

Nitrosonium Complexes of [2.2]Paracyclophane*

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Abstract—The reaction of [2.2]paracyclophane with nitrosonium tetrachloroaluminate was studied by NMR (^1H , ^{13}C) spectroscopy using deuterium isotopic perturbation technique. The resulting cationic complexes containing one and two nitrosonium ions are involved in fast (on the NMR time scale) interconversion. Quantum-chemical calculations performed on the DFT level (using triple zeta basis set) indicate the higher stability of 2η single-charged π -complexes relative to σ complexes corresponding to the addition of NO^+ ion at the *ipso* and *ortho* positions. The formation of the single-charged π -complex is energetically more favorable, compared to the double-charged π -complex. The affinity of NO^+ for [2.2]paracyclophane is much greater than for *p*-xylene, presumably due to stacking interaction between the aromatic rings in the π -complex.

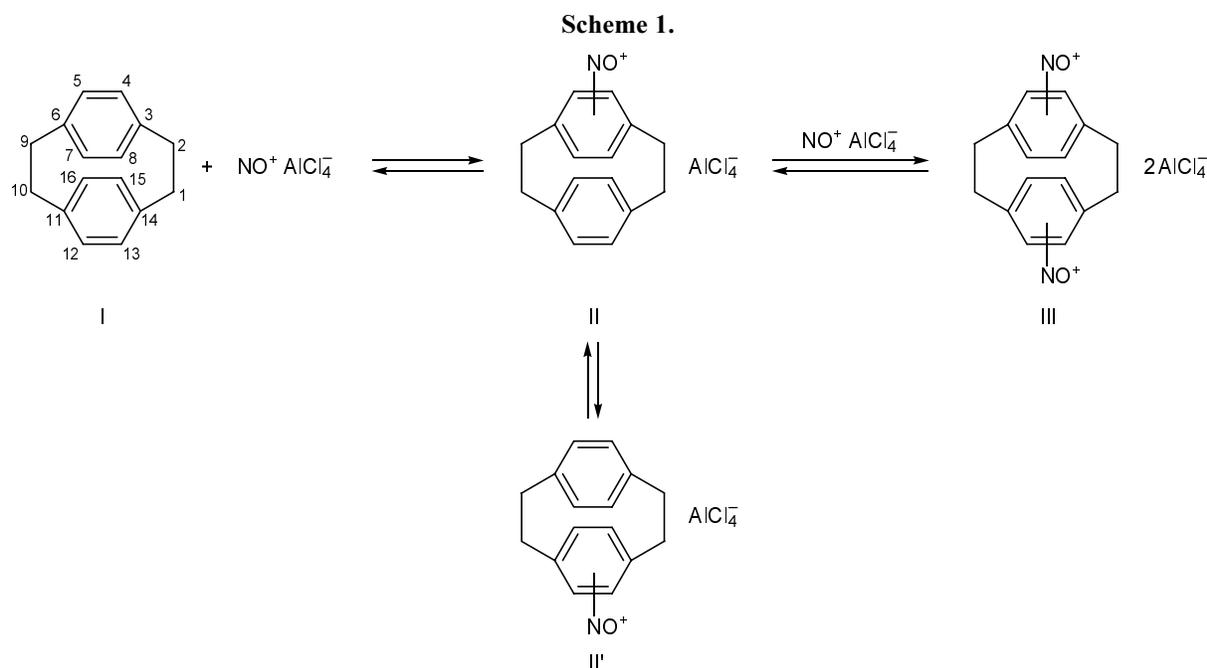
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Nitrosonium complexes of aromatic compounds have long attracted researchers' attention [2]. In the recent time, interest in such complexes increased due to discovery of a unique role of NO molecules in processes occurring in living organisms [3]. It was presumed that NO molecules may be involved in biological processes in the oxidized form, i.e., as nitrosonium cation NO^+ [4]. Up to now, the structure and reactivity of numerous complexes derived from aromatic compounds and NO^+ ion have been studied [1, 2, 5, 6]. However, only a few published data are available on nitrosonium complexes of cyclophanes [1, 5] (cf. [7]), though such complexes attract specific interest taking into account unusual structure of a number of cyclophanes. The aromatic rings therein are arranged in such a way that stacking interaction between them becomes possible. Analogous interactions play an important role in the formation of supramolecular structures and largely determine their properties [8]. Stacking interactions together with interactions like cation- π -aromatic system underlie biological processes responsible for molecular recognition, neurological signalization, and other important events in living nature [9–11].

The goal of the present work was to study the structure and reactivity of [2.2]paracyclophane nitrosonium complexes by theoretical and experimental methods.

The geometric parameters of [2.2]paracyclophane {the distance between the aromatic rings is considerably shorter than the sum of the van der Waals radii, 3.099(1) and 3.40 Å, respectively [12]} suggest a strong interaction between the aromatic rings. The reaction of [2.2]paracyclophane (**I**) with $\text{NO}^+ \text{AlCl}_4^-$ in $\text{SO}_2\text{-CD}_2\text{Cl}_2$ at -80°C gives rise to single- and double-charged nitrosonium complexes which are likely to originate from π - π interaction and undergo fast interconversion on the NMR time scale (Scheme 1). This follows from the ^1H and ^{13}C NMR data. Addition of an equimolar amount of $\text{NO}^+ \text{AlCl}_4^-$ to a solution of compound **I** induces a relatively small downfield shift of signals from the aromatic hydrogen and carbon atoms, as compared to their positions in the spectra of initial [2.2]paracyclophane (Table 1) (cf. [13–15]). It is known that ^{13}C chemical shifts of charged π -electron systems are related to the electron density on the corresponding carbon atoms [16]. The calculated overall positive π -charges on the aromatic carbon atoms in π -complex **II** (Table 1) are similar to those found for π -complexes formed by nitrosonium ion with naphthalene and methylnaphthalenes ($q_\pi^+ = 0.34\text{--}0.54$) [14] but appreciably lower than for [2.2]paracyclophane protonated at the *ipso* position ($q_\pi^+ \approx 1$) [17]. Raising the $\text{NO}^+ \text{AlCl}_4^-$ -to-**I** molar ratio (n) from 1 to 6 leads to further displacement of the aromatic proton and carbon signals to a weaker field. The smaller gain in $\Delta\delta_{\text{C}}$ on

* For preliminary communication, see [1].



the plot of $\Delta\delta_C$ versus n in the n range from 1 to 6, as compared to the n range from 0 to 1, and the subsequent flattening of the plot may be regarded as an evidence that dicationic π -complex **III** is involved in equilibrium (Scheme 1, Fig. 1) (cf. [18]). The formation of complex **III** is also supported by the data obtained for complex **V** derived from *p*-xylene (**IV**) and NO⁺ ion, which is a close analog of nitrosonium [2.2]paracyclophane complex. As might be expected, the plot of $\Delta\delta_C$ versus the NO⁺ AlCl₄⁻–**IV** ratio flattens out at a smaller value of n (~2) (Fig. 2), and the calculated value of q_π^+ is considerably lower (Table 1).

Additional experimental proofs for the formation of π -complexes **II** and **III** rather than σ complexes **VI** and **VII** involved in fast interconversion (Schemes 2, 3) were obtained using isotopic perturbation technique [19, 20]. Addition of a suspension of 4-deutero[2.2]-paracyclophane in CD₂Cl₂ to a solution of NO⁺ AlCl₄⁻ in SO₂ at –60°C led to formation of complexes which showed a weak isotope effect on the aromatic carbon signals in the ¹³C NMR spectrum ($\delta_C \approx 0.3$ ppm at –50°C); these data are inconsistent with the version implying fast interconversion of σ complexes (cf. [13, 14, 19–22]).

Table 1. ¹H and ¹³C NMR spectra of [2.2]paracyclophane (**I**), *p*-xylene (**IV**), and nitrosonium complexes **II**, **III**, and **V** in SO₂–CD₂Cl₂ (–75°C) and calculated total π charges (q_π^+) on the aromatic carbon atoms

Compound no.	Ratio ArH–NO ⁺ AlCl ₄ ⁻	$\delta(^1\text{H})$, ppm		$\delta(^{13}\text{C})$, ppm			$\Delta\Sigma\delta(\text{C}_{\text{arom}})$, ppm	q_π^+ ^a
		CH ₂ (CH ₃)	H _{arom}	CH ₂ (CH ₃)	C ⁱ	C ^o		
I	–	3.01	6.48	34.54	140.33	133.38		
II	1:1	3.27	7.09	34.35	149.90	137.52	71.40	0.45
II, III	1:2	3.33	7.18	34.34	150.54	137.89	76.92	0.48
II, III	1:4	3.41	7.34	34.20	154.00	139.37	102.60	0.64
II, III	1:6	3.41	7.34	34.14	153.96	139.33	102.12	0.64
IV	–	2.22	7.04	20.10	135.30	129.50		
IV, V	1:1	2.46	7.52	20.61	145.02	136.86	48.88	0.31
V	1:2	2.57	7.74	20.85	149.61	138.88	66.14	0.41
V	1:4	2.57	7.74	20.87	149.66	138.90	66.32	0.41
V	1:6	2.57	7.74	20.86	149.64	138.88	66.24	0.41

^a Calculated assuming 160 ppm per unit π charge [14, 16].

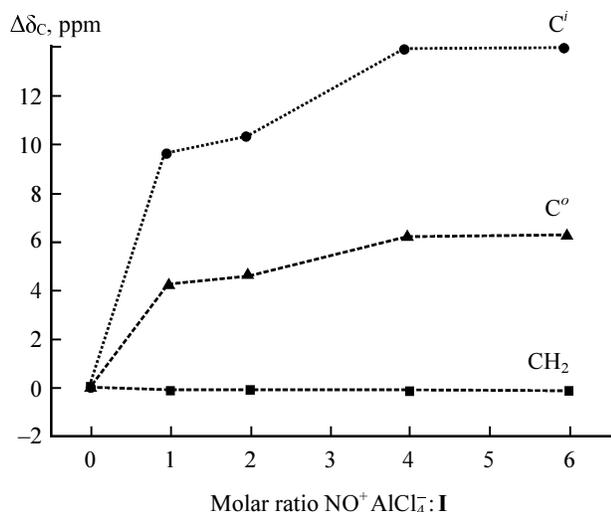


Fig. 1. Plot of the ^{13}C chemical shift differences between π -complexes **II** and **III** and [2.2]paracyclophane versus $\text{NO}^+ \text{AlCl}_4^-$:**I** molar ratio.

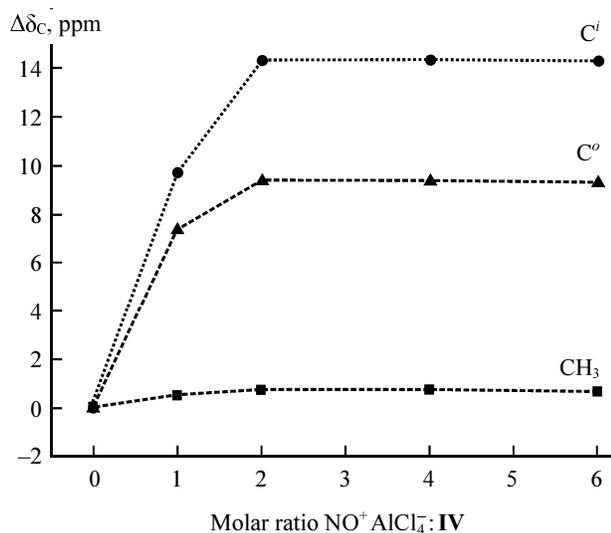
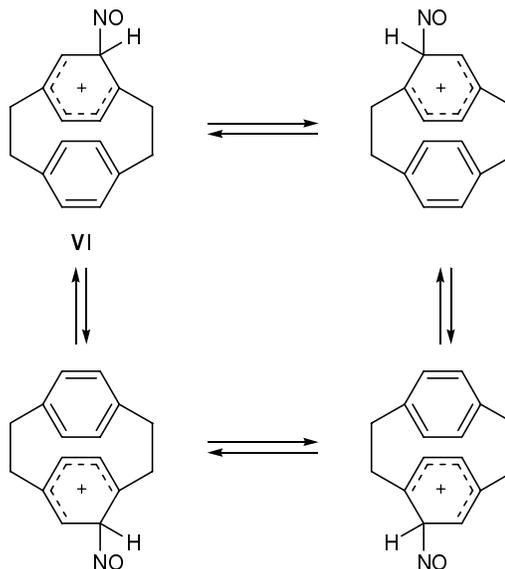


Fig. 2. Plot of the ^{13}C chemical shift differences between π -complex **V** and *p*-xylene versus $\text{NO}^+ \text{AlCl}_4^-$:**IV** molar ratio.

Our DFT calculations (3Z basis set) [23] also indicated greater stability of π -complexes as compared to σ complexes. Starting from structures **VI** and **VII** with standard geometry, optimization at a fixed length of the C–N bond (1.5 Å) gave structures with higher energies than those of 2η π -complexes; moreover, these structures did not occupy minima on the potential energy surface. Further optimization with removal of limitations on the C–N bond length led to π -complexes having considerably extended C–NO bonds (2.3–2.5 Å to the nearest ring carbon atoms and 2.7–3.4 Å to more distant atoms) and occupying minima on the potential energy surface (Table 2, Fig. 3). The NO group in

these complexes is oriented at a certain angle with respect to the aromatic ring plane and is directed either outside or inside ($2\eta_a$ and $2\eta_b$ complexes, respectively). Analogous results were obtained by the calculations performed on the B3LYP level [6-31G(*d*) basis set] [24]; they showed that the σ complex derived from benzene and NO^+ does not correspond to an energy minimum on the potential energy surface. Among the optimized structures, the $2\eta_a$ π -complex is the most energetically favorable, and its geometric parameters are similar to those obtained experimentally by X-ray analysis of the π -complexes formed by NO^+ ion with hexamethylbenzene [25] and other arenes [2, 6, 26] (Table 2). Complexes of this type are characterized by angular orientation of the NO group with respect to the normal to the benzene ring plane,

Scheme 2.



Scheme 3.

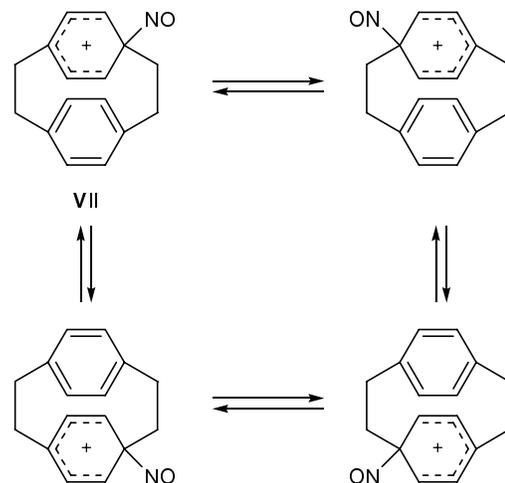


Table 2. Calculated (DFT) energies of formation (E), affinities of NO^+ ion for [2.2]paracyclophane and p -xylene (A_{NO^+}), charges on the NO group (q_{NO^+}), and some geometric parameters of nitrosonium complexes

Complex	E , ^a a.u.	A_{NO^+} , kJ/mol	$l(\text{NO})$, Å	$l(\text{CC})$, ^b Å	d , ^c Å	ϕ , ^d deg	q_{NO^+}
2 η a	-748.28017	312.8	1.130	1.409	2.13	29	0.29
2 η b	-748.27236	292.3	1.127	1.408	2.30	68	0.32
NO^+ ArH ^c	–	–	1.09±0.02	1.41±0.01	2.12±0.07	36±15	
III	-877.74317	1.7 ^f	1.116	1.411	2.17	28	0.43
V	-440.13770	275.2	1.124	1.410	2.13	30	0.35
VIII	-748.25994	259.7	1.139	1.408	1.80	86	0.29

^a 1 a.u. = 2625.5 kJ/mol.

^b Arithmetic mean of the bond lengths in the aromatic ring bearing the NO^+ ion.

^c Distance from the nitrogen atom to the aromatic ring plane.

^d Angle between the NO bond and normal to the aromatic ring plane.

^e Average data obtained by the X-ray diffraction method for the π -complexes formed by NO^+ ion with toluene, o -xylene, p -xylene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene [26].

^f Affinity of NO^+ cation for π -complex **II**.

sp^2 hybridization of the aromatic carbon atoms, and considerably extended C–N bonds between the NO nitrogen atom and the nearest carbon atoms of the corresponding ring (2.0–2.5 Å).

According to the calculations, the formation of 2 η a π -complex from [2.2]paracyclophane and NO^+ cation is a strongly exothermic process ($\Delta E = 312.8$ kJ/mol), while the addition of the second NO^+ cation to that complex with formation of π -complex **III** is accompanied by very small gain in energy ($\Delta E = 1.7$ kJ/mol). This is consistent with the above data on variation of $\Delta\delta_{\text{C}}$ depending on the $\text{NO}^+ \text{AlCl}_4^-$ -**I** ratio (Fig. 1). It should be noted that double-charged complex **III** resembles 2 η a π -complex in geometric parameters (Fig. 3, Table 2). The NO^+ groups in complex **III** are characterized by transoid arrangement, and each of these groups possesses a greater positive charge than that on the NO^+ group in 2 η a π -complex.

The addition of NO^+ to [2.2]paracyclophane with formation of 2 η a π -complex shortens the distance between the benzene rings ($l_{3-14} = 2.73$, $l_{4-15} = 3.08$ Å) relative to that distance in initial [2.2]paracyclophane ($l_{3-14} = 2.82$, $l_{4-15} = 3.14$ Å). Analogous pattern was observed in the complex formation between [2.2]paracyclophane and $\text{Cr}(\text{CO})_3$ fragment [27, 28]. Theoretical study of [2.2]paracyclophane showed that approach of its benzene rings to each other increases the outer parts of the carbon atomic orbitals in the e_{1u} molecular orbital, which should enhance the donor power of those rings [28]. In fact, comparison of the calculated A_{NO^+} values for [2.2]paracyclophane and p -xylene (Table 2) indicates greater donor power of [2.2]para-

cyclophane with respect to NO^+ , and the difference is fairly large ($\Delta A_{\text{NO}^+} = 37.6$ kJ/mol). This is consistent with our experimental data on competing interactions of [2.2]paracyclophane and p -xylene with NO^+ . As follows from the ^1H and ^{13}C NMR spectra, addition of an equimolar amount of $\text{NO}^+ \text{AlCl}_4^-$ to a suspension of [2.2]paracyclophane and p -xylene in CD_2Cl_2 - SO_2 (1:1, by volume) at -75°C leads to formation of complexes **II** and **III**, while the chemical shifts of p -xylene almost do not change. The geometric parameters of nitrosonium complex **V** are fairly similar to those of 2 η a π -complex (Fig. 3, Table 2); therefore, increased affinity of [2.2]paracyclophane to NO^+ ion is likely to originate from stacking interaction of the aromatic rings in the π -complex.

A specific property of [2.2]paracyclophane is its ability to form inner nitrosonium complexes in which the NO^+ ion is located between the aromatic rings (cf. [5]). An attempt to simulate this structure on the DFT level, followed by geometry optimization, gave π -complex **VIII**. The NO group in structure **VIII** resides at one side of the carbon skeleton, and the C–N bonds between the nitrogen atom and carbon atoms of the aromatic ring are relatively short (Fig. 3). The formation of complexes where the NO^+ ion is coordinated to two aromatic molecules was previously revealed by spectral methods, as well as by X-ray analysis [2, 6].

Thus [2.2]paracyclophane is capable of forming both single- and double-charged nitrosonium π -complexes, and its increased affinity for NO^+ ion may be rationalized in terms of stacking interaction between the benzene rings in the resulting π -complex.

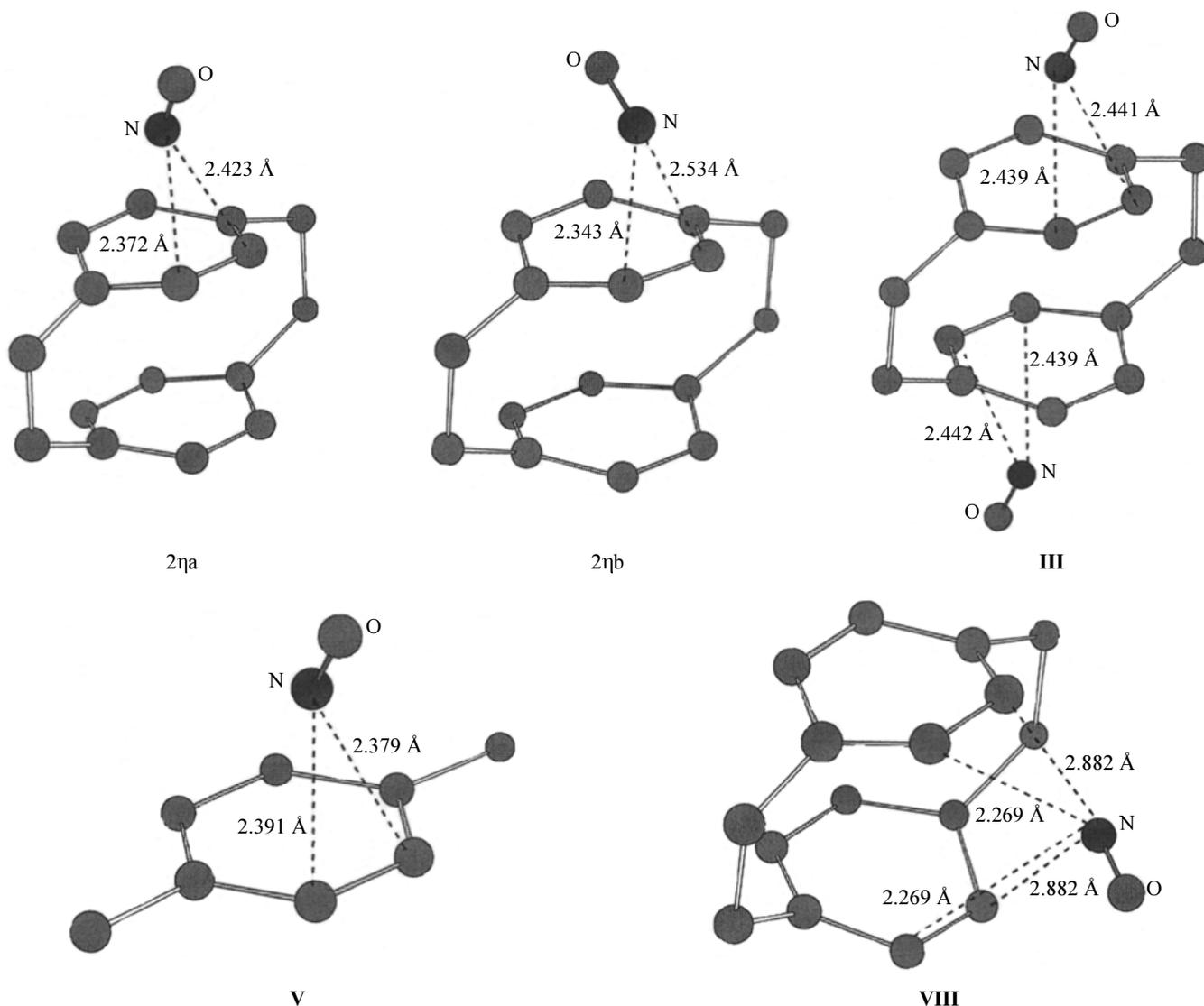


Fig. 3. Structures of π -complexes **II**, **III**, **V**, and **VIII** optimized on the DFT level.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 and AC-200 spectrometers (400 and 200 MHz for ^1H and 100.6 and 50.3 MHz for ^{13}C , respectively). The chemical shifts were referenced to the solvent signals (CD_2Cl_2 : δ 5.33, δ_{C} 53.6 ppm).

[2.2]Paracyclophane from Fluka (purum, >99%) was used; *p*-xylene of pure grade was distilled and dried by keeping over 4-Å molecular sieves; CD_2Cl_2 containing 99% of deuterium was distilled over P_2O_5 . 4-Deutero[2.2]paracyclophane was synthesized according to the procedure described in [29] by treatment of 4-bromo[2.2]paracyclophane [30] with butyllithium, followed by reaction of the organolithium derivative

thus formed with D_2O . Sulfur dioxide [31] and nitrosonium tetrachloroaluminate [32] were prepared by known methods. Solutions of nitrosonium complexes **II** and **III** for NMR studies were prepared by adding a suspension of [2.2]paracyclophane in CD_2Cl_2 to a solution of $\text{NO}^+\text{AlCl}_4^-$ in SO_2 ($c = 0.1$ M), cooled to -80°C . The CD_2Cl_2 – SO_2 volume ratio was 1:1. Next portions of $\text{NO}^+\text{AlCl}_4^-$ were then added to the solution thus obtained, and its NMR spectra were recorded. The molar ratios $\text{NO}^+\text{AlCl}_4^-$ –[2.2]paracyclophane are given in Table 1. Solutions of the deuterated complex and nitrosonium complex of *p*-xylene were prepared in a similar way.

Quantum-chemical calculations by the DFT method using the PBE potential were performed with the aid of

Priroda software package [23]. Triple zeta basis set $\{(11s6p2d)/[6s3p2d]$ for the carbon, oxygen, and nitrogen atoms and $(5s1p)/[3s1p]$ for hydrogen atoms} was used in geometry optimization. Critical points on potential energy surfaces were identified by calculating Hesse's matrix [33].

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REFERENCES

- Borodkin, G.I., Elanov, I.R., and Shubin, V.G., *Abstracts of the 13th IUPAC Conference on Physical Organic Chemistry*, Inchon, 1996, p. 243.
- Borodkin, G.I. and Shubin, V.G., *Usp. Khim.*, 2001, vol. 70, p. 241.
- Murad, F., *Angew. Chem., Int. Ed.*, 1999, vol. 38, p. 1857.
- Stamler, J.S., Singel, D.J., and Loscalzo, J., *Science*, 1992, vol. 258, p. 1898.
- Rathore, R., Lindeman, S.V., Rao, K.S.S.P., Sun, D., and Kochi, J.K., *Angew. Chem., Int. Ed.*, 2000, vol. 39, p. 2123; Zyryanov, G.V., Kang, Y., Stampf, S.P., and Rudkevich, D.M., *Chem. Commun.*, 2002, p. 2792; Rosokha, S.V., Lindeman, S.V., Rathore, R., and Kochi, J.K., *J. Org. Chem.*, 2003, vol. 68, p. 3947; Zyryanov, G.V., Kang, Y., and Rudkevich, D.M., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 2977; Zyryanov, G.V. and Rudkevich, D.M., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 4264.
- Rosokha, S.V., Lindeman, S.V., and Kochi, J.K., *J. Chem. Soc., Perkin Trans. 2*, 2002, p. 1468.
- Laali, K.K., Borodkin, G.I., Okazaki, T., Hayashida, Y., Nakamura, Y., and Nishimura, J., *J. Chem. Soc., Perkin Trans. 2*, 2000, p. 2347.
- Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, Weinheim: VCH, 1995. Translated under the title *Supramolekulyarnaya khimiya*, Novosibirsk: Nauka, Sib. Predpr. Ross. Akad. Nauk, 1998, pp. 111, 167.
- Ma, J.C. and Dougherty, D.A., *Chem. Rev.*, 1997, vol. 97, p. 1303.
- Hu, J., Barbour, L.J., and Gokel, G.W., *New J. Chem.*, 2004, vol. 28, p. 907.
- Ansems, R.B.M. and Scott, L.T., *J. Phys. Org. Chem.*, 2004, vol. 17, p. 819.
- Lyssenko, K.A., Antipin, M.Yu., and Antonov, D.Yu., *Eur. J. Chem. Phys., Phys. Chem.*, 2003, vol. 4, p. 817.
- Borodkin, G.I., Elanov, I.R., Shakirov, M.M., and Shubin, V.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1992, p. 2104.
- Borodkin, G.I., Elanov, I.R., Shakirov, M.M., and Shubin, V.G., *J. Phys. Org. Chem.*, 1993, vol. 6, p. 153.
- Borodkin, G.I., Podryvanov, V.A., Shakirov, M.M., and Shubin, V.G., *J. Chem. Soc., Perkin Trans. 2*, 1995, p. 1029.
- Koptyug, V.A., *Arenonievye iony. Stroenie i reaktivnaya sposobnost' (Arenium Ions. Structure and Reactivity)*, Novosibirsk: Nauka, 1983, p. 83.
- Laali, K. and Filler, R., *J. Fluorine Chem.*, 1989, vol. 43, p. 415.
- Heo, G.S., Hillman, P.E., and Bartsch, R.A., *J. Heterocycl. Chem.*, 1982, vol. 19, p. 1099.
- Saunders, M., Chandrasekhar, J., and Schleyer, P.v.R., *Rearrangements in Ground and Excited States*, de Mayo, P., Ed., New York: Academic, 1980, vol. 1, p. 1; Saunders, M. and Kronja, O., *Carbocation Chemistry*, Olah, G.A. and Prakash, G.K.S., Eds., Hoboken: Wiley, 2004, p. 213.
- Hansen, P.E., *Annu. Rep. NMR Spectrosc.*, 1983, vol. 15, p. 105; Siehl, H.-U., *Adv. Phys. Org. Chem.*, 1987, vol. 23, p. 63.
- Borodkin, G.I., Elanov, I.R., Podryvanov, V.A., Shakirov, M.M., and Shubin, V.G., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 12863.
- Borodkin, G.I., Elanov, I.R., Shakirov, M.M., and Shubin, V.G., *Zh. Org. Khim.*, 1991, vol. 27, p. 889.
- Laikov, D.N., *Chem. Phys. Lett.*, 1997, vol. 281, p. 151.
- Skokov, S. and Wheeler, R.A., *J. Phys. Chem. A*, 1999, vol. 103, p. 4261.
- Borodkin, G.I., Nagi, Sh.M., Gatilov, Yu.V., Mamatyuk, V.I., Mudrakovskii, I.L., and Shubin, V.G., *Dokl. Akad. Nauk SSSR*, 1986, vol. 288, p. 1364; Brownstein, S., Gabe, E., Lee, F., and Piotrowski, A., *Can. J. Chem.*, 1986, vol. 64, p. 1661.
- Gwaltney, S.R., Rosokha, S.V., Head-Gordon, M., and Kochi, J.K., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 3273.
- Kai, Y., Yasuoka, N., and Kasai, N., *Acta Crystallogr., Sect. B*, 1978, vol. 34, p. 2480.
- Papoyan, G.A., Butin, K.P., Khoffman, R., and Rozenberg, V.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, p. 151.
- Yeh, Y.L. and Gorham, W.F., *J. Org. Chem.*, 1969, vol. 34, p. 2366.
- Cram, D.J. and Day, A.C., *J. Org. Chem.*, 1966, vol. 31, p. 1227.
- Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva (Pure Chemicals)*, Moscow: Khimiya, 1974, p. 56.
- Rheinboldt, H. and Wasserfuhr, R., *Chem. Ber.*, 1927, vol. 60, p. 732.
- Minkin, V.I., Simkin, B.Ya., and Minyaev, R.M., *Kvantovaya khimiya organicheskikh soedinenii. Mekhanizmy reaktsii (Quantum Chemistry of Organic Compounds. Reaction Mechanisms)*, Moscow: Khimiya, 1986, p. 10.