Nitrosonium Complexes of Fluorene and 9,9-Dimethylfluorene

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Abstract—The reaction of fluorene and 9,9-dimethylfluorene with nitrosonium tetrachloroaluminate was investigated using ^{1}H and ^{13}C NMR spectroscopy with deuterium perturbation. The arising positively charged complexes with one and two nitrosonium cations are involved into an interconversion fast in the NMR time scale. The data of quantum-chemical calculations performed by DFT method (basic Λ02) indicate the higher stability of single-charged π-complexes of 2η type compared with the π-complexes corresponding to the addition of two NO⁺ cations. In the dication π-complexes the transoid position of the NO groups is more favorable than the cisoid position.

Nitrosonium arene complexes for a long time attract the rapt attention of researchers [1]. Up till now the structure and reactivity of numerous complexes of aromatic compounds with NO⁺ were investigated [1–9]. However the data on the nitrosonium complexes of polycyclic aromatic compounds are limited [1–9] (cf. [10]).

The goal of this study was the theoretical and experimental investigation of the structure and dynamics of the nitrosonium complexes of fluorene and 9,9-dimethylfluorene. The special feature of these complexes is the possibility of an interring migration of the NO group, and the presence of test NMR signals from groups CH_2, CMe_2 makes it possible to establish the relative occurrence of the intra- and intermolecular transfer of the NO group.

The reaction of NO⁺AlCl₄⁻ with fluorene (**I**) or 9,9-dimethylfluorene (**II**) in SO_2–CD_2Cl_2 at –80°C yielded mono- and double-charged nitrosonium complexes in all likelihood of the π-complex character that suffered interconversion fast in the NMR time scale (Scheme 1).

This statement is confirmed by the data of ^{1}H and ^{13}C NMR spectroscopy. On the addition of an equimolar amount of the salt NO⁺AlCl₄⁻ to the solutions of compounds **I** and **II** the averaged signals of hydrogen and carbon atoms of the aromatic rings suffered relatively small downfield shift compared to the cor-responding

signals in the spectra of the precursor compounds (Tables 1, 2) (cf. [4, 7–9]). The chemical shifts of ^{13}C atoms in the charged π-electron systems are known to correlate with the π-electron density [13]. The calculated values of the overall positive π-charge on the carbon atoms of the aromatic rings in π-complexes **III** and **IV** (Table 2) are close to the corresponding charges for the π-complexes of the nitrosonium reaction with naphthalene and its methyl derivatives (q_π^+ 0.34–0.64)[8], and they are considerably less than those of the arenonium ions (q_π^+ ~1) [13]. On increasing the molar ratio NO⁺AlCl₄⁻ : (**I**) or NO⁺AlCl₄⁻ : (**II**) from 1 to 7 and from 1 to 5 respectively an additional downfield shift is observed for the signals of hydrogen and carbon atoms of the aromatic rings. This fact might be regarded as an indication of the involvement into a dynamic equilibrium of dication π-complexes **VII** and **VIII** (Scheme 1, Figs. 1, 2) (cf. [4]).

An additional experimental proof of the formation of π-complexes of NO⁺ cation with the fluorene and not the formation of the corresponding σ-complexes suffering a fast interconversion was obtained by the method of isotope perturbation of the resonance equilibrium [16, 17]. On addition of a mixture of fluorene and 2-deuterofluorene (at a molar ratio 1:1) dissolved in CD_2Cl_2 to a solution of salt NO⁺AlCl₄⁻ in SO_2 at –60°C complexes were generated in whose ^{13}C NMR spectra a slight isotope

Scheme 1.

R = H (**I, III, III', V, VII, VII'**), Me (**II, IV, IV', VI, VIII, VIII'**).
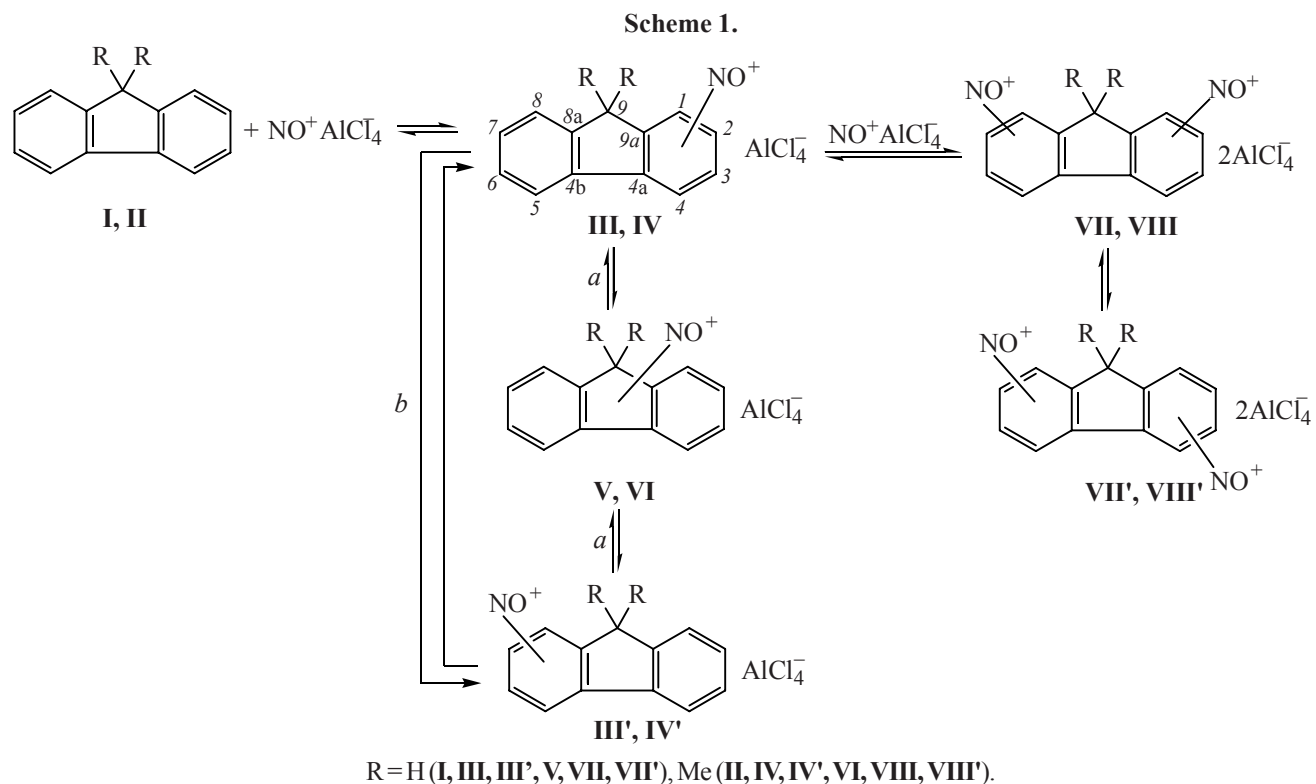
Table 1. ^{1}H NMR spectra of fluorene, 9,9-dimethylfluorene, and their nitrosonium complexes in SO_2–CD_2Cl_2 at $-70°C^a$

Compound no.	Molar ratio ArH:$NO^+AlCl_4^-$	δ, ppm			
		CH_2 $(CH_3)^b$	$H^{1,8\,c}$	$H^{2,7\,c}$, $H^{3,6\,c}$	$H^{4,5\,c}$
I^d	–	3.99	7.62	7.34, 7.42	7.83
III, VII	1:1	4.04	7.82	7.63, 7.67	8.05
III, VII	1:2	4.19	7.98	7.82, 7.86	8.25
III, VII	1:3	4.27	8.06	7.92	8.29
III, VII	1:4	4.33	8.14	7.99	8.37
III, VII	1:5	4.37	8.18	8.02	8.41
III, VII	1:6	4.40	8.21	8.05	8.45
III, VII	1:7	4.41	8.23	8.07	8.47
IIe	–	1.46	7.52	7.33, 7.37	7.77
IV, VIII	1:1	1.52	7.75	7.66	8.03
IV, VIII	1:2	1.59	7.84	7.84	8.19
IV, VIII	1:3	1.60	7.89	7.89	8.24
IV, VIII	1:4	1.61	7.93	7.93	8.28
IV, VIII	1:5	1.62	7.96	7.96	8.32

^{a} Chemical shifts are reported in ppm with respect to an internal reference CH_2Cl_2 (δ_H 5.33 ppm). ^{b} Broadened singlet. ^{c} Broadened multiplets. ^{d} Cf. [11]. ^{e} Cf. [12].

Table 2. ^{13}C NMR spectra of fluorene, 9,9-dimethylfluorene, and their nitrosonium complexes in SO_2–CD_2Cl_2 at $-70°$ C^a, and also the calculated values of the overall π-charge on the carbon atoms of aromatic rings $(q_{\pi}^{+})^b$

Compd. no..	Molar ratio ArH:$NO^+AlCl_4^-$	δ, ppm								$\Delta\Sigma\delta(C_{arom})$ ppm	q_{π}^{+}
		C^9	CH_3	$C^{1,8}$ C	$C^{2,7}$ C	$C^{3,6}$ C	$C^{4,5}$ C	$C^{8a,9a}$ d	$C^{4a,4b}$ d		
I^e	–	36.11		125.95	127.69	127.46	120.76	143.92	141.22	–	–
III, VII	1:1	36.43		128.95	132.07	130.90	124.54	148.12	143.04	41.24	0.26
III, VII	1:2	36.82		130.77	134.41	132.89	126.72	150.41	144.05	64.50	0.40
III, VII	1:3	37.09		131.48	135.08	133.58	127.47	151.07	144.31	71.98	0.45
III, VII	1:4	37.30		132.07	135.62	134.15	128.09	151.61	144.50	78.08	0.49
III, VII	1:5	37.42		132.52	136.05	134.61	128.58	152.02	144.63	82.82	0.52
III, VII	1:6	37.56		132.77	136.28	134.82	128.84	152.24	144.69	85.28	0.53
III, VII	1:7	37.63		132.95	136.44	134.99	129.02	152.40	144.73	87.06	0.54
II^f	–	46.73	26.25	123.66	128.04	127.70	120.67	154.08	138.89	–	–
IV, VIII	1:1	47.64	25.78	126.66	132.53	131.27	124.48	158.03	140.90	41.66	0.26
IV, VIII	1:2	48.17	25.64	128.23	134.71	133.07	126.41	160.01	141.88	62.54	0.39
IV, VIII	1:3	48.28	25.60	128.65	135.09	133.51	126.85	160.38	141.99	66.86	0.42
IV, VIII	1:4	48.37	25.60	128.98	135.41	133.88	127.22	160.67	142.07	70.38	0.44
IV, VIII	1:5	48.45	25.62	129.31	135.71	134.19	127.55	160.93	142.16	73.62	0.46

[a] Chemical shifts in ppm from TMS were recalculated from the internal reference CD_2Cl_2 (δ_C 53.6 ppm).
[b] In the calculation a value of 160 ppm was taken per a unit of p-chargeзаряеа [13].
[c,d] The chemical shifts probably should be interchanged.
[e] Cf. [14].
[f] Cf. [15].

effect was observed for atoms $C^{1,8}$, $C^{3,6}$ [δ(–50°C) 0.06, 0.07 ppm respectively]. The small values of the isotope effect cannot correspond to the fast interconversion of σ-complexes **IX, IX'** that the most likely are the most stable among the isomeric nitrosonium σ-complexes of fluorene (cf. [4, 7, 8, 16–19]). The calculations by the DFT method (basis Λ02) [20–23] showed that no minima on the potential energy surface (PES) corresponded to the addition of cation NO^+ at the positions 1–4 of fluorene. In contrast, the PM3 method [24] indicated the preference of the σ-complexes formation, and the most stable among them appeared to be 2-nitrosofluorenyl cation (the enthalpy of formation of 1-, 2-, 3- and 4-nitroso-fluorenyl cations amounted respectively to 1091.3, 1054.8, 1083.4, and 1064.8 kJ mol^{-1}).

As already mentioned, the calculations by DFT method (basis Λ02) showed larger energy preference of the π-complexes compared to σ-complexes. We found minima on the PES corresponding to single-charged π-complexes of the 2η type with fairly elongated bonds C–NO (2.3–2.5 Å to the nearest carbon atoms of the rings and 2.7–3.4 Å to more remote atoms of the same ring) (Table 3, Figs. 3, 4). The NO group in these complexes is located at an angle to the plane of the aromatic ring and is "connected" to atoms C^3, C^4, or C^{4a}, C^{9a} (complexes **A1**, **B1** and **A2**, **B2** respectively) (Figs. 3, 4). The geometrical data obtained are in agreement with the results of calculations by the method B3LYP [basis 6-31G(d)] of a benzene complex with the

Scheme 2.


IXa, IXb   **IX'a, IXb**
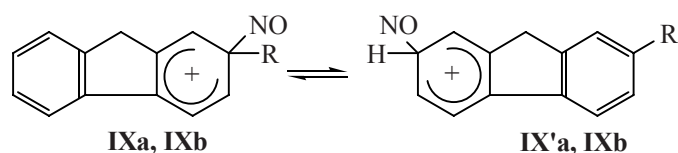
R = H (**a**), D (**b**).
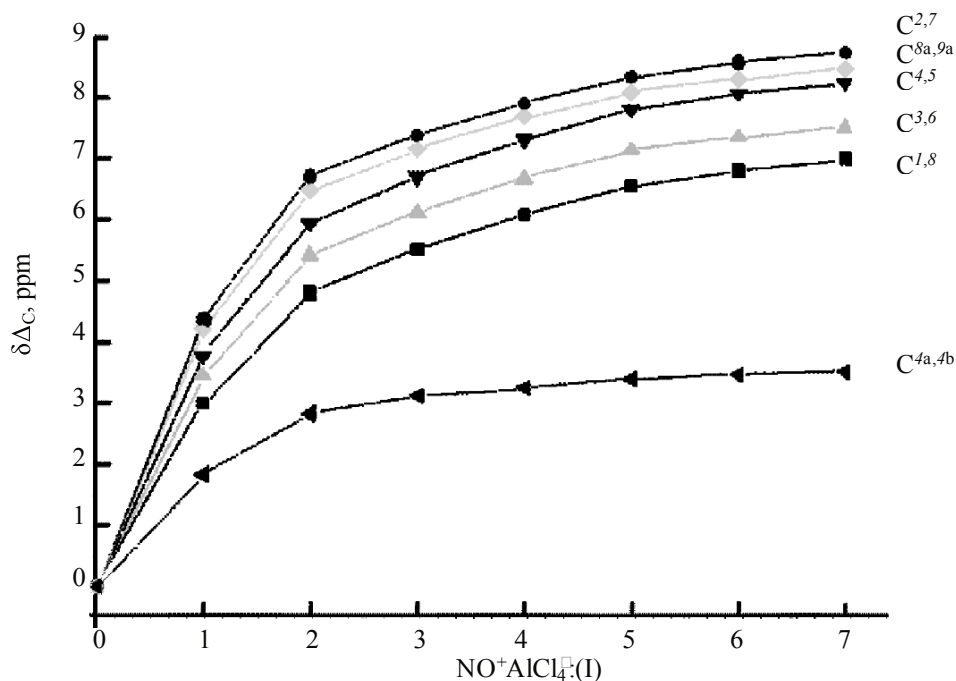
Fig. 1. The dependence of the differences of the ^{13}C chemical shifts for π-complexes **III**, **VII**, and fluorene on the molar ratio $NO^+AlCl_4^-$: **(I)**.
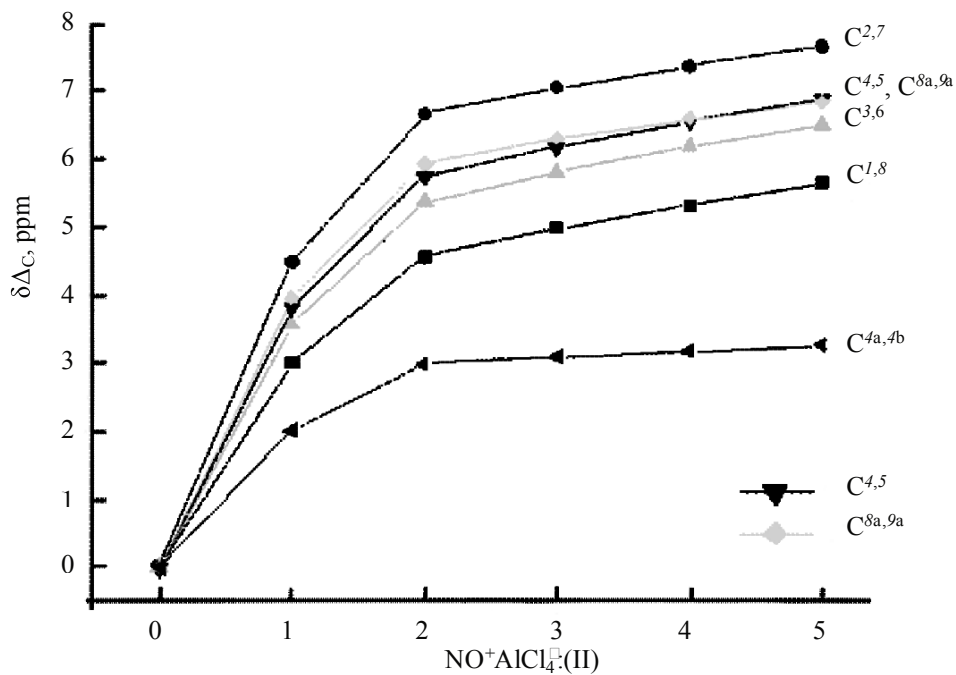

Fig. 2. The dependence of the differences of the ^{13}C chemical shifts for π-complexes **IV, VIII**, and 9,9-dimethylfluorene on the molar ratio $NO^+AlCl_4^-$: **(II)**.

NO^+ cation [25]. The most energetically feasible among the optimized structures are π-complexes **A1** and **B1**. The geometrical parameters of these complexes are close to those obtained by XRD study of the π-complex of the NO^+ cation with hexamethylbenzene [26] and other arenes [1, 6, 27] (Table 3). The common for this type complexes is the angular location of the NO group with respect to the perpendicular to the benzene ring plane, sp^2-hybridization of the carbon atoms of the aromatic ring, and fairly elongated bonds between the nitrogen of
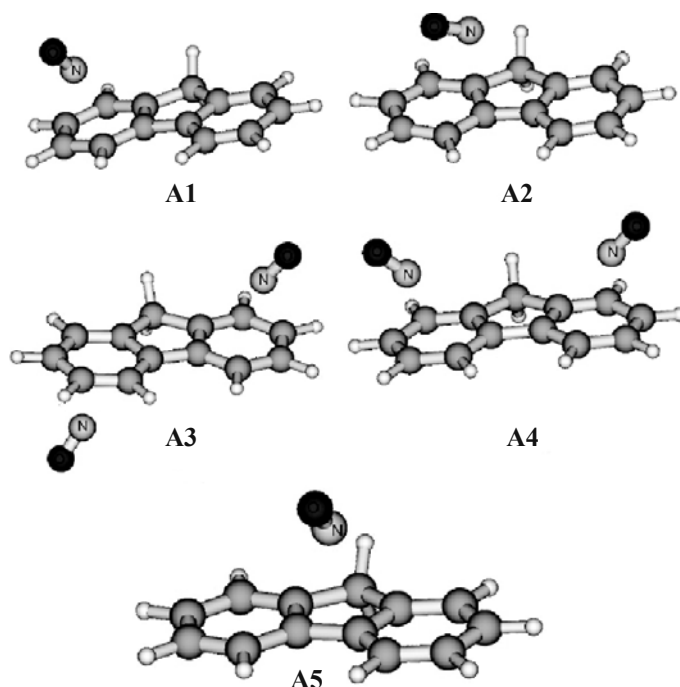
Fig. 3. Structures of fluorene nitrosonium complexes optimized by DFT method.
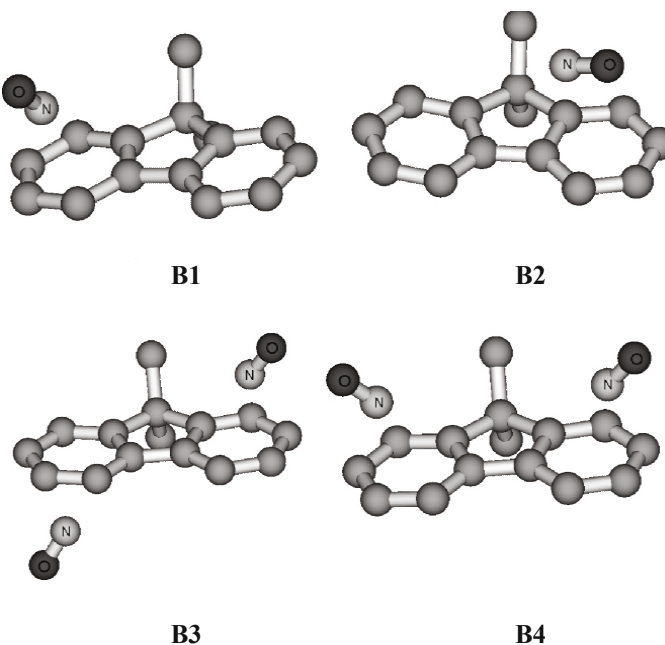
Fig. 4. Structures of 9,9-dimethylfluorene nitrosonium complexes optimized by DFT method (hydrogen atoms are not shown).

Table 3. Calculated by DFT method energies of formation (E), the affinity of NO^+ cation to fluorene and 9,9-dimethylfluorene (A_{NO}^+), the charge on the NO group (q_{NO}^+), and some geometrical parameters of nitrosonium complexes

Complex	E, a.u.[a]	A_{NO}^+, kJ mol^{-1}	l(NO), Å	l(NC^i), Å[b]	d, Å[c]	φ, deg[d]	q_{NO}^+
A1	–630.52925	286.4	1.126	2.373 (C^3), 2.423 (C^4)	2.153	33	0.33
A2	–630.52280	269.5	1.124	2.270 (C^{9a}), 2.479 (C^{4a})	2.237	64	0.37
A3	–759.97932	245.1	1.113	2.434 (C^2), 2.445 (C^3)	2.234	36	0.46
			1.113	2.434 (C^7), 2.446 (C^6)	2.233	36	0.46
A4	–759.97732	239.9	1.114	2.404 (C^2), 2.437 (C^3)	2.234	39	0.45
			1.114	2.399 (C^7), 2.447 (C^6)	2.227	39	0.45
A5	–630.52130	265.6	1.124	2.456 (C^{4a}), 2.455(C^{4b})	2.213	43	0.36
B1	–709.07442	291.6	1.127	2.380 (C^3), 2.409 (C^4)	2.151	33	0.32
B2	–709.06652	270.8	1.122	2.410 (C^{9a}), 2.495 (C^{4a})	2.330	70	0.38
B3	–838.52776	258.9	1.114	2.430 (C^2), 2.436 (C^3)	2.223	36	0.45
			1.114	2.430 (C^7), 2.436 (C^6)	2.225	36	0.45
B4	–838.52592	254.1	1.114	2.400 (C^2), 2.428 (C^3)	2.216	38	0.44
			1.115	2.397 (C^7), 2.432 (C^6)	2.217	38	0.44
NO$^+$ArH[e]	–	–	1.09 ± 0.02	2.0–2.5	2.12 ± 0.07	36 ± 15	–

[a] 1 a.u. = 2625.5 kJ mol^{-1}.
[b] The lengths of C–N bonds corresponding to the carbon atoms (C^i) nearest to cation NO$^+$.
[c] The distance from the nitrogen atom to the plane of the aromatic ring.
[d] The angle between the N–O bond and the perpendicular to the plane of the aromatic ring .
[e] Average values measured by XRD method for π-complexes of NO$^+$ with toluene, o-xylene, p-xylene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene [4, 27].

the NO group and the nearest carbon atoms of this ring (2.0–2.5 Å).

By means of DFT (basis Λ02) we revealed the minima on the PES corresponding to the dication π-complexes **A3**, **B3**, **A4,** and **B4** (Figs. 3, 4). According to the quantum-chemical calculations the formation of single-charged π-complexes **A1**, **B1**, **A2,** and **B2** of fluorine and 9,9-dimethylfluorenewith the NO^+ cation is a strongly exothermal process, whereas the addition of two NO^+ cations to these hydrocarbons to give π-complexes **A3**, **B3**, **A4,** and **B4** provides a smaller gain in the energy (Table 3). This result is consistent with the above presented data on the change of $\Delta\delta_C$ values at variations of the ratios $NO^+AlCl_4^-$:(**I**) and $NO^+AlCl_4^-$:(**II**) (Figs. 1, 2) (cf. [4]).

Dication complexes **A3**, **B3**, **A4,** and **B4** are similar in their geometrical characteristics to π-complexes **A1**, **B1** and **A2**, **B2** (Figs. 3, 4, Table 3). The NO groups in these complexes take both transoid and cisoid positions, the former being more stable. As should be expected, in the dication complexes the fraction of the positive charge on the NO group was larger than in the case of the single-charged p-complexes.

An interesting feature of the nitrosonium complexes of fluorene and 9,9-dimethylfluorene is the possibility of the interring migration of the NO group that can occur both by intramolecular and intermolecular pathway (Scheme 1, paths *a* and *b* respectively) (cf. [4]). The calculations by DFT method (basis Λ02) shows that complex **A5** (Fig. 3) which evidently lies on the path of the transition of the NO group from one six-membered ring to another has one imaginary frequency and goes over π-complex **A2**.*

The energy difference for these complexes is only 3.9 kJ mol^{-1} indicating the possibility of a fast interring migration of the NO group. Actually, in the ^{13}C NMR spectrum of the solution of complex **III** even at –70°C appeared averaged by pairs signals of atoms $C^{1,8}$, $C^{2,7}$, $C^{3,6}$, $C^{4,5}$, $C^{4a,4b}$, and $C^{8a,9a}$. A similar pattern is observed for the nitrosonium complex of 9,9-dimethylfluorene, and the rearrangement in this complex is not "frozen out" even at –100°C (in the system SO_2–SO_2ClF–CD_2Cl_2). The proton signals of CH_2 and CMe_2 groups in the ^1H NMR spectra and of carbon atoms of the methyl groups of complexes **III** and **IV** are also averaged indicating

the greater rate of the intermolecular rearrangement compared to the intramolecular (Scheme 1, paths *a* and *b* respectively).

Hence the fluorene and 9,9-dimethylfluorene in reaction with nitrosonium tetrachloroaluminate form dynamic π-complexes, and the transfer of the NO group from one ring to another occurs with a high rate in the NMR time scale even at low temperature.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometers Bruker AC-200 and DRX-500 (operating frequencies 200 and 500 MHz for ^1H, 50.3 and 125.8 MHz for ^{13}C respectively). As internal references were used the signals of residual protons and of carbon atoms of CD_2Cl_2 (δ_H 5.33, δ_C 53.6 ppm).

The following reagents were used in the study: fluorene of "pure" grade, CD_2Cl_2 (with deuterium content 99 at%) distilled over P_2O_5. 9,9-Dimethylfluorene was synthesized by procedure [28]. 2-Deuterofluorene was obtained by treating 2-iodofluorene with BuLi [29] followed by quenching of the obtained organolithium compound with D_2O (cf. [4]). SO_2, SO_2ClF, and $NOAlCl_4$ were prepared as described in [30], [31], and [32] respectively.

The solutions of nitrosonium complexes **III** and **IV** for the registering of ^1H and ^{13}C NMR spectra were obtained by adding salt $NO^+AlCl_4^-$ to the solution of fluorene or 9,9-dimethylfluorene in CD_2Cl_2–SO_2, cooled to–75°C (*C* 0.2 mol l^{-1}). Volume ratio of CD_2Cl_2:SO_2 1:3. Then additional portions of salt $NO^+AlCl_4^-$ was successively added, and the NMR spectra were registered. The molar ratios $NO^+AlCl_4^-$:hydrocarbon are listed in Tables 1, 2. The solution of the nitrosonium complex of 2-deuterofluorene was prepared analogously. The registering of NMR spectra of complex **IV** at –100°C was carried out in a mixture SO_2–SO_2ClF–CD_2Cl_2, 2:2:1 by volume.

Quantum-chemical calculations were performed by DFT method with potential PBE using software "Priroda" [20–23]. In the optimization of the structures geometry basis Λ02 was employed {(12s8p4d2f)/[4s3p2d1f] for atoms C, O, N and (8s4p2d)/[3s2p1d] for atom H}. The determination of critical points on PES was performed by calculating Hesse matrix [33].

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* We failed to localize on PES a similar nitrosonium complex of 9,9-dimethylfluorene evidently due to the unfeasible interaction between CH_3 and NO groups.

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