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Synthesis and structure of bis(*N*-methylaza-15-crown-5)-fused 2,5-dibenzylidenecyclopentanone and its novel bis-sandwich complex with Ba^{2+} ions

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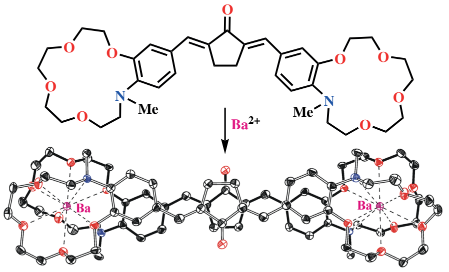
A symmetrical cyclopentanone-based dienone containing two *N*-methylbenzoaza-15-crown-5 ether moieties was synthesized. The structures of the dienone and its bis-sandwich complex with barium perchlorate were investigated using X-ray diffraction and electronic spectroscopy.



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Dibenzylidene cycloalkanone derivatives (cross-conjugated dienones) are relatively easily accessible *via* organic synthesis[1,2] and exhibit a number of useful properties. These compounds are used as precursors for the synthesis of numerous heterocyclic compounds.[1] They efficiently absorb visible light and exhibit intense fluorescence,[3–5] form liquid crystals,[6] serve as photoswitchable organic semiconductors,[7] undergo [2+2] photocycloaddition in solution[8] and solid phase[9] and exhibit pharmacological activity.[10]

Symmetrical bis(*N*-phenylazacrown)-containing dienones derived from cyclobutanone, cyclopentanone and cyclohexanone have been reported earlier.[11–14] They are characterized by efficient absorption in the visible region (370–520 nm) and intense fluorescence in the 500–700 nm range. They are capable of binding alkali and alkaline earth metal cations, as well as α,ω-alkanediammonium ions, which is accompanied by considerable changes in the absorption and emission spectra. Therefore, these compounds can be considered optical molecular sensors for these ions. However, the stability of bis(*N*-phenylazacrown)-containing dienone complexes is moderate.

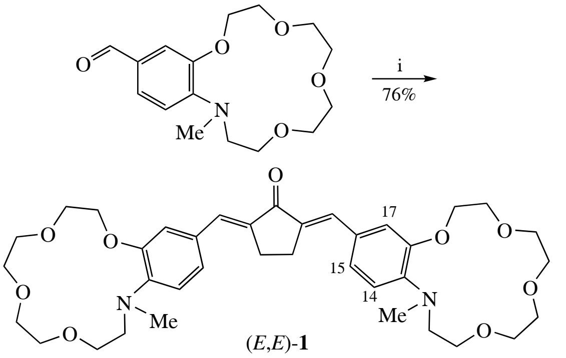
We previously proposed a new strategy for synthesizing functional derivatives of 1-aza-2,3-benzocrown ethers *via* stepwise transformation of the macrocycle into benzocrown ether derivatives.[15] *N*-Alkylbenzoazacrown ethers were shown to possess significantly higher binding capacity for metal and ammonium cations than *N*-phenylazacrown ethers with the same macrocycle size. Their complexing properties are comparable to those of benzocrown ethers. Using formyl-*N*-methylbenzoazacrown ether derivatives, we synthesized azacrown-containing styryl dyes, which demonstrated high efficiency as optical molecular sensors for alkali and alkaline earth metal cations.[15] In this regard, the use of 5′-formyl-*N*-methylbenzoazacrown ethers for the synthesis of cross-conjugated dienones as effective photoactive complexing agents seems promising.

In this communication, we present the synthesis, X-ray diffraction and electronic spectroscopy study of the structure and spectral properties of a new symmetrical cross-conjugated bis(*N*-methylbenzoaza-15-crown-5)-containing cyclopentanone-based dienone **1**[†] and its complex with barium perchlorate. It should be noted that X-ray diffraction data for crown-containing dienones and their complexes are unavailable from the literature.

Dienone **1** was prepared by aldol condensation of cyclopentanone with two molar equivalents of 5′-formyl-*N*-methylbenzoaza-15-crown-5-ether[†,15] in aqueous ethanol in the presence of sodium hydroxide (Scheme 1 and experimental details in Online Supplementary Materials). According to ^{1}H NMR spectroscopy, the dienone is formed as the (*E*,*E*)-isomer, since the spectrum contains only one set of signals for each proton type, and the protons of the methine groups appear as a singlet at δ 7.39 ppm, which corresponds to the (*E*,*E*)-isomer.[1]

Figure 1 shows the absorption spectra of dienone (*E*,*E*)-**1** in MeCN as a function of the concentration of added barium perchlorate. Free dienone absorbs at $\lambda_{max} = 453$ nm (curve *1*). The addition of excess $Ba(ClO_4)_2$ induces a pronounced blue shift ($\Delta\lambda_{max} = -74$ nm), indicating the coordination of Ba^{2+} ions to dienone aza-15-crown-5 ether moieties. Curve *10* in Figure 1

[†] The systematic IUPAC names of dienone **1** and its precursor are (2*E*,5*E*)-2,5-bis[(13-methyl-2,3,5,6,8,9,12,13-octahydro-11*H*-benzo[*k*][1,4,7,10]tetraoxa[13]azacyclopentadecin-16-yl)methylidene]-cyclopentan-1-one and 13-methyl-2,3,5,6,8,9,12,13-octahydro-11*H*-benzo[*k*][1,4,7,10]tetraoxa[13]azacyclopentadecine-16-carbaldehyde, respectively.



Scheme 1 *Reagents and conditions*: i, cyclopentanone, NaOH, EtOH–H_2O, room temperature.

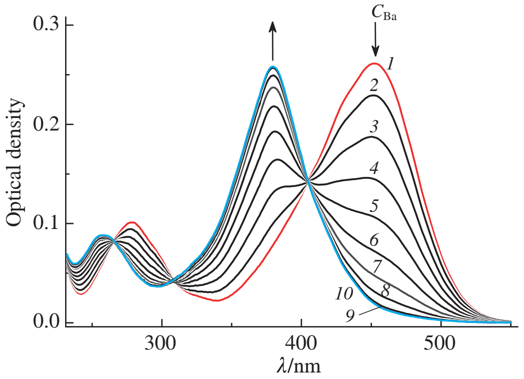


Figure 1 Absorption spectra of dienone (*E*,*E*)-**1** for various relative concentrations (C_{Ba}/C_1) of added $Ba(ClO_4)_2$: (*1*) 0, (*2*) 0.27, (*3*) 0.54, (*4*) 0.79, (*5*) 1.03, (*6*) 1.26, (*7*) 1.48, (*8*) 1.73, (*9*) 2.31 and (*10*) 2.98; curve *10* is the spectrum of $[(E,E)\text{-}\mathbf{1}\cdot Ba^{2+}]_2$. Conditions: $C_1 = 5.1\times10^{-6}$ M, MeCN, 0.01 M Bu_4NClO_4, quartz cell, *l* = 1 cm, room temperature.

corresponds to the fully complexed form of (*E*,*E*)-**1**, since a further increase in the metal salt concentration does not cause any spectral changes. This spectrum has a profile characteristic of H-aggregates of dyes: an intense narrowed band with a clear-cut long-wavelength shoulder,[16] attesting to interactions of two chromophores located closely one above the other. Typical examples demonstrating the effect of these interactions on the spectral properties of unsaturated compounds are stacking dimers of functionalized styryl dyes.[17] We hypothesized that in the presence of Ba^{2+} ions, dienone (*E*,*E*)-**1** initially forms 1 : 1 complexes, which immediately dimerize to give highly stable bis-sandwich 2 : 2 complexes. Other possible complexes (1 : 2, 2 : 1 or both) appear to make minor contributions to the spectra presented in Figure 1. Thus, curve *10* in this Figure corresponds to the spectrum of the $[(E,E)\text{-}\mathbf{1}\cdot Ba^{2+}]_2$ dimer.

By spectrophotometric titration of dienone (*E*,*E*)-**1** with $Ba(ClO_4)_2$ in MeCN, we determined the stability constants of the 1 : 1 and 2 : 2 complexes to be $\log(K_{1:1}/M^{-1}) = 5.2$ and $\log(K_{2:2}/M^{-3}) = 17.5$. A similar spectrophotometric titration in a MeCN–water mixture (100 : 1, v/v) gave $\log(K_{1:1}/M^{-1}) = 3.9$ and $\log(K_{2:2}/M^{-3}) = 16.3$ (see Online Supplementary Materials). No complexation occurred in a MeCN–water mixture (10 : 1, v/v).

Previously, unusual bis-sandwich 2 : 2 complexes were found for bis-crown stilbenes and large-radius metal cations or alkanediammonium ions.[13] For bis(15-crown-5)stilbene with K^+ ions and bis(18-crown-6)stilbene with Cs^+ ions, the structures of the bis-sandwich complexes were confirmed by X-ray diffraction analysis.

The structures of dienone (*E*,*E*)-**1** and its complex with barium perchlorate, $(E,E)\text{-}\mathbf{1}\cdot Ba(ClO_4)_2\cdot 4.5\,C_6H_6$, were studied by X-ray diffraction analysis.‡ The resulting structures are shown in Figures 2 and S2 (see Online Supplementary Materials). The crystal data and details of the X-ray diffraction experiment are summarized in Table S1, and selected bond lengths and dihedral angles are given in Tables S2 and S3 (see Online Supplementary Materials).

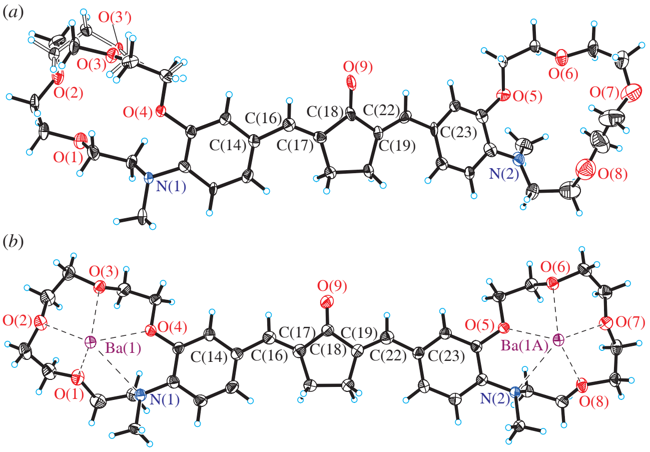


Figure 2 Structures of (*a*) dienone (*E*,*E*)-**1** and (*b*) the major component of its complex $(E,E)\text{-}\mathbf{1}\cdot Ba(ClO_4)_2\cdot 4.5\,C_6H_6$. Thermal ellipsoids are drawn at the 50% probability level. Coordination bonds are shown as dashed lines.

The bond length distributions in the dienone moiety, C(14)–C(16)=C(17)–C(18)–C(19)=C(22)–C(23), are similar for both structures. The C(16)=C(17) and C(19)=C(22) bonds, which are markedly shortened [on average 1.344(8) Å] compared to the neighboring formally single bonds [on average 1.472(8) Å], attest to a significant localization of the former bonds (see Table S2).

In the structure of the complex, the conjugated dienone moiety is nearly planar: the twist angle between the two benzene rings is only 4.4°, whereas in free (*E*,*E*)-**1**, the chromophore is more twisted. This is apparently caused by the requirement for close packing in the crystal (see Table S2). Generally, the presence of two *N*-methylazacrown ether moieties in dienone **1** does not disrupt effective conjugation in the molecule, as

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‡ *Crystal data for* (*E*,*E*)-**1**. $C_{37}H_{50}N_2O_9$, $M = 666.79$, monoclinic, space group $P2_1$, $a = 14.951(2)$, $b = 7.6562(11)$ and $c = 15.708(2)$ Å, $\beta = 109.441(4)°$, $V = 1695.6(4)$ Å^3, $T = 100(2)$ K, $Z = 2$, $d_{calc} = 1.306$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.093$ mm^{-1}, goodness-of-fit on F^2 is 1.024, 22242 collected reflections including 7132 independent ones ($R_{int} = 0.1332$), *R* indices for $I > 2\sigma(I)$ $R_1 = 0.1057$ and $wR_2 = 0.1932$, for all reflections $R_1 = 0.1970$ and $wR_2 = 0.2261$, residual electron density (min/max) is –0.375/0.616 ē Å^{-3}.

Crystal data for $(E,E)\text{-}\mathbf{1}\cdot Ba(ClO_4)_2\cdot 4.5\,C_6H_6$. $C_{64}H_{77}BaCl_2N_2O_{17}$, $M = 1354.51$, triclinic, space group $P\bar{1}$, $a = 12.1915(5)$, $b = 14.4273(6)$ and $c = 20.1461(8)$ Å, $\alpha = 96.864(1)°$, $\beta = 101.241(1)°$ and $\gamma = 113.400(1)°$, $V = 3112.4(2)$ Å^3, $T = 150(2)$ K, $Z = 2$, $d_{calc} = 1.445$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.796$ mm^{-1}, goodness-of-fit on F^2 is 1.030, 41665 collected reflections including 13802 independent ones ($R_{int} = 0.0683$), *R* indices for $I > 2\sigma(I)$ $R_1 = 0.0506$ and $wR_2 = 0.1093$, for all reflections $R_1 = 0.0761$ and $wR_2 = 0.1197$, residual electron density (min/max) is –1.397/1.142 ē Å^{-3}.

Red crystals of (*E*,*E*)-**1** were grown by slow evaporation of its solution in MeOH in the dark. Yellow crystals of the $(E,E)\text{-}\mathbf{1}\cdot Ba(ClO_4)_2\cdot 4.5\,C_6H_6$ complex were obtained by slow saturation of a solution of an equimolar mixture of the components in MeCN with benzene vapor in the dark. The X-ray diffraction experiments were carried out on a D8 Venture diffractometer [MoKα radiation (λ = 0.71073 Å), graphite monochromator, ω-scan mode]. The structures were solved by the direct method and refined anisotropically using full-matrix least-squares fitting on F^2. Hydrogen atom positions were calculated geometrically and refined using the riding model. All calculations were carried out using the SHELXL software.[18]

CCDC 2451890 and 2451891 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

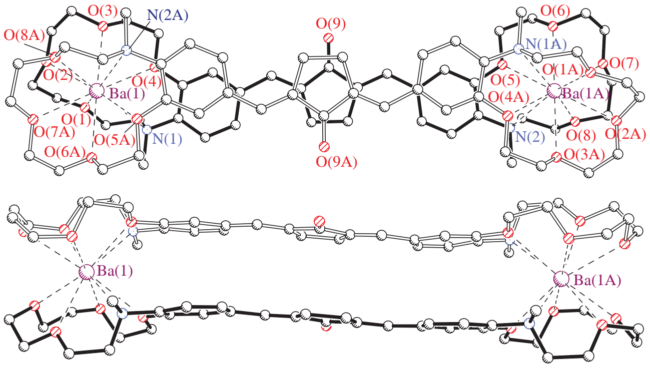

Figure 3 Structure of the bis-sandwich tetracation $[(E,E)\text{-}\mathbf{1}\cdot\mathrm{Ba}^{2+}]_2$ in two projections.

was also observed in the case of substituted 2,5-dibenzylidenecyclopentanone derivatives addressed in our previous studies.[5,13]

In the structure of $(E,E)\text{-}\mathbf{1}\cdot\mathrm{Ba(ClO_4)_2}\cdot 4.5\,\mathrm{C_6H_6}$, two dienone molecules and two barium cations form the centrosymmetric bis-sandwich tetracation $[(E,E)\text{-}\mathbf{1}\cdot\mathrm{Ba}^{2+}]_2$ (Figure 3). In this complex, the conjugated moieties of the dienone molecules are arranged in parallel planes at a distance of ~3.5 Å and project well onto each other, which implies an effective stacking interaction between them.

Particular attention should be paid to the conformation of the macroheterocycles in free (*E*,*E*)-**1** and its change as a result of complex formation. In (*E*,*E*)-**1**, the conformations of the two macroheterocycles are markedly dissimilar, which is clearly visible when superimposing the *N*-methylbenzoazacrown ether moieties over the benzene rings [Figure S1(*a*)]. The conformation of the first macrocycle with the N(1) atom was found for all *N*-methylbenzoaza-15-crown-5 ethers and their metal complexes investigated in our previous works.[15]

In the structure of $(E,E)\text{-}\mathbf{1}\cdot\mathrm{Ba(ClO_4)_2}\cdot 4.5\,\mathrm{C_6H_6}$, the conformations of the two macroheterocycles coordinated to barium differ little from each other [Figure S1(*b*)] and are similar to the conformation of the first macrocycle in (*E*,*E*)-**1**. This fact demonstrates that *N*-methylbenzoaza-15-crown-5 ethers in their most typical conformation are pre-organized for binding metal cations.

Thus, we synthesized a previously unknown symmetrical cross-conjugated cyclopentanone-based dienone containing two *N*-methylbenzoaza-15-crown-5 ether moieties, which exhibited a strong optical response upon complexation with Ba^{2+} ions. X-ray diffraction analysis revealed a high degree of pre-organization of dienone macroheterocycles for binding metal cations and determined the structure of the unusual bis-sandwich tetracation $[(E,E)\text{-}\mathbf{1}\cdot\mathrm{Ba}^{2+}]_2$. The obtained results are of undoubted interest for further study of the complex-forming and photochemical properties of dienones of similar structure with different sizes of alkanone rings and azacrown ether moieties. Bis(*N*-methylbenzoazacrown)-containing cross-conjugated dienones are promising chromoionophores and can serve as effective molecular sensors for metal cations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7851.

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