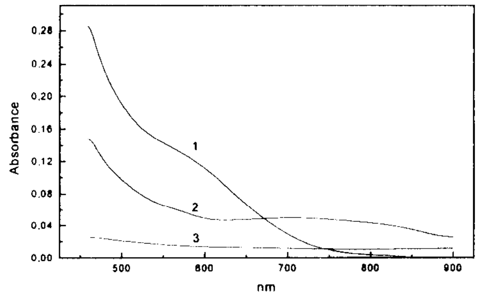
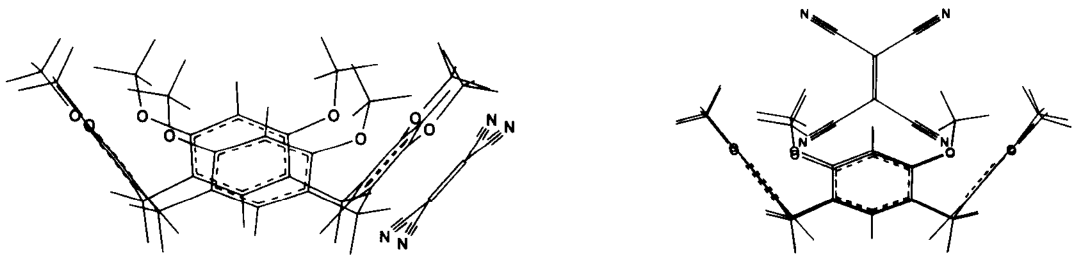


Fig. 5. A comparison of absorption spectra in chloroform, of TCNQ complexes with: 1) 1,3-DMB; 2) OMRA crown conformer; 3) OMRA diamond conformer.

The ^{1}H-NMR spectra of the OMRA conformers in the presence of equimolar amounts of TCNE do not show any substantial changes in comparison to the non-complexed OMRA conformers ($\Delta\delta_{max.}$ = 0.002). This technique, therefore, cannot support the proposed structure of the complex. The quantum-mechanical calculations using the AM1 method (MOPAC 6.0[7]) were conducted in order to decide 1) whether the crown conformer of OMRA binds TCNE outside the cavity (exterior complex) or whether the inclusion complex is formed (Scheme 2); 2) whether the 1:1 exterior complex can form a stable complex with the second TCNE molecule. For the sake of simplicity, the calculations were performed for the crown conformer of OMRA with a methylene bridge.



exterior complex

inclusion complex

Scheme 2

The calculated π-electron densities at the particular aromatic carbon atoms of 1,3-DMB and the crown conformer of OMRA are shown in Fig. 6. The higher π-electron density of the crown conformer of OMRA, resulting from the presence of additional electron donor groups, explains the red shift of the ultraviolet CT band of the OMRA - TCNE complex compared to the 1,3-DMB - TCNE complex.

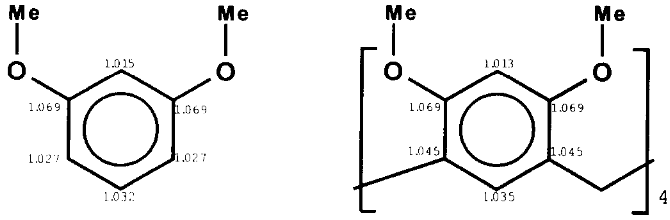


Fig. 6. π-electron densities at the particular aromatic carbon atoms of 1,3-DMB and the crown conformer of OMRA with a methylene bridge.

The heat of formation of the 1,3-DMB - TCNE complex was computed in relation to the separation of the complex components. The optimal computed distance between these components is 3.62 Å. This value agrees very well with the literature data on the CT complexes formed by TCNE[8]. Fig. 7 shows the change in the energy of the 1,3-DMB - TCNE complex in relation to the separation of the components, as well as their optimal arrangement.

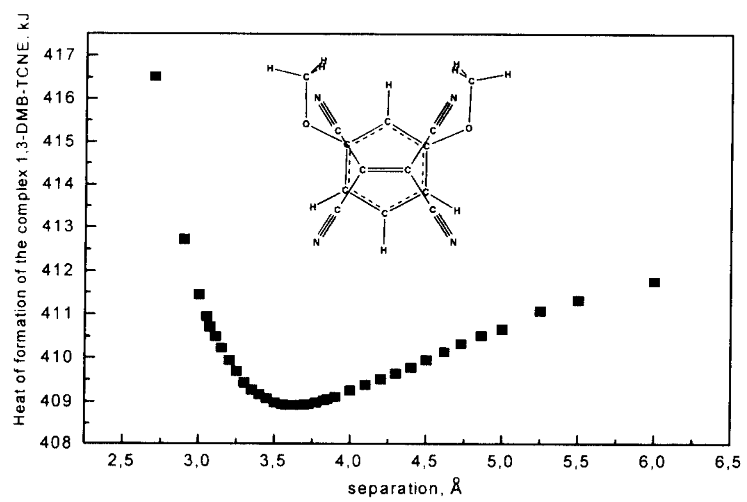


Fig. 7. Heat of formation of the 1,3–DMB - TCNE complex in relation to the separation of the complex components.

In the case of the exterior complex, the calculations indicate only limited charge transfer from OMRA to the TCNE molecule. This results in slight changes of the π-electron density of the complexed OMRA molecule compared to the non-complexed molecule as well as the ionization potentials of the complex. Fig. 8 shows the changes of the heat of formation of the complex from the crown conformer of OMRA with TCNE in relation to the component distance. The equilibrium distance in this complex is 4.55 Å. These data indicate formation of the stable complex of the outer-sphere type via the π···π interaction between an aromatic ring of OMRA and TCNE. In addition, the sandwich arrangement, which is observed for CT complexes with TCNE, favors the formation of such a complex type.

An identical equilibrium distance was calculated for the complex of TCNE with 1,3-dimethoxy-(4,6-dimethyl)-benzene, which is a structural analog of the octamethoxy-resorc[4]arene unit.

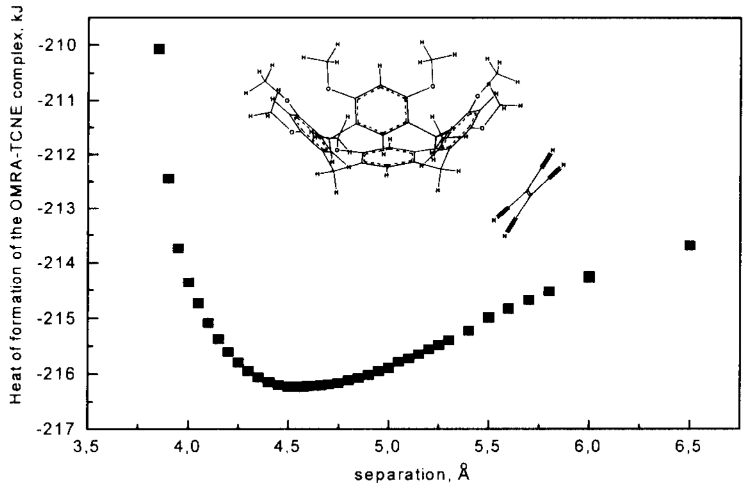


Fig. 8. Heat of formation of the OMRA - TCNE complex in relation to the separation of the complex components.

In the case of the exterior complex with the second TCNE molecule attached, the calculations suggest a low probability of formation of such a complex. Such a system is not stable, with no minimum of the heat of formation in relation to the separation of the complex components. Therefore, reduction of the π-electron density of the complexed OMRA molecule makes the attachment of the second TCNE molecule impossible. As a consequence, only the 1:1 complex is formed. Such a complex type was also proposed by Shinkai and co-workers to describe the interactions of calix[4,6,8]arenes with TCNE[9].

The theoretical calculations were also conducted for the inclusion complex of the crown conformer of OMRA with TCNE. The results exclude formation of a stable CT complex. The TCNE molecule is pushed out of the calixarene cavity; the curve of heat of formation for the inclusion complex in relation to the separation of the components has no minimum.

In the case of the diamond conformer, the only one existing complex is probably the exterior complex resulting from attaching one TCNE molecule to one of the OMRA aromatic rings. The lower formation constant compared to the crown conformer of OMRA can testify to the greater steric hindrance in formation of this complex.

The observed formation constants of the complexes of OMRA conformers with TClQ and TCNQ, which are lower than those of the complexes with TCNE, can be explained by: 1) the weaker electron-acceptor properties of these molecules compared to TCNE; 2) greater steric hindrance in formation of the OMRA complexes with TClQ and TCNQ, which are larger molecules than TCNE.

In summary, complexation of octamethoxyresorc[4]arene with strong electron acceptors was investigated. The compositions of complexes were determined using the Job method. The formation constants for these complexes were evaluated by the nonlinear least-squares regression analysis method. The structure of the complexes with TCNE as modelled using the AM1 method was discussed, and an exterior mode of complexation proposed.

Experimental

General: ^{1}H-NMR spectra of solutions in $CDCl_3$ (internal standard: Me_4Si) were recorded with a Bruker AM-300 spectrometer. UV-VIS spectra were taken on an Specord 500 spectrophotometer.

Materials: OMRA conformers were synthesized according to the literature[3]. 1,3-dimethoxy-benzene (Acros) and chloroform for UV-spectroscopy (Fluka) were used as received. TCNE, TClQ and TCNQ were purified by sublimation.

Spectroscopic measurements: The continuous variation method was employed to estimate the stoichiometry of the complexes at 25°C. The concentration of [OMRA + TCNE] was kept constant ($5 \cdot 10^{-2}$ M). For the determination of formation constants, a series of solutions containing TCNE, TClQ and TCNQ ($5.0 \cdot 10^{-2}$ M) and varying concentrations of crown and diamond conformer OMRA ($3.8 \cdot 10^{-3}$ – $1.1 \cdot 10^{-2}$ M) was prepared in a cell of 1.0 cm path length. The formation constants K for the 1:1 complexes were determined by nonlinear least-squares regression analysis using Eqs. (1) and (2)

$$A(\lambda_i)/b = (S_0 \cdot K \cdot \varepsilon_C(\lambda_i) \cdot [L])/(1+K \cdot [L]) \qquad (1)$$

$$L_0 = [L] + (S_0 \cdot K \cdot [L])/(1+K \cdot [L]) \qquad (2)$$

in which $A(\lambda_i)$ is the complex absorbance, $\varepsilon_C(\lambda_i)$ is the molar absorptivity for the complex at *i* nm, S_0 is the total concentration of TCNE, L_0 and L are the total and equilibrium concentrations of OMRA respectively, b is the path length. The formation constants are summarized in Table 1.

Acknowledgment

This work was supported by the Polish State Committee for Scientific Research (Project 3T09A00613).

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