

Stacking structures of complexes between bis(crown)azobenzene and a dipyridylethylene derivative in a crystal and in solution

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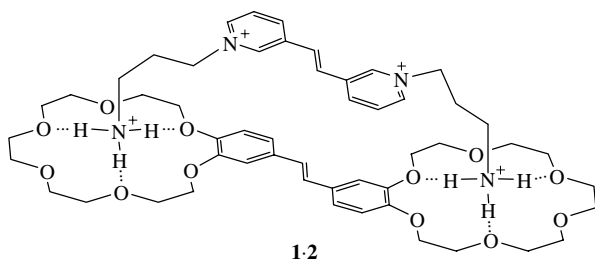
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Bis(18-crown-6)azobenzene and *N,N'*-di(ammoniopropyl)di(3-pyridiniumyl)ethylene form stacking bimolecular and termolecular complexes in acetonitrile solutions; their stability and crystal structure of the bimolecular complex were studied.

The host–guest complexation involving hydrogen bonds is considered an efficient way of molecular self-assembly in solutions, films, or crystals.¹ Bis(crown)-containing azobenzenes capable of strongly binding metal and ammonium cations are attractive for studying the self-assembly.² Because of the ability to undergo reversible *trans*–*cis* photoisomerization at the N=N bond, these compounds have been proposed as molecular switches for the photocontrolled extraction and membrane transport of metal ions, in synzymes and in the design of molecular devices in nanotechnology.^{2,3} However, the potential of bis(crown)-containing azobenzenes as components of supramolecular ensembles consisting of organic molecules remains unused.

The strategy of self-assembly of photosensitive supramolecular systems based on bis(crown)stilbenes (donors, D) and di(ammonioalkyl) derivatives of viologen analogues (acceptors, A) allows one to carry out forced self-assembly of components due to a cooperative effect of a large number of weak interactions, namely, hydrogen bonds or ion–dipole, donor–acceptor and stacking interactions.⁴ Note that this strategy gives rise to exceptionally stable D–A complexes even with weak acceptor compounds. For example, in acetonitrile bis(18-crown-6)stilbene (*E*)-**1** forms a stable 1:1 complex with *N,N'*-di(ammoniopropyl)di(3-pyridyl)ethylene (*E*)-**2** (lg $K_{1:1}$ = 8.67) in which, owing to the proximity of the donor and acceptor fragments, charge transfer takes place in the ground state, giving rise to absorption in the visible region (λ_{max} = 405 nm) and changing the redox potentials of both components.^{4,5} However, the spatial structure of **1**·**2** complexes has not been proven.



It was found that, with an excess stilbene **1**, relatively stable termolecular complex (**1**)₂·**2** can also be formed (lg $K_{2:1}$ = 2.02).

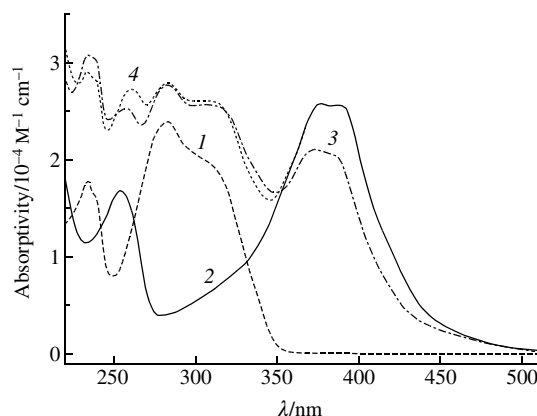


Figure 1 Absorption spectra of (1) (*E*)-**2**, (2) (*E*)-**3** and (3) their 1:1 mixture in MeCN; concentrations of the reactants are 5×10^{-5} M. Curve 4 is the sum of spectra 1 and 2.

We assumed that weak electron-donating bis(crown)azobenzenes can also be used to prepare stable supramolecular D–A complexes with the derivatives of viologen analogues.

Here we report the complexation of bis(18-crown-6)-containing azobenzene (*E*)-**3**, which is structurally related to stilbene **1**, with weak electron-donating dipyridylethylene derivative **2** and prove, for the first time, the structure of bimolecular complex **3**·**2** by X-ray diffraction.

The syntheses of **2** as a tetraperchlorate salt and **3** have been reported.^{4,6} The ability of dipyridylethylene **2** to form host–guest complexes with azobenzene **3** in acetonitrile was studied by spectroscopy. Free compounds **2** and **3** show intense long-wavelength absorption with maxima at 283 and 388 nm, respectively (Figure 1, curves 1 and 2).[†] A comparison of the spectrum of an equimolar mixture of **2** and **3** with the arithmetic sum of the spectra of free components (Figure 1, curves 3 and 4) shows a 4-nm hypsochromic shift of the long-wavelength absorption band. This change indicates that the ammonium groups of **2** are bound by crown-ether fragments of **3**, which hampers the

[†] UV–VIS spectra were recorded on a UV-3101PC spectrophotometer (Shimadzu) in a range of 200–600 nm with an increment of 0.5 nm (MeCN, 1 cm cell, room temperature).

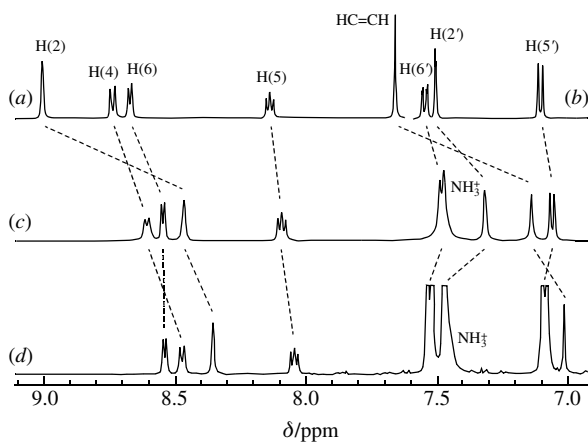


Figure 2 ^1H NMR spectra (aromatic region) of (a) (E)-**2**, (b) (E)-**3** ($C = 1 \times 10^{-3}$ M), and their mixtures (c) 1:1 and (d) 1:10 ($C_2 = 1 \times 10^{-3}$ M) in CD_3CN , 30 $^\circ\text{C}$.

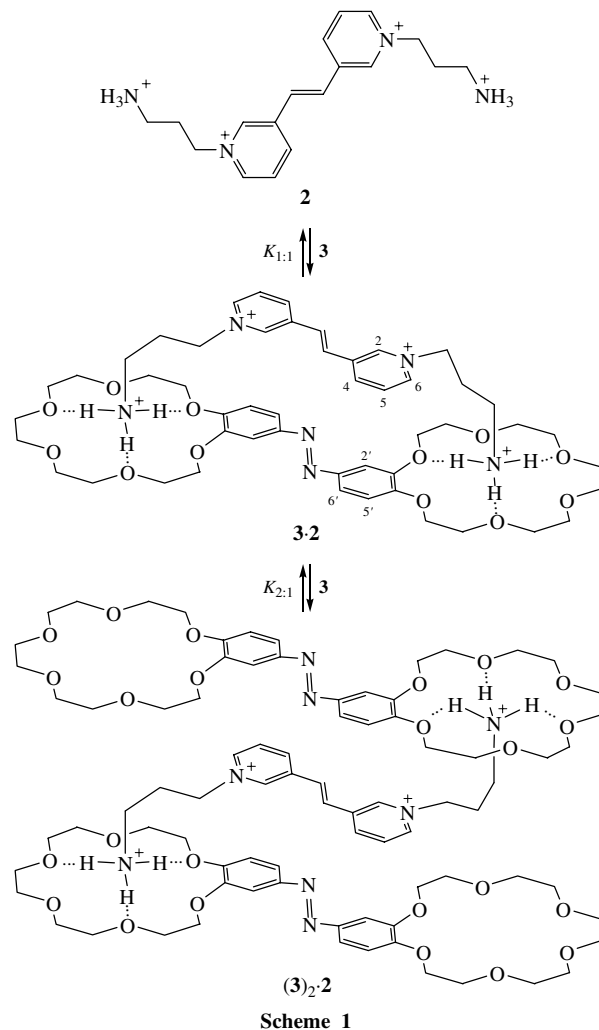
intramolecular charge transfer from the donor benzocrown-ether residue to the central $\text{N}=\text{N}$ group in **3**. A similar spectral behaviour was observed upon the formation of a bimolecular complex between azobenzene **3** and the model diammonium compound $\text{NH}_3^+(\text{CH}_2)_{10}\text{NH}_3^+ \cdot 2\text{ClO}_4^-$ (**4**).[‡] The through-space interaction of chromophoric fragments in the **3/2** system is manifested in the absorption spectrum as a slight decrease in the intensity of long-wavelength absorption, apparently, due to a weak donor–acceptor interaction.

An ^1H NMR study of the complexation of **2** with **3** proved to be more informative. The mixing of components in equimolar amounts induced an upfield shift (up to 0.54 ppm) of the signals from ethylene protons and all aromatic protons in both components [Figure 2(a)–(c)]. Owing to the homoditopic interaction of the ammonium groups of dipyriddyethylene with the 18-crown-6 fragments of azobenzene in the **3:2** complex, the conjugated fragments of the components are proximate to each other (Scheme 1); this results in mutual shielding of their protons. In the presence of an excess of **3**, the equilibrium shifts toward the formation of the termolecular complex (**3**)₂·**2**, which induces a further upfield shift of the proton signals of **2** [Figure 2(d)]. This fact is indicative of a stacked arrangement of components in (**3**)₂·**2**.

The stability constants of the complexes were determined by ^1H NMR titration.[§] Due to the very high stability constants of the bimolecular complexes formed by bis(18-crown-6)azobenzene with diammonium compounds that exceed the upper limit of applicability of direct titration ($K_{1:1} > 10^5 \text{ M}^{-1}$), competitive titration was carried out, which simultaneously takes into account two equilibria of the type $\text{D} + \text{A} \rightleftharpoons \text{D} \cdot \text{A}$ (1) in a ternary system with a fixed stability constant for one of the complexes. First, the stability constant of the complex of model

[‡] 1,10-Decanediammonium diperchlorate **4** was prepared by the addition of an excess of 70% aqueous HClO_4 to 1,10-decanediamine (Aldrich) in methanol followed by quantitative precipitation with diethyl ether; white solid, mp 262–265 $^\circ\text{C}$ (decomp.). Found (%): C, 32.14; H, 6.94; N, 7.37. Calc. for $\text{C}_{10}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_8$ (373.23) (%): C, 32.18; H, 7.02; N, 7.51.

[§] ^1H NMR titration experiments were performed on a Bruker DRX500 instrument in CD_3CN at 30 $^\circ\text{C}$. For competitive titration in the **3/1/4** system, the concentrations of **3** and **4** were maintained at 1×10^{-3} M, and the concentration of **1** was varied from 0 to 1×10^{-2} M. For competitive titration in the **3/2/4** system, the concentrations of **2** and **3** were maintained at 1×10^{-3} M, and the concentration of **4** was varied from 0 to 1×10^{-2} M. For titration in the **3/2** system, the concentration of **2** was maintained at 1×10^{-3} M, and the concentration of **3** was varied from 1×10^{-3} to 1×10^{-2} M. The stability constants were measured to within $\pm 20\%$ by analysing changes in the proton positions of reactants **2** and **3** using the HYPNMR program.⁷



compound **4** with azobenzene **3**, $\lg K_{1:1} = 7.34$, was determined by titration in the **3/1/4** system using the known stability constant of complex **1·4** ($\lg K_{1:1} = 7.58$).⁸ The resulting stability constant of complex **3·4** was used to calculate the constant of complex **3·2** from competitive titration data obtained in the **3/2/4** system. The stability constant of complex **3·2** found in this way, $\lg K_{1:1} = 8.07$, is four times lower than that of related complex **1·2**. This is attributable to the electron-withdrawing effect of the $\text{N}=\text{N}$ bond, which decreases the ability of oxygen atoms conjugated with the azobenzene π system to participate in binding of the NH_3^+ group and to less pronounced π -donor properties of **3** with respect to stilbene **1**. Bimolecular complex **3·2** is apparently subjected to substantial steric strain caused by incomplete geometric fitting of the components required for effective stacking interaction of their conjugated systems. This strain may be relieved upon the addition of a second molecule of **3** to the bimolecular complex to give complex (**3**)₂·**2**, in which the ammonium groups of **2** are coordinated to the 18-crown-6 fragments of two azobenzene molecules (Scheme 1). Direct ^1H NMR titration in the **3/2** system at $C_3 > C_2$ allowed us to determine the stability constant of termolecular complex (**3**)₂·**2**, which was $\lg K_{2:1} = 1.81$ [only one equilibrium of type (1) was taken into account], *i.e.*, also lower than that of the analogous complex based on stilbene **1**. The simplified complexation model is applicable in this case due to the high stability constant of bimolecular complex **3·2**, which permits one to consider that, at $C_3 > C_2$, the concentration of free acceptor **2** is negligibly low.

The structure of bimolecular complex **3·2** was established by X-ray diffraction.[¶] Figure 3 shows the structure of the major

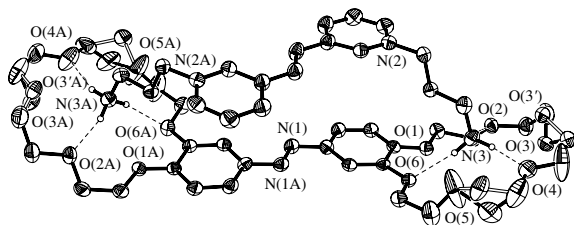


Figure 3 Structure of complex **3·2·5C₆H₆** is drawn with anisotropic displacement parameters at a 40% probability level. Perchlorate anions, benzene solvate molecules and most of hydrogen atoms are omitted for clarity. Hydrogen bonds are shown with dashed lines.

components of the complex, which form a double-decker structure. In this complex, both ammonium groups of the acceptor molecule are coordinated by the 18-crown-6 fragments of the donor molecule through the $N^+-H\cdots O$ hydrogen bonds. The chromophore fragments of the donor and the acceptor are projected one onto another on slight twisting. The planes of the pyridine residues in **2** are rotated with respect to each other through an angle of 10.6° ; the dihedral angle between the benzene rings in **3** is 7.7° . A 2-fold axis passes through the midpoint of the ethylene bond in the dipyriddyethylene molecule **2** and the midpoint of the $N=N$ bond in the azobenzene molecule **3**. Therefore, the mean planes of the donor and acceptor conjugated fragments are parallel and separated by a distance of ~ 4.7 Å, which is greater than twice the van der Waals radius of the carbon atom (~ 3.8 Å) or the sum of the van der Waals radii of nitrogen and carbon atoms (~ 3.4 Å). This is indicative of an essential weakening of the stacking interaction between these chromophores.

† Yellow lamellar single crystals of complex **3·2** were grown by the slow saturation of an acetonitrile solution of a mixture of **2** and **3** ($\sim 1:1$ molar ratio) with benzene through a gas phase at room temperature. The X-ray experiment was carried out on a Bruker SMART-CCD diffractometer [MoK α radiation ($\lambda = 0.71073$ nm), graphite monochromator, ω -scanning, θ range 1.83 – 28.99°]. The X-ray intensity data were processed using the Bruker SAINT software.⁹ The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares against F^2 . The crystallographically independent two perchlorate anions and three solvate benzene molecules were also found in the unit cell. Rotational disorder of both perchlorate anions together with a pronounced anisotropy of the thermal atomic vibrations of some crown-ether fragments and disorder of some of their chains were revealed. One of the benzene molecules is disordered over two closely spaced 2-fold axis-related positions. The positions of hydrogen atoms were calculated geometrically (excluding the hydrogens of the disordered benzene molecule) and refined using a riding model. All the calculations were carried out with the use of the SHELXTL-PLUS program package.¹⁰

For **3·2·5C₆H₆**: $C_{80}H_{104}Cl_4N_6O_{28}$, $M = 1739.49$, monoclinic, space group $P2_1/c$, $a = 15.387(2)$, $b = 8.2974(13)$ and $c = 32.364(5)$ Å, $\beta = 90.000(4)^\circ$, $V = 4131.9(11)$ Å³, $T = 120(2)$ K, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.229$ mm⁻¹, goodness-of-fit on F^2 is 1.086, 39971 collected reflections including 10966 independent ones ($R_{\text{int}} = 0.0835$), R indices for $I > 2\sigma(I)$ $R_1 = 0.1100$ and $wR_2 = 0.3144$, for all reflections $R_1 = 0.1968$ and $wR_2 = 0.3528$, residual electron density (min/max) is $-0.634/0.706$ eÅ⁻³.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 643904. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

In a crystal, complexes **3·2** form $\cdots D-A \cdots D-A \cdots$ type stacks. The chromophore fragments of the donor and acceptor components of the neighbouring complexes are projected onto one another in the same way as within a double-decker complex, but they are arranged in parallel planes at a ~ 3.6 Å distance, which undoubtedly implies a very strong stacking interaction between them. Thus, the homoditopic coordination of NH_3^+ groups to crown-ether fragments in a bimolecular complex weakens the donor–acceptor and stacking interaction of the conjugated systems of the components, which may account for the formation of relatively strong termolecular complexes $D-A-D$, in which the chromophores can approach one another to a shorter distance.

Thus, we demonstrated the possibility of forced formation of supramolecular $D-A$ and $D-A-D$ complexes between a weak donor, bis(18-crown-6)azobenzene, and a weak acceptor, a viologen analogue containing two terminal ammonium groups. The spatial structure of the highly stable bimolecular complex was established for the first time; this confirmed its double-decker structure, in which the ammonium groups of the acceptor molecule are involved in host–guest complexes with the crown-ether fragments of the azobenzene molecule, and their π -conjugated fragments are arranged one above another. The rules of construction of the stacking-type $D-A$ complexes that we found can be used to design photosensitive architectures in nanotechnology.

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References

- 1 J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, 1995.
- 2 S. Shinkai, in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001, ch. 9.
- 3 V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 3348.
- 4 S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Botsmanova, L. G. Kuz'mina, A. V. Churakov, Yu. A. Strelenko, M. V. Alfimov, J. A. K. Howard, D. Johnels and U. G. Edlund, *New J. Chem.*, 2005, **29**, 881.
- 5 K. P. Butin, A. A. Moiseeva, S. P. Gromov, A. I. Vedernikov, A. A. Botsmanova, E. N. Ushakov and M. V. Alfimov, *J. Electroanal. Chem.*, 2003, **547**, 93.
- 6 R. Cacciapaglia, S. Di Stefano and L. Mandolini, *J. Am. Chem. Soc.*, 2003, **125**, 2224.
- 7 C. Frassinetti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, *Anal. Biochem.*, 1995, **231**, 374.
- 8 E. N. Ushakov, S. P. Gromov, A. I. Vedernikov, E. V. Malysheva, A. A. Botsmanova, M. V. Alfimov, B. Eliasson, U. G. Edlund, J. K. Whitesell and M. A. Fox, *J. Phys. Chem. A*, 2002, **106**, 2020.
- 9 SAINT, Version 6.02A, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- 10 SHELXTL-PLUS, Version 5.10, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.

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