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Unusual three-decker structure of a D–A–D complex between bis(crown)stilbene and a di(quinolyl)ethylene derivative

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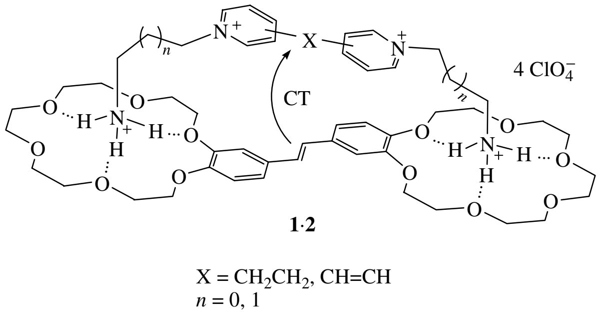
Bis(18-crown-6)stilbene and *N*,*N*′-di(ammoniopropyl)di(4-quinoliniumyl)ethylene form bimolecular (D–A) and sandwich-like termolecular (D–A–D) complexes; the complex stabilities and crystal structure of the termolecular complex were studied.

The host–guest complexation is considered as a promising way of self-assembly of organic molecules in solutions, films or crystals.[1] An advantage of self-assembly at the molecular level is that it gives a way for stabilization of unstable compounds and intermediates of chemical reactions by fine adjustment of the components to one another through deliberate modification of their structure. A most efficient way of self-assembly is the formation of supramolecular complexes involving hydrogen bonds.

The reactions of electron-excessive (D) and electron-deficient (A) molecules to give charge-transfer complexes (CTC) are of interest due to substantial changes in the electronic spectra and redox potentials of the components,[2] the capacity for photoinduced electron transfer,[3] and to the prospects for using these systems in molecular electronics. However, a study of the CTC in solutions is most often restricted by low stability of bimolecular D–A complexes ($\lg K_{1:1} < 2$); no relatively stable termolecular D–A–D complexes based on organic compounds have been described so far.

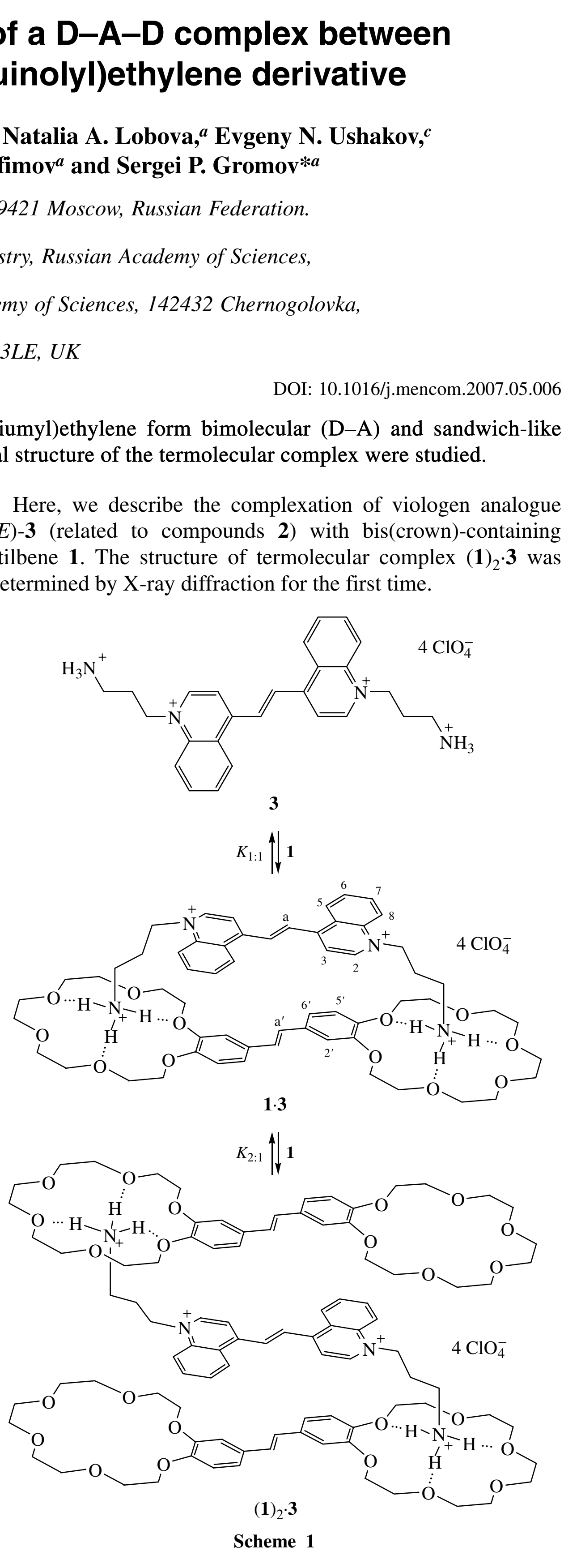
Recently,[4] we reported an improved synthesis of symmetric bis(crown)-containing stilbenes and a study of their spatial structure. It was found that in acetonitrile bis(18-crown-6)-stilbene [(*E*)-**1**] forms exceptionally stable 1:1 complexes with *N*,*N*′-di(ammonioalkyl) derivatives of viologen analogues **2** ($\lg K_{1:1}$ = 8.67–9.42) in which charge transfer takes place in the ground state[5] and electron transfer takes place in the excited state,[6] owing to the proximity of the donor and acceptor fragments. With excess stilbene **1**, relatively stable termolecular CTC $(\mathbf{1})_2\cdot\mathbf{2}$ can also be formed ($\lg K_{2:1}$ = 2.02–3.27).



1·2

X = CH_2CH_2, CH=CH
n = 0, 1

Here, we describe the complexation of viologen analogue (*E*)-**3** (related to compounds **2**) with bis(crown)-containing stilbene **1**. The structure of termolecular complex $(\mathbf{1})_2\cdot\mathbf{3}$ was determined by X-ray diffraction for the first time.



Scheme 1

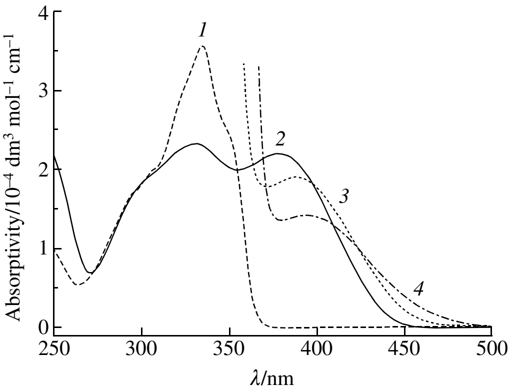


Figure 1 Absorption spectra of (*1*) (*E*)-**1**, (*2*) (*E*)-**3** ($C = 5\times10^{-5}$ M), and their (*3*) 1:1 and (*4*) 10:1 mixtures ($C_3 = 2\times10^{-4}$ M) in MeCN–water (93:7).

The synthesis of diquinolylethylene **3** as the tetraperchlorate salt has been described previously.[7] The ability of **3** to form host–guest complexes with bis(18-crown-6)stilbene in acetonitrile was studied by spectroscopy. Free compounds **1** and **3** exhibit strong long-wavelength absorption with peaks at 335 and 378 nm, respectively (Figure 1, curves *1* and *2*).[†] On mixing **3** with **1** in 1:1 and 1:10 ratios, the long-wavelength band of the acceptor undergoes a slight bathochromic shift to 387 and 395 nm, respectively, accompanied by gradual broadening and decrease in intensity (Figure 1, curves *3* and *4*). A comparison with the results obtained previously[5] for systems based on dipyridylethylene derivatives in which the formation of complexes **1**·**2** and $(\mathbf{1})_2\cdot\mathbf{2}$ was accompanied by the appearance of a broad weak charge transfer band (CTB) in the region 500–550 nm attests to a similar behaviour of system **1/3**. In this case, the position of the CTB implies that the charge transfer is less beneficial than that in systems **1/2**.

The ^{1}H NMR study of complexation of **1** with **3** has shown that the mixing of equimolar amounts of the components induces an upfield shift (up to 0.69 ppm) of the signals of ethylene and most of aromatic protons of both components [Figure 2(*a*)–(*c*)]. Owing to the homoditopic interaction of the ammonium groups of the acceptor with the 18-crown-6 ether moieties of the donor, the conjugated fragments of the components in complex **1**·**3** are arranged closely in space (Scheme 1), which results in mutual shielding of their protons. In the presence of excess **1**, the equilibrium shifts toward the formation of termolecular complex $(\mathbf{1})_2\cdot\mathbf{3}$, resulting in a further upfield migration of the proton signals of the acceptor [Figure 2(*d*)]. This fact points to a stack-type arrangement of the components in $(\mathbf{1})_2\cdot\mathbf{3}$. The stability constants of the complexes were determined using ^{1}H NMR titration.[‡] The resulting stability constant for complex **1**·**3**, lg $K_{1:1} = 5.1\pm0.3$, proved to be much lower than that for the related bimolecular system based on *N*,*N*′-di(ammoniopropyl) derivative of dipyridylethylene (lg $K_{1:1} = 9.08$). This is attributable to the strong steric interaction of the annelated benzene ring with the N-substituent and a fixed orientation of the ethylene bond with respect to the quinoline system in **3**, resulting in substantial strain in the complex **1**·**3** formed. This strain can be removed upon the addition of a second molecule of **1** to the bimolecular complex to give $(\mathbf{1})_2\cdot\mathbf{3}$; therefore, its stability (lg $K_{2:1} = 3.13\pm0.05$) is comparable with that of the complexes formed by **2**.[5]

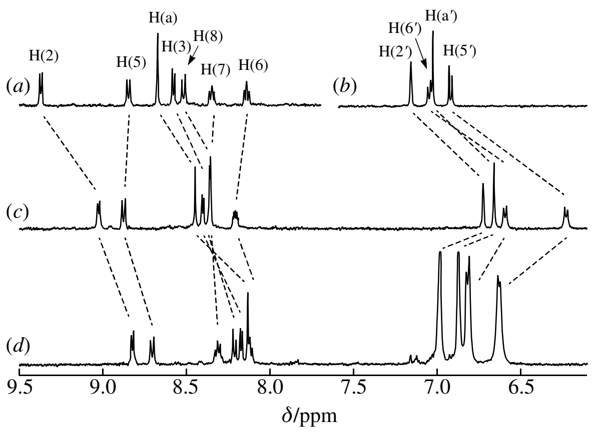


Figure 2 ^{1}H NMR spectra (aromatic region) of (*a*) (*E*)-**3**, (*b*) (*E*)-**1** ($C = 5\times10^{-4}$ M), and their (*c*) 1:1 and (*d*) 1:6 mixtures ($C_3 = 5\times10^{-4}$ M) in CD_3CN–D_2O (93:7), 30°C.

The structure of termolecular complex $(\mathbf{1})_2\cdot\mathbf{3}$ was established by X-ray diffraction.[§] The complex has a centrosymmetrical structure; Figure 3 shows the structures of the main components. The stilbene molecule of **1** occupies a general position; its multiplication through the symmetry center accommodating the acceptor gives a complex with the component ratio 2(**1**):1(**3**). Thus, the acceptor molecule is packed between two donor molecules to give three-decker sandwich **1**·**3**·**1**. In this triad, each ammonium group of **3** is coordinated by one 18-crown-6 ether fragment of a neighbouring molecule of **1** through three N^+–H···O hydrogen bonds. The H_2O(1W) water molecule resides in the cavity of the second crown ether fragment of **1** and forms hydrogen bonds with the O(1), O(4) and O(6) atoms. The chromophore fragment of **3** is non-planar: the planes of the

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[†] UV-VIS spectra were recorded on a UV-3101PC spectrophotometer (Shimadzu) in a range of 230–550 nm with an increment of 0.5 nm (MeCN–water, 93:7; 1 cm cell; room temperature).

[‡] ^{1}H NMR titration experiment was performed on a Bruker DRX500 instrument in CD_3CN–D_2O (93:7) solution at 30 °C. The concentration of **3** was maintained at 5×10^{-4} M, and the concentration of **1** was varied from 0 to 2.5×10^{-3} M. The stability constants were determined by analysis of changes in the positions of signals for the protons of both reactants *vs.* varied concentrations of **1**. The HYPNMR program[8] was used for the calculations.

[§] Deep-green single crystals of complex $(\mathbf{1})_2\cdot\mathbf{3}$ were grown by slow saturation of an acetonitrile solution (~5% water) of a mixture of **1** and **3** (at a nearly 2:1 molar ratio) with benzene and dioxane through a gas phase at room temperature. The X-ray experiment was carried out on a Bruker SMART-CCD diffractometer [MoKα radiation ($\lambda = 0.71073$ nm), graphite monochromator, ω-scanning, θ range 2.74–29.00°]. The X-ray intensity data were processed using the Bruker SAINT software.[9] The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method against F^2. The unit cell was found to contain two crystallographically independent perchlorate anions, three dioxane molecules and two water molecules. The hydrogen atoms of the water molecule H_2O(1W) found in the crown ether cavity of **1** were located from difference Fourier syntheses and refined isotropically. The positions of other hydrogen atoms were calculated geometrically and then refined isotropically, excluding the hydrogens of disordered and located at symmetry center dioxane molecules (these were refined using a riding model) and water molecule O(2W). All calculations were carried out with the use of the SHELXTL-Plus program package.[10]

For $(\mathbf{1})_2\cdot\mathbf{3}\cdot5C_4H_8O_2\cdot3H_2O$: $C_{114}H_{174}Cl_4N_4O_{53}$, $M = 2590.37$, triclinic, space group $P\bar{1}$, $a = 11.4047(3)$, $b = 14.3824(3)$ and $c = 19.9734(5)$ Å, $\alpha = 79.2720(10)$, $\beta = 80.6520(10)$ and $\gamma = 76.2880(10)$ °, $V = 3103.06(13)$ Å^3, $T = 120(2)$ K, $Z = 1$, μ(MoKα) = 0.191 mm^{-1}, 22765 collected reflections including 15144 independent ones ($R_{\mathrm{int}} = 0.0157$), R factors based on reflections with $I > 2\sigma(I)$ $R_1 = 0.0537$ and $wR_2 = 0.1466$, based on all reflections – $R_1 = 0.0685$ and $wR_2 = 0.1547$.

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 644450. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

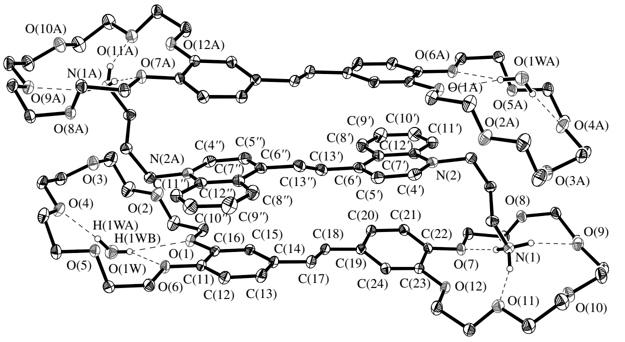

Figure 3 Structure of complex $(\mathbf{1})_2\cdot\mathbf{3}\cdot5C_4H_8O_2\cdot3H_2O$ drawn with anisotropic displacement parameters at the 50% probability level. Perchlorate anions, dioxane and water O(2W) solvate molecules, and most of hydrogen atoms are omitted for clarity. Hydrogen bonds are shown by dashed lines.

quinoline residues are rotated with respect to the plane of the ethylene group through a 30.1° angle, and the quinoline residues themselves are strictly parallel. The chromophore fragment of **1** shows a noticeable deviation from planarity, the dihedral angle between the benzene rings, C(11)···C(16)/C(19)···C(24), equals 15.5°, while the chromophore of free **1** is planar.[4] This geometry of the donor component of the complex is a compromise that ensures the best conditions for simultaneous interaction of the p_z-orbitals of the quinoline residue of **3** with the benzene rings of two neighbouring stilbene molecules. The chromophore fragments of triad **1·3·1** are projected exactly onto one another but they are not parallel, the dihedral angle between the mean planes of the conjugated fragments of **1** and **3** being 10.7°. With this geometry, the C(11)···C(16) benzene ring of molecule **1** and the N(2A),C(4″)···C(12″) quinoline residue of molecule **3** are more proximate than the other pair, the C(19)···C(24) benzene ring – the N(2), C(4′)···C(12′) quinoline residue. Evidently, this levels off the possible strain characterizing bimolecular complex **1·3**.

In the crystal, the termolecular complexes form ···D–A–D··· ···D–A–D··· type stacks. Trimer **1·3·1** contacts with neighbouring trimers through the stacking of the stilbene systems of molecules **1** related by another center of symmetry and located in parallel planes at a distance of ~3.5 Å. Each stack is surrounded by perchlorate ions and dioxane solvate molecules and is in gentle contact with neighbouring stacks through the crown ether fragments.

Thus, we demonstrated an appreciable dependence of the stability of supramolecular D–A complexes based on donor bis(18-crown-6)stilbene on the structure of the acceptor component. The spatial structure of the termolecular D–A–D complex was determined for the first time, and its sandwich structure was confirmed. The ammonium groups of the acceptor molecule are bound into host–guest complexes with the crown ether fragments of two neighbouring stilbene molecules, while their π-conjugated fragments are proximate and arranged exactly one above another with the maximum overlap of the p_z-orbitals favourable for stacking. These rules of construction of stacking architectures in charge transfer complexes can be used in the design of organic semiconductors and conductors in molecular electronics.

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