Intramolecular π-complexes based on nitroaryl derivatives of furotroponimine: structure and stereodynamics*

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Neutral aromatic electrophiles, such as trinitrobenzene and dinitrobenzofuroxane, covalently bound to the furotroponimine moiety form intramolecular through-space charge-transfer π-complexes both in solution and in the crystalline state. The kinetic and activation parameters of stereodynamic processes were determined by dynamic NMR spectroscopy. These parameters provide quantitative estimates of the kinetic stability of the π-complexes. The electronic and geometric characteristics of the π-complexes were calculated by the B3LYP/6-31G** method.

Key words: intramolecular π-complex, dinitrobenzofuroxane, furotroponimine, electrophile, nucleophilic substitution, stacking interactions, DFT, B3LYP/6-31G**.

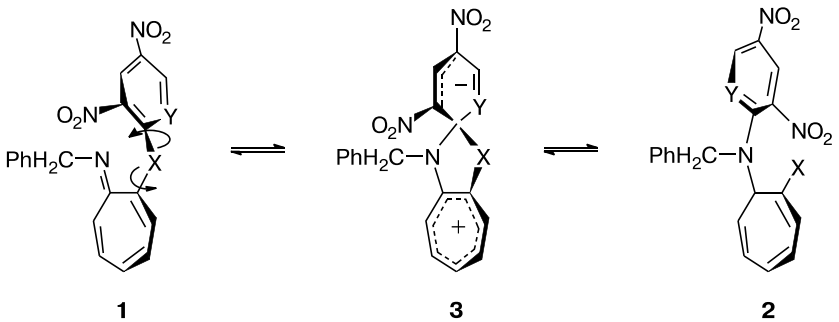
As opposed to anionic σ-complexes, which were experimentally detected as intermediates in the nucleophilic aromatic substitution reactions,[1—3] the existence of π-complexes of aromatic electrophiles with nucleophiles preceding the formation of σ-complexes is often only postulated. The preparative isolation and characterization have so far been documented only for a π-complex of trinitrobenzene with the indole-3-carboxylate anion (a precursor of the σ-adduct known as a Meisenheimer complex)[4] and a π-complex of nitrobenzodifuroxane with anthracene (a precursor of the Diels—Alder σ-adduct).[5]

The intramolecular nucleophilic aromatic substitution **1** ⇄ **2** affords bipolar spirocyclic σ-complexes **3** (Scheme 1) as intermediates.[6,7]

Depending on the structures of the nucleophilic moiety (tropolone and its heteroanalogs) and the electrophilic moiety (π-deficient aryls and hetaryls), either open-chain isomers **1** and **2** or zwitterionic spirocyclic compounds **3** can be thermodynamically more stable.[6,8] The tautomerism and stereodynamics of the degenerate and non-degenerate transformations **1** ⇄ **3** ⇄ **2** were studied in detail[9—11] by dynamic NMR spectroscopy. The mapping of the reaction channel **1** ⇄ **3** was performed based on the X-ray diffraction data for the key structures.[12] However, the formation of an intramolecular π-complex has not been experimentally observed.

An analysis of the structures of the synthesized stable bipolar spirocyclic σ-complexes based on derivatives of

Scheme 1



1 **3** **2**

X = O, S, NR; Y = CNO_2, CSO_2CF_3, N

* Dedicated to the Academician of the Russian Academy of Sciences S. M. Aldoshin on the occasion of his 60th birthday.

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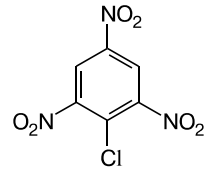
tropolone **3**, benzimidazole,[13] aminoquinoline,[14] and indolizine[15] shows that for the structures with efficient intramolecular charge transfer to be formed, the molecule should contain the following quite evident moieties, the combination of which is often difficult to achieve by synthetic methods: 1) an aromatic electrophile capable of delocalizing a negative charge, 2) a nucleophile prone to the formation of an aromatic cation, and 3) a conjugated linker, which can direct the reaction centers to the reaction channel.

We report on the structures and stereodynamics of two intramolecular contact-charge-transfer π-complexes, which were synthesized using the above-described approaches. We used picryl chloride **4**, which forms preparatively isolated bipolar spirocyclic compounds,[6,12,13] and superelectrophilic dinitrochlorobenzofuroxane **5** (see Refs 10, 16, and 17) as electrophiles. Stable aromatic diethoxyfurotropylium cation **6**, which is a synthetic equivalent of furotropone, readily reacts with aromatic amines.[18]



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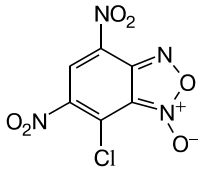

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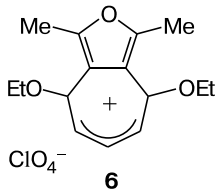

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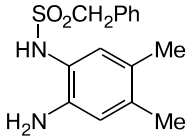

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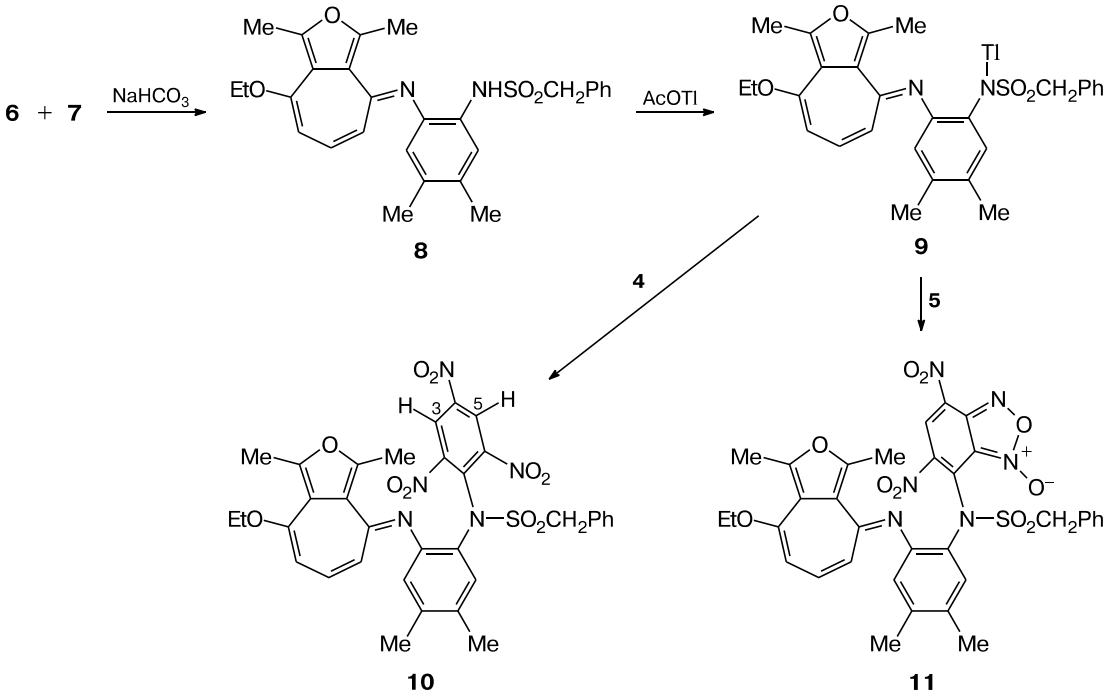
Therefore, the reaction of perchlorate **6** with *N*-(phenylmethanesulfonyl)-2-phenylenediamine **7** affords furotroponimine **8** (Scheme 2). The latter compound satisfies the conditions necessary for the formation of intramolecular charge-transfer systems. First, compound **8** contains the seven-membered conjugated ring bound to the electron-donating ethoxy group and annulated with the π-excessive furan ring. Hence, taking into account the stability of cation **6**, compound **8** would be expected to be effectively involved in the delocalization of the positive charge in the reactions with electrophiles. Second, compound **8** contains the RSO_2NH group, in which the proton can be easily replaced by the nitroaryl group.

The reaction of compound **8** with AcOTl gives salt **9**. We used thallium salts **9** because their reactivity is similar to that of silver salts but they are stable to light. The reaction of equivalent amounts of thallium salt **9** and the corresponding nitroaryl chloride produces intramolecular charge-transfer complexes **10** and **11** (see Scheme 2).

The benzylsulfonyl group in compounds **10** and **11** fulfills two main functions: 1) accepts the electron density from the N atom, thus preventing a decrease in the electrophilicity of the nitroaryl group and 2) the chiral states of the molecule are fixed by the diastereotopic methylene group, thus making it possible to study the tautomerism and stereodynamics by dynamic NMR spectroscopy.[9]

Scheme 2



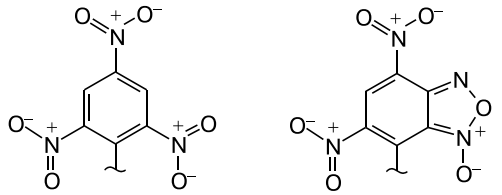
The characteristic feature of the ^{1}H NMR spectrum of complex **10** is that, at temperatures close to room temperature, the signals of the protons H(3) and H(5) of the picryl group appear as two broadened one-proton singlets rather than as a narrow two-proton singlet characteristic of all spirocyclic and open-chain trinitrobenzene derivatives studied earlier. The magnetic nonequivalence indicates that the protons H(3) and H(5) are in a substantially different environment and, consequently, the rapid reversible exchange between their positions is impossible.

In the ^{1}H NMR spectrum of compound **10** in $CDCl_3$, the signals of the protons H(3) and H(5) reversibly coalesce to a two-proton single averaged signal at 40 °C and are split into two one-proton signals at −35 °C. The kinetic and activation parameters of the process, in which the protons H(3) and H(5) in complex **10** exchange their positions, are $k_{298} = 1.0 \cdot 10^2$ s^{-1}, $\Delta G^{\neq}_{298} = 61.5$ kJ mol^{-1}, $\Delta H^{\neq} = 48$ kJ mol^{-1}, $\Delta S^{\neq} = -45$ J mol^{-1} K^{-1}.

The X-ray diffraction data (Fig. 1) provide insight into the factor responsible for the magnetic nonequivalence of the protons H(3) and H(5) and the nature of the observed stereodynamic process. The donor and acceptor groups of molecule **10** are almost parallel to each other, and there is a considerable attractive interaction between these groups in the crystal structure. This interaction is manifested, in particular, in the shortened contacts between the N(1) and C(22), N(1) and C(27), C(3) and C(23) atoms.

Figure 2 shows the X-ray diffraction structure of π-complex **11**. The donor and acceptor groups of molecule **11**, like those in picryl derivative **10**, are almost parallel to each other. Noteworthy are the shortened C(1)...C(22) and C(3)...C(23) contacts. The higher electrophilicity of the dinitrobenzofuroxane ring[2,3,10] compared to that of the trinitrophenyl group and, consequently, the stronger attractive interaction between the nitroaryl and furotropone groups are responsible for higher kinetic stability of π-complex **11**. Upon heating of compound **11** in $C_6D_5NO_2$, the AB quartet belonging to the protons of the diastereotopic methylene group exhibits reversible coalescence to a single signal (Fig. 3).

The kinetic and activation parameters of this stereodynamic process are $k_{298} = 5.2 \cdot 10^{-2}$ s^{-1}, $\Delta G^{\neq}_{298} = 80.3$ kJ mol^{-1}, $\Delta H^{\neq} = 107$ kJ mol^{-1}, $\Delta S^{\neq} = 90$ J mol^{-1} K^{-1}. It should be noted that the picryl (**12**) and dinitrobenzofuroxyl (**13**) groups create similar steric hindrance to the rotation around the electrophile—N bond. Consequently, the observed increase in the barrier to rotation can be



12 **13**

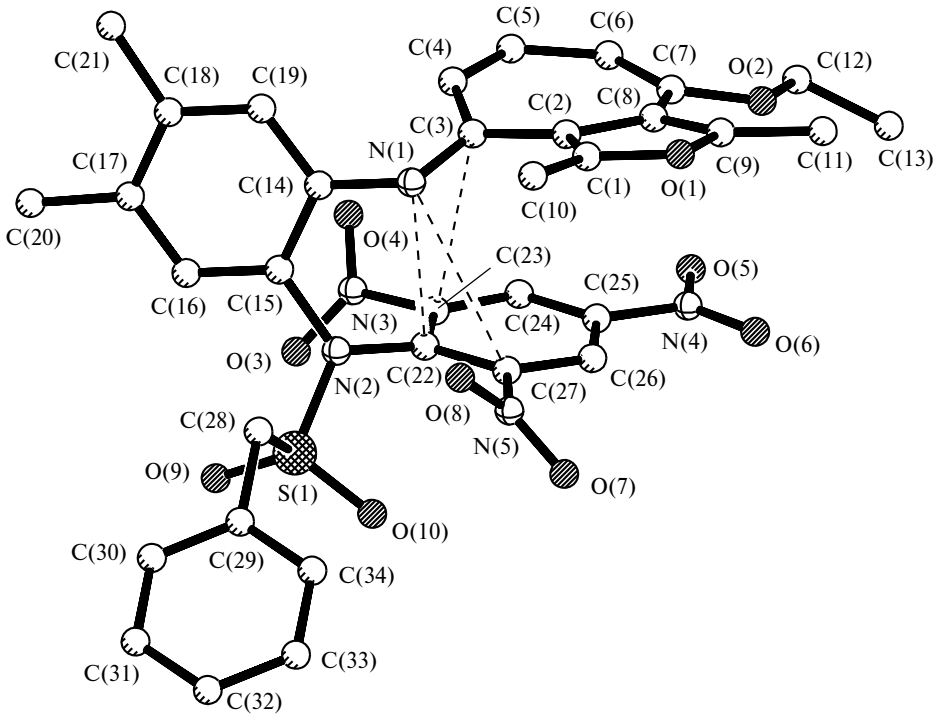


Fig. 1. X-ray diffraction structure of compound **10**. Here and in Fig. 2, the shortened contacts are indicated by dashed lines. The interatomic distances and the sums of the van der Waals radii[19] (in parentheses) (Å): N(1)...C(22), 2.76 (3.21); N(1)...C(27), 3.16 (3.21); C(3)...C(23), 3.34 (3.42).

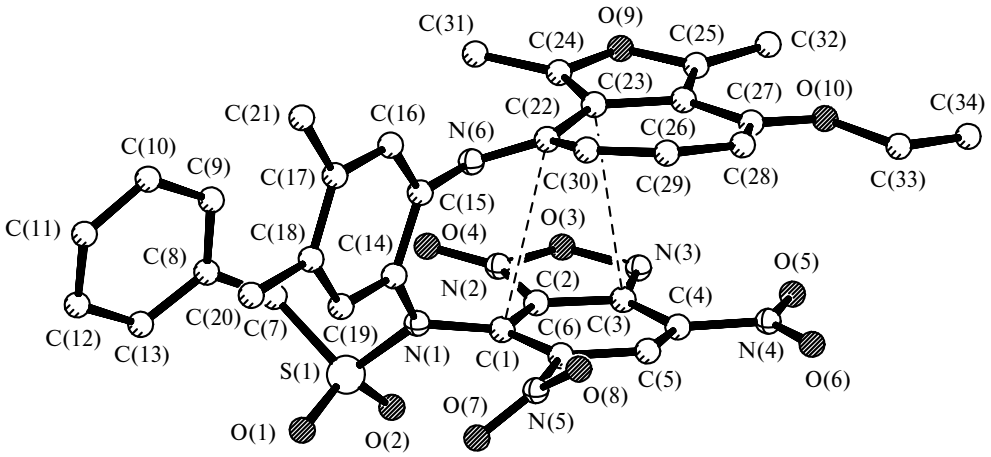


Fig. 2. X-ray diffraction structure of compound **11**. The interatomic distances and the sums of the van der Waals radii[19] (in parentheses) (Å): C(1)...C(22), 3.25 (3.42); C(3)...C(23), 3.39 (3.42).

attributed only to stronger donor-acceptor interactions. According to the quantum chemical calculations at the B3LYP/6-31G** level of theory taking into account the solvent effect of CH_2Cl_2 with the use of the PCM model,[20] the global electrophilicity index[21,22] is 3.8 and 5.5 eV for picryl group **12** and dinitrobenzofuroxyl group **13**, respectively. These values correspond to the expected direction of the electron density transfer in the resulting π-complex.

The protons H(3) and H(5) in compound **10**, as well as the methylene protons in **11**, exchange their positions. Hence, the rotation of the nitroaryl group around the C—NSO_2R bond and, consequently, the cleavage of donor-acceptor π bonds are required. The rate of these stereodynamic processes reflects the intensity of interactions under consideration.

An analysis of interatomic distances smaller than the sums of the corresponding van der Waals radii is very informative in studying molecules prone to tautomeric and stereodynamic transformations, because shortened contacts often provide information on the pathway of the tautomeric transformation.[6] For the systems under consideration, the X-ray diffraction data combined with an increase in the barrier to rotation around the electrophile—N bond are, in our opinion, reliable evidence for the π-complex formation. It should be noted that shortened intramolecular interatomic contacts may be a consequence solely of the molecular packing in the crystal. This fact can be clarified by analyzing the electron density distribution in terms of the topological theory of Atoms in Molecules (AIM)[23] and comparing the total energies of different conformers of compounds **10** and **11** in a solvent.

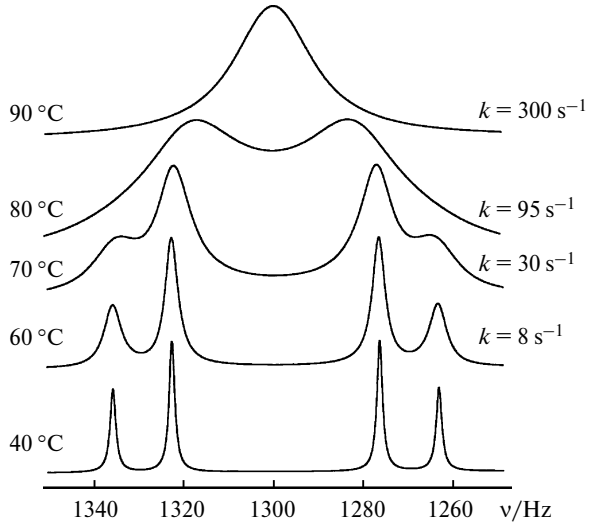


Fig. 3. Temperature-dependent evolution of the signals of the CH_2 group in the ^1H NMR spectra ($C_6D_5NO_2$) of compound **11**.

In terms of the AIM theory, the presence of the saddle critical point (3,−1) between the corresponding atoms is a necessary and sufficient condition of the existence of the binding interaction (chemical bond). It is assumed that the electron density at this point usually denoted as $\rho_b(\mathbf{r})$ is proportional to the bond strength and order.[23]

The AIM analysis[23] with the use of the wavefunction obtained by the B3LYP/6-31G** method revealed two critical points (3,−1) in the region of weak binding interactions characteristic of the shortened C(6)...C(25) ($\rho(\mathbf{r}) = 3.0 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 9.2 \cdot 10^{-3}$ a.u.), C(4)...C(23) ($\rho(\mathbf{r}) = 4.9 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 1.32 \cdot 10^{-2}$ a.u.), and N(1)...O(8) ($\rho(\mathbf{r}) = 6.8 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 2.27 \cdot 10^{-2}$ a.u.) contacts for picryl compound **10** and the shortened C(6)...C(30) ($\rho(\mathbf{r}) = 4.9 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 1.34 \cdot 10^{-2}$ a.u.) and C(4)...C(28) ($\rho(\mathbf{r}_c) = 3.2 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 9.5 \cdot 10^{-3}$ a.u.) contacts for dinitrobenzofuroxane derivative **11** (Fig. 4). In addition to these interactions, the AIM analysis revealed weak binding interactions (bond paths) between the H atoms of the donor group and the nitro O atoms of the acceptor group.

The X-ray diffraction data and the results of quantum chemical calculations are indicative of very short interatomic distances along the bond paths (see Fig. 4 and

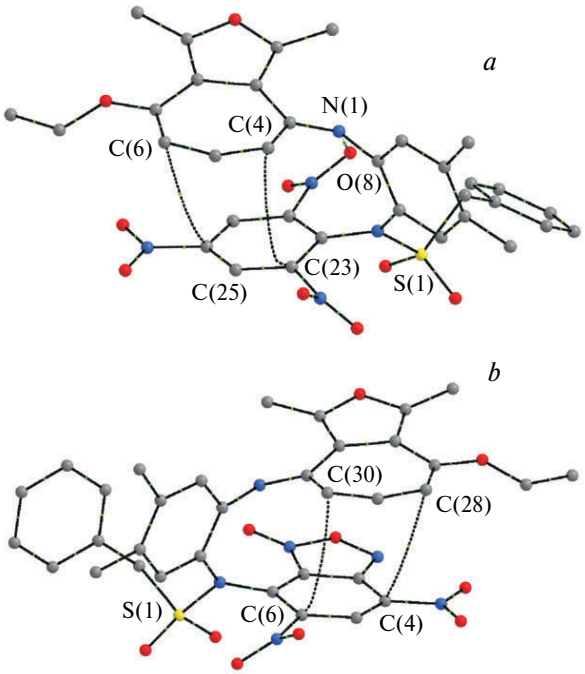


Fig. 4. Selected bond paths for systems **10** (*a*) and **11** (*b*) determined by the AIM analysis.
Note. Fig. 4 is available in full color in the on-line version of the journal (http://www.springerlink.com).

Table 1). However, the interatomic distances found for the crystalline phase, are overestimated by the DFT calculations for solution (for example, C(3)...C(23) is 3.612 Å and N(1)...C(27) is 3.316 Å for **10** (*cf.* Fig. 1) and C(1)...C(22) is 3.344 Å and C(3)...C(23) is 3.735 Å for **11** (*cf.* Fig. 2)).

The positive values of the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ characterize the above-mentioned bonds as weak attractive interactions between the closed electron shells, which occur, in particular, in the case of the formation of hydrogen bonds and van der Waals contacts.[23] This is confirmed by a comparison of the calculated values with those typical of the Ne...HF and Ar...HF complexes ($\rho(\mathbf{r}) = 9.9 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 4.84 \cdot 10^{-2}$ a.u. and $\rho(\mathbf{r}) = 7.7 \cdot 10^{-3}$, $\nabla^2\rho(\mathbf{r}) = 3.11 \cdot 10^{-2}$ a.u., respectively).[23]

Table 1. Calculated (B3LYP/6-31G**, solvent CH_2Cl_2) and experimental interatomic distances in compounds **10** and **11**

Distance	*d*/Å	
	Calculation	X-ray
	Compound **10**	
N(1)...O(8)	3.192	3.273
C(4)...C(23)	3.523	3.456
C(6)...C(25)	3.815	3.854
	Compound **11**	
C(6)...C(30)	3.523	3.552
C(4)...C(28)	3.791	3.800

The conformers of compounds **10** and **11**, which are energetically most stable according to the results of calculations, are depicted in Fig. 5. The integral values of the stacking interactions were estimated as the total energy differences between the conformers presented in Fig. 5, *a* and the most stable forms, in which stacking interactions are absent (see Fig. 5, *b*). The systems with an eclipsed arrangement of the donor and acceptor groups in **10** and **11** are more stable (by 2.4 and 2.3 kcal mol^{-1}, respectively).

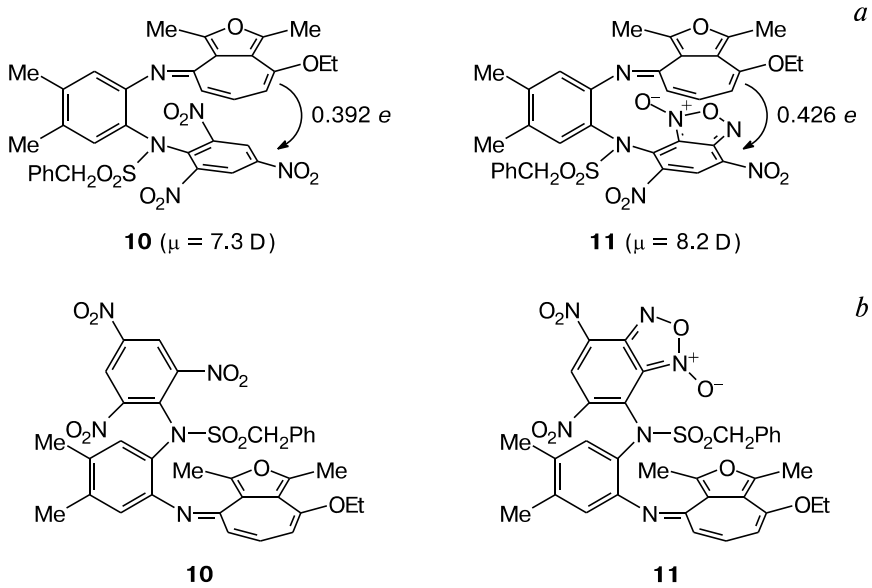


Fig. 5. Structures **10** and **11** with stacking interactions (*a*) and without these interactions (*b*). The charge transfer is indicated by an arrow.

There is a considerable charge transfer between the donor and acceptor groups of the π-complexes (in both cases, ~0.4 *e*, see Fig. 5, *a*). The charges and dipole moments presented in Fig. 5, *a*, correlate with both the activation barriers to rotation about the N—nitroaryl bond and the experimentally observed higher kinetic stability of the dinitrobenzofuroxane derivative.

There is a much greater number of attractive interactions in the stable conformers of compounds **10** and **11** than those shown in Fig. 4. It is due to the accumulation of these interactions in the intramolecular space and the high polarity of the systems that the eclipsed conformations are favorable. This fact was confirmed even by the molecular mechanics method (the MM+ force field), the calculated energies of the stacking interactions being of the same order of magnitude as those estimated by DFT calculations (4.6 kcal mol^{-1} for compound **10** and 9.6 kcal mol^{-1} for compound **11**).

Therefore, the experimentally observed high-polarity systems based on nitroaryl derivatives of furotroponimine are stabilized as π-complexes both in solution and in the crystalline state. The structures of the latter are determined by attractive stacking interactions and a considerable intramolecular charge transfer. The methods of synthesis and investigations of intramolecular π-complexes proposed in the present study provide a deeper insight into the nature of stacking interactions that play an important role in the formation of supramolecular structures, the coordination of pharmacons to biological targets, and the photochemically controlled behavior of supramolecular ensembles.

Experimental

The ^{1}H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) in CD_2Cl_2 using Me_4Si as the internal standard. The temperature-dependent spectra of compounds **10** and **11** were recorded in $CDCl_3$ and $C_6D_5NO_2$, respectively. The computer simulation of the spectra was carried out and the rate constants were calculated using the gNMR 5.1 software.[24] The Gibbs energies ($\Delta G^{\neq}$) were calculated using the Arrhenius equation for each rate constant. The enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation were determined by the linear least-squares fitting with the correlation coefficient not smaller than 0.98. According to our estimates based on the results of the study,[25] the error of the determination was not larger than 15% for *k*, 0.6 kJ mol^{-1} for $\Delta G^{\neq}$, 2 kJ mol^{-1} for $\Delta H^{\neq}$, and 8 J mol^{-1} K^{-1} for $\Delta S^{\neq}$.

The methods of molecular mechanics and quantum chemical calculations were reported in the study.[26]

[2-(8′-Ethoxy-1′,3′-dimethylfuro[*c*]tropylidene-4′-imino)-4,5-dimethylphenyl](phenylmethanesulfonyl)(2″,4″,6″-trinitrophenyl)amine (10). A mixture of thallium salt **9** (see Ref. 18) (0.1 g, 0.145 mmol), picryl chloride (0.036 g, 0.145 mmol), and pyridine (0.025 mL) in acetonitrile (10 mL) was stirred at room temperature for 30 min and then refluxed for 15 min. The precipitate of TlCl was separated by hot filtration. The mother liquor was concentrated *in vacuo*. The yield was 0.03 g (28%). Red crystals, m.p. 240—242 °C (MeCN). Found (%): C, 58.08; H, 4.29; N, 9.76. $C_{34}H_{31}N_5O_{10}S$. Calculated (%): C, 58.20; H, 4.45; N, 9.98. ^{1}H NMR (CD_2Cl_2), δ: 1.47 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.7 Hz); 2.11 (s, 3 H, CH_3); 2.20 (s, 3 H, CH_3); 2.37 (s, 3 H, CH_3); 2.53 (s, 3 H, CH_3); 3.85 (q, 2 H, OCH_2, J = 7.7 Hz); 4.67 (s, 2 H, $C\underline{H}_2$Ph); 5.04 (d, 1 H, H(7′), J = 9.3 Hz); 5.81 (d, 1 H, H(5′), J = 12.6 Hz); 5.95 (dd, 1 H, H(6′), J = 12.6 Hz, J = 9.3 Hz); 6.37 (s, 1 H, H(3)); 7.30—7.55 (m, 5 H, Ph); 7.74 (s, 1 H, H(6)); 8.46 (br.s, 2 H, H(3″), H(5″)).

I[2-(8′-Ethoxy-1′,3′-dimethylfuro[*c*]tropylidene-4′-imino)-4,5-dimethylphenyl](phenylmethanesulfonyl)(4″,6″I-dinitrobenzofuroxane-7″)amine (11). A mixture of thallium salt **9** (see Ref. 18) (0.2 g, 0.29 mmol) and 7-chloro-4,6-dinitrobenzofuroxane[27] (0.075 g, 0.29 mmol) in toluene (10 mL) was heated for 30 min. The precipitate containing the reaction product and TlCl was filtered off. The product was extracted with $CHCl_3$, and the solvent was removed *in vacuo*. The crystals that formed were suspended in an aqueous solution of sodium dodecyl sulfate (0.2%), heated with stirring for 10 min, and filtered off. The precipitate was washed with distilled water and acetone (3×1 mL). The yield was 0.03 g (14%). Black crystals with a green tint, m.p. 254—257 °C. Found (%): C, 57.30; H, 4.09; N, 11.43. $C_{34}H_{30}N_6O_{10}S$. Calculated (%): C, 57.14; H, 4.23; N, 11.76. ^{1}H NMR (CD_2Cl_2), δ: 1.55 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.7 Hz); 2.15 (s, 3 H, CH_3); 2.25 (s, 3 H, CH_3); 2.37 (s, 3 H, CH_3); 2.53 (s, 3 H, CH_3); 3.93 (q, 2 H, OCH_2, J = 7.7 Hz); 4.23 (d, 1 H, $C\underline{H}_2$Ph, J = 13.4 Hz); 4.43 (d, 1 H, $C\underline{H}_2$Ph, J = 13.4 Hz); 5.15 (d, 1 H, H(7′), J = 9.4 Hz); 5.77 (d, 1 H, H(5′), J = 12.5 Hz); 6.03 (dd, 1 H, H(6′), J = 12.5 Hz, J = 9.4 Hz); 6.44 (s, 1 H, H(3)); 7.35—7.50 (m, 5 H, Ph); 7.74 (s, 1 H, H(6)); 8.35 (s, 1 H, H(5″)).

X-ray diffraction analysis. Single crystals of **10** were obtained by the crystallization from acetonitrile ($C_{34}H_{31}N_5O_{10}S$, M = 701.7); at 110 K, monoclinic, space group $P2_1/n$, a = 11.2196(19) Å, b = 12.933(2) Å, c = 22.323(4) Å, β = 97.466(4)°, V = 3211.7(9) Å^3, Z = 4, d_{calc} = 1.451 g cm^{-3}, μ(Mo-Kα) = 3.57 cm^{-1}, $F(000)$ = = 1464. The intensities of 26737 reflections were measured on a Bruker SMART 1000 CCD diffractometer (λ(Mo-Kα) = = 0.71073 Å, ω-scanning technique, 2θ < 60°); 9350 unique reflections (R_{int} = 0.0404) were used in the refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic and isotropic displacement parameters. The final R factors for compound **10** are wR_2 = 0.1175 and GOF = 1.082 based on all independent reflections (R_1 = 0.0603 based on F for 5264 observed reflections with $I > 2\sigma(I)$). All calculations were carried out using the SHELXTL PLUS 5.0 program package.[28] The X-ray diffraction data for π-complex **10** were deposited with the Cambridge Crystallographic Data Centre (CCDC 915832).

Single crystals of **11** were obtained by the crystallization from chloroform ($C_{34}H_{30}N_6O_{10}S$, M = 714.7); at 163 K, monoclinic, space group $P2_1/c$, a = 19.757(4) Å, b = 11.857(3) Å, c = = 13.939(4) Å, β = 96.262(19)°, V = 3245.9(14) Å^3, Z = 4, d_{calc} = 1.463 g cm^{-3}, μ(Mo-Kα) = 3.57 cm^{-1}, $F(000)$ = 1488. The intensities of 3294 reflections were measured on a Siemens P3 diffractometer (λ(Mo-Kα) = 0.71073 Å, ω-scanning technique, 2θ < 40°); 3049 unique reflections (R_{int} = 0.0424) were used in the refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic and isotropic displacement parameters. The hydrogen atoms were positioned geometrically and refined using a riding model. The final R factors for compound **11** are

$wR_2 = 0.1274$ and GOF = 1.023 based on all independent reflections ($R_1 = 0.0855$ based on F for 1540 observed reflections with $I > 2\sigma(I)$). All calculations were carried out using the SHELXTL PLUS 5.0 program package.[28] The X-ray diffraction data for π-complex **11** were deposited with the Cambridge Crystallographic Data Centre (CCDC 915831).

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