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Synthesis of Polyfluorinated Tetraoxacalix[4]arenes by Reaction of Pentafluoronitrobenzene with Resorcinol, Orcinol, and Tetrafluororesorcinol

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Abstract—Successive reactions of pentafluoronitrobenzene with resorcinol, orcinol, and tetrafluororesorcinol in acetonitrile in the presence of triethylamine afforded polyfluorinated ABAB and ABAC tetraoxacalix[4]-arenes. Analysis of the ^{1}H and ^{19}F NMR spectra of the synthesized oxacalixarenes indicated high conformational mobility of the resorcinol and tetrafluororesorcinol fragments of their molecules due to interaction with the solvent.

Keywords: polyfluorinated tetraoxacalixarenes, pentafluoronitrobenzene, resorcinol, orcinol, tetrafluoro-resorcinol, conformational behavior

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Tetraoxacalixarenes are among scaffolds used in supramolecular chemistry to study host–guest intermolecular interactions [1]. A number of chemosensors for neutral organic compounds [2–4], cations [5–7], and anions [8–11] have been obtained on the basis of tetraoxacalixarenes. The possibility of using oxacalixarenes as ion pair transporters through cell membranes has been demonstrated [12–15]. Some oxacalixarenes have been found to exhibit physiological activity [16].

Fluorinated tetraoxacalixarenes were synthesized previously via [3 + 1] two-step fragment coupling approach by reaction of 4-substituted tetrafluoropyridines with resorcinol and orcinol [17, 18], as well as by reaction of dichlorotriazines with perfluorinated dihydroxybenzenes [19].

In this work we examined a fragment coupling approach to the synthesis of polyfluorinated tetraoxacalixarenes via reaction of pentafluoronitrobenzene with resorcinol, orcinol, and tetrafluororesorcinol. This approach has been utilized by us in the synthesis of A_3B perfluorinated tetraoxacalixarenes [20]. Recently, we have also shown that polyfluorinated ABAC tetraoxacalixarenes can be obtained by successively reacting perfluorinated *m*-xylene and pentafluorobenzonitrile with resorcinol and tetrafluororesorcinol [21, 22]. Likewise, successive reactions of pentafluoronitrobenzene with resorcinol and tetrafluororesorcinol in acetonitrile in the presence of triethylamine gave triphenyl ethers **1a** and **3a** and tetraoxacalixarenes **4a**–**8a** containing an impurity of the corresponding isomers (Scheme 1). Diether **3a** was synthesized previously in a moderate yield (37%) by heating pentafluoronitrobenzene with tetrafluororesorcinol in acetonitrile in the presence of potassium carbonate [23].

The synthesis of tetraoxacalixarenes **4a**–**8a** can be performed both with intermediate isolation of triphenyl ethers **1a**, **1b**, **3a**, and **3b** and via reaction of orcinol with 2 equiv of pentafluoronitrobenzene under mild conditions, followed by heating of the resulting mixture of triphenyl ethers **2a** and **2b** with 1 equiv of orcinol or tetrafluororesorcinol.

The structure of polyfluorinated tetraoxacalixarenes **4**–**8** was determined on the basis of spectral and analytical data. It was previously shown that the ^{1}H and ^{19}F NMR spectra of polyfluorinated tetraoxacalixarenes are characterized by a significant upfield shift of the ^{1}H and ^{19}F signals of the lower rim atoms of the resorcinol fragments due to shielding by the neighboring aromatic rings [20–22]. In the ^{1}H and ^{19}F NMR spectra of **4**–**8** we also observed upfield shifts of the 25-H and

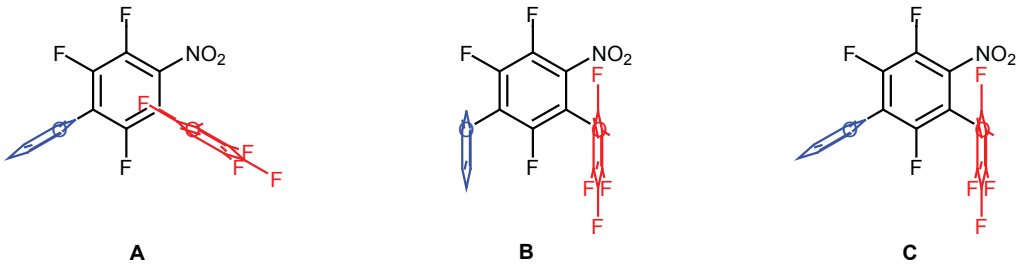

Fig. 1. Possible conformations of tetraoxacalixarene **5a** in $CDCl_3$ and $(CD_3)_2CO$ solutions.

27-F signals. Here, the signal of 2-H located between two 4-$O_2NC_6F_4O$ fragments of **1a** can be used as reference in the ^{1}H NMR spectrum. However, the magnitude of the observed upfield shift depends on the solvent. In the ^{1}H NMR spectra of **1a** and **5a** in $CDCl_3$, the difference between the chemical shifts of 2-H in **1a** and 25-H in **5a** is 0.96 ppm, whereas the corresponding difference in the spectra recorded in acetone-d_6 is 0.42 ppm. Likewise, the 27-F chemical shift of **5a** also strongly depends on the solvent and is δ_F 7.1 ppm in $CDCl_3$ and 11.5 ppm in acetone-d_6. The signal of 2-F (located between the aryloxy groups) in the ^{19}F NMR spectra of perfluorinated triphenyl ethers is observed at δ_F ~11–14 ppm, and its position weakly depends on the solvent (cf. [21] and the data for ethers **3a** and **3b**). Presumably, tetraoxacalixarene **5a** molecules in $CDCl_3$ and $(CD_3)_2CO$ solutions adopt different equilibrium conformations characterized by different degrees of magnetic shielding of the lower-rim protons and fluorines of the resorcinol fragments by the neighboring aromatic rings. The limiting cases of this shielding are illustrated by conformers **A**–**C** in Fig. 1. It should be noted that the position of the lower-rim 26-F and 28-F signals of the nitrobenzene fragments in the ^{19}F NMR spectra almost does not depend on the solvent. A similar solvent dependence was observed for the 25-H and 27-H signals in the ^{1}H NMR spectra of **6a**. Apart from the steric factor (conformation), variation of the chemical shifts may be related to electronic effects arising from conjugation between the lone electron pairs on the bridging oxygen atoms and aromatic rings.

Scheme 1.

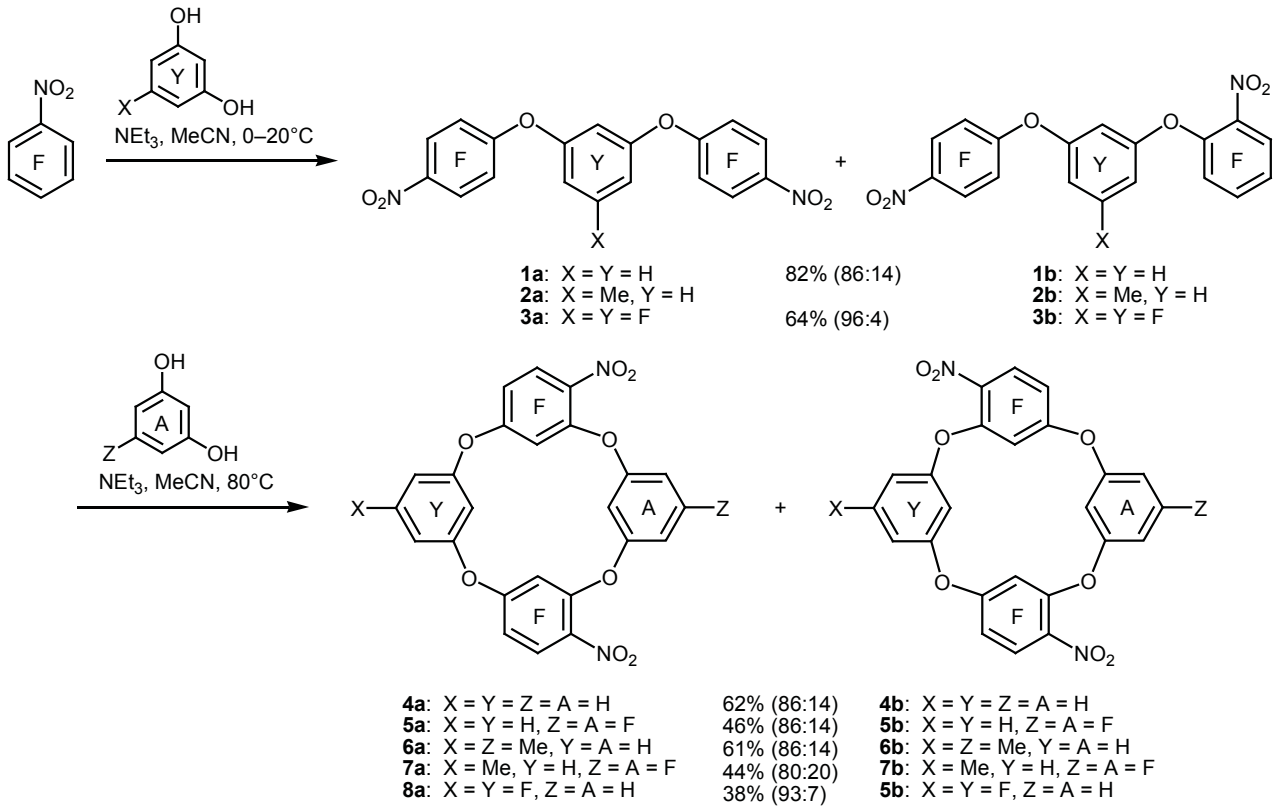

Table 1. Chemical shifts (δ, δ_F, ppm) of some nuclei in the ^1H and ^{19}F NMR spectra of triphenyl ether **1a** and tetraoxacalixarene **5a** in different solvents

Solvent	2-H (**1a**)	25-H (**5a**)	$\Delta\delta(2\text{-}H_{1a} - 25\text{-}H_{5a})$	27-F (**5a**)
Carbon tetrachloride	6.83	5.96	0.87	6.6
Chloroform	6.84	5.93	0.91	7.1
Methylene chloride	6.84	5.93	0.91	8.2
Benzyl chloride	6.71	5.76	0.95	8.1
Chlorobenzene		5.88		8.0
Toluene		5.74		8.5
Diethyl ether	7.06	6.23	0.83	9.3
Nitrobenzene	7.06	6.38	0.68	9.2
Acetone	7.21	6.85	0.36	11.4
Acetonitrile	6.97	6.29	0.68	11.6

The ^1H and ^{19}F NMR spectra of triphenyl ether **1a** and tetraoxacalixarenes **5a** were also recorded in other solvents (Table 1). The results showed that the solvents used can be arbitrarily divided into three groups. The first group of solvents includes chloroform and carbon tetrachloride, where the NMR spectra of **5a** displayed a significant upfield shift of both 25-H (resorcinol) and 27-F (tetrafluororesorcinol) signals. This may be due to the existence of molecule **5a** in these solvents as equilibrium conformer **A** (Fig. 1). In going to acetone and acetonitrile (second group), the magnitude of the upfield shift of the 25-H and 27-F signals is significantly lower, which suggests shift of the conformational equilibrium toward structure **B** (Fig. 1). Solvents of the third group (chlorobenzene, toluene, and benzyl chloride) give rise to a significant upfield shift of the 25-H signal but a smaller shift of the 27-F signal, presumably due to partial withdrawal of the fluorine atom from the area shielded by the neighboring nitrobenzene fragments (conformer **C** in Fig. 1). The above groups of solvents are likely to differ from each other in the mode of interaction with tetraoxacalixarene **5a** molecules. Aromatic solvents are characterized by a substantial contribution of π–π interaction with tetrafluorobenzene ring, whereas the interaction of **5a** with chloromethanes could involve mainly insertion of the solvent molecules into the calixarene cavity between the resorcinol and tetrafluororesorcinol fragments. Various interaction modes, in particular π–π interaction between tetraoxacalixarenes and aromatic compounds, were previously discussed in [24].

The molecular structure of a crystalline 2:1 complex of tetraoxacalixarene **5a** with chlorobenzene was studied by X-ray diffraction (Fig. 2). It was similar to the structure of polyfluorinated tetraoxacalixarenes described by us in [20–22]. The dihedral angle between the opposite nitrobenzene rings is 40.4°, and the dihedral angle between the other two rings is 74.5°. Chlorobenzene molecule is involved in π–π stacking interaction with the tetrafluorobenzene rings of the two neighboring tetraoxacalixarene molecules **5a**. The distance between the centroids of the tetrafluorobenzene rings to the chlorobenzene ring plane is 3.49 Å, and the intercentroid distances are 3.60 and 3.82 Å, respectively. In addition, there are π–π interactions between pairs of the nitrobenzene rings with disordered nitro groups and benzene rings of the neighboring molecules (intercentroid distances 3.86 and 3.74 Å; centroid–

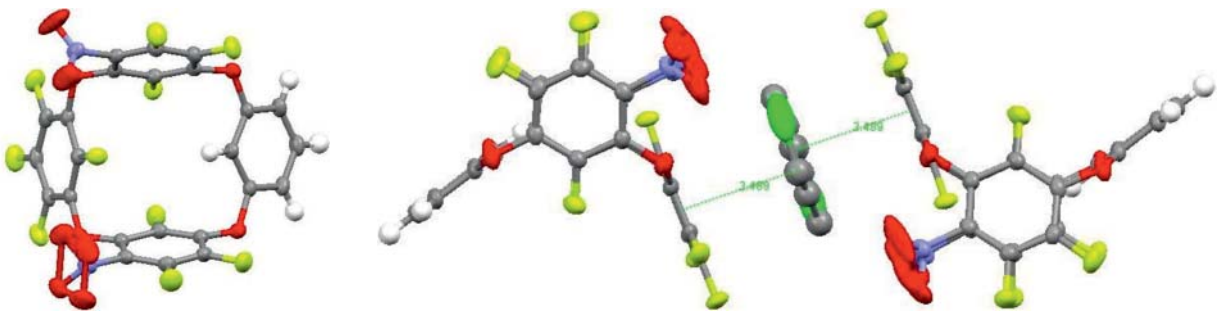

Fig. 2. Molecular structure of tetraoxacalixarene **5a** according to the X-ray diffraction data.

plane distances 3.42 and 3.47 Å). Unlike the resorcinol fragment, π–π stacking interaction is likely to partially force the tetrafluorobenzene ring out of the overlap zone with the neighboring nitrobenzene rings. The X-ray diffraction data for compound **5a** are consistent with its behavior in aromatic solvents according to the NMR data.

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were recorded on a Bruker AV-300 spectrometer at 282.36 MHz (relative to C_6F_6 as internal standard) and 300 MHz, respectively. The ^{13}C NMR spectrum of **5a** was measured with a Bruker AV-400 spectrometer at 100.6 MHz. The solvent effect on the ^{19}F and ^{1}H NMR spectra of **1a** and **5a** was studied using a coaxial insert (o.d. 4.1 mm) made of tetrafluoroethylene–hexafluoropropylene copolymer, which was placed in a standard NMR ampule filled with D_2O; the chemical shifts were measured relative to hexamethyldisiloxane (^{1}H) and hexafluorobenzene (^{19}F) as internal standards. The IR spectra were recorded on a Bruker Vector 22 IR spectrometer. The elemental compositions of polyfluorinated tetraoxacalix[4]arenes **4a**–**8a** were determined by classical methods, as well as from the high-resolution mass spectra (electron impact, 70 eV) which were obtained with a Termo Scientific DFS instrument. The progress of reactions was monitored by TLC on silica gel 60 F_{254} plates (Merck). Silica gel with a particle size of 0.063–0.200 mm (Merck) was used for column chromatography.

The X-ray diffraction data for a single crystal of **5a**·0.5(C_6H_5Cl) were obtained on a Bruker KAPPA Apex II diffractometer (Mo K_α radiation, 296 K). A correction for absorption was applied by SADABS program. The structure was solved by the direct method and was refined by the full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were refined in isotropic approximation according to the riding model. All calculations were performed using SHELXTL and SHELXL-2018/3 packages. One nitro group in molecule **5a** is disordered by two positions with a population ratio of 0.638:0.362. The chlorobenzene solvate molecule is located in the symmetry center and is disordered by two positions with equal populations. Triclinic crystal system; $C_{24}H_4N_2O_8 \cdot 0.5C_6H_5Cl$, M 694.57; space group P-1; unit cell parameters: a = 9.0585(3), b = 11.1141(4), c = 14.4280(5) Å; α = 67.442(2), β = 81.899(2), γ = 76.750(2)°; V = 1303.45(8) Å^3; Z = 2; d_{calc} = 1.770 g/cm^3; μ = 0.225 mm^{-1}. Total of 31470 reflection intensities were measured in the range 1.5° < θ < 27.9°, including 6187 independent reflections (R_{int} = 0.0405) and 4400 reflections with $I > 2\sigma(I)$; number of variables 441. Final divergence factors: R_1 = 0.0659 [reflections with $I > 2\sigma(I)$], wR_2 = 0.2229 (all independent reflections); goodness of fit S = 1.059. The coordinates of atoms and their thermal displacement parameters were deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1986975) [25].

1,3-Bis(2,3,5,6-tetrafluoro-4-nitrophenoxy)-benzene (1a) and 1,2,3,4-tetrafluoro-5-nitro-6-[3-(2,3,5,6-tetrafluoro-4-nitrophenoxy)phenoxy]-benzene (1b) (mixture of isomers**).** A solution of 0.22 g (2 mmol) of resorcinol and 0.85 g (4 mmol) of pentafluoronitrobenzene in 15 mL of acetonitrile was cooled to 0°C, a solution of 1.0 g (10 mmol) of triethylamine in 5 mL of acetonitrile was added with stirring, and the mixture was stirred for 2 h at 0°C and for 1 h at room temperature. The solvent was distilled off under reduced pressure (~20 mm Hg), and the residue was subjected to silica gel column chromatography using carbon tetrachloride–chloroform (~5:1 by volume) as eluent. The product was 0.94 g (82%) of a viscous material containing triphenyl ethers **1a** and **1b** at a ratio of 86:14 (according to the GC/MS data). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$: **1a**: 11.7 m (4F, *o*-F), 16.2 m (4F, *m*-F); **1b**: 6.2 t (1F, 3-F, J = 21.0 Hz), 11.7 m (2F, 2′-F, 6′-F), 13.9 d.d (1F, 1-F, J = 20.0, 8.0 Hz), 14.5 t.d (1F, 2-F, J = 20.0, 4.0 Hz), 15.9 d.d.d (1F, 4-F, J = 22.0, 8.0, 4.0 Hz), 16.1 m (2F, 3′-F, 5′-F); in acetone-d_6: **1a**: 11.2 m (4F, *o*-F), 16.2 m (4F, *m*-F); **1b**: 5.4 t (1F, 3-F), 11.2 m (2F, 2′-F, 6′-F), 13.4 d.d (1F, 1-F), 14.2 t.d (1F, 2-F), 15.8 d.d.d (1F, 4-F), 16.2 m (2F, 3′-F, 5′-F). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: **1a**: 6.80 d.d (2H, 4-H, 6-H, J = 8.2, 2.2 Hz), 6.86 t (1H, 2-H, J = 2.2 Hz), 7.35 t (1H, 5-H, J = 8.2 Hz); **1b**: 6.70–6.82 m (3H, 2-H, 4-H, 6-H), 7.32 t (1H, 5-H, J = 8.2 Hz); in acetone-d_6: **1a**: 7.13 d.d (2H, 4-H, 6-H), 7.28 t (1H, 2-H), 7.53 t (1H, 5-H); **1b**: 7.00–7.21 m (3H, 2-H, 4-H, 6-H), 7.50 t (1H, 5-H). Mass spectrum: m/z 496 $[M]^+$).

1,3-Bis(2,3,5,6-tetrafluoro-4-nitrophenoxy)-2,4,5,6-tetrafluorobenzene (3a) and 1,2,4,5-tetrafluoro-3-nitro-6-[2,3,4,6-tetrafluoro-5-(2,3,4,5-tetrafluoro-6-nitrophenoxy)phenoxy]benzene (3b) (mixture of isomers**).** A solution of 1.0 g (10 mmol) of triethylamine in 5 mL of acetonitrile was added with stirring at room temperature to a solution of 0.36 g (2 mmol) of tetrafluororesorcinol and 0.85 g (4 mmol) pentafluoronitrobenzene in 15 mL acetonitrile. The

mixture was stirred for 4 h at room temperature and was then refluxed for 4 h (80°C). The solvent was distilled off under reduced pressure (~20 mm Hg), and the residue was subjected to silica gel column chromatography using carbon tetrachloride–chloroform (~5:1 by volume) as eluent. The product was 0.65 g (57%) of a viscous material containing triphenyl ethers **3a** and **3b** at a ratio of 96:4 (GC/MS). ^{19}F NMR spectrum (CCl_4–$CDCl_3$), δ_F, ppm: **3a**: 2.0 t (1F, 5-F), 8.2 m (4F, 2′-F, 2″-F, 6′-F, 6″-F), 10.6 d (2F, 4-F, 6-F), 12.8 s (1F, 2-F), 16.4 m (4F, 3′-F, 3″-F, 5′-F, 5″-F); **3b**: 1.8 t (1F, 3′-F), 6.3 t (1F, 4″-F), 8.1 m (2F, 1-F, 5-F), 9.8 m and 9.9 m (2F, 2′-F, 4′-F), 12.2 s (1F, 6′-F), 13.8 m (1F, 2″-F), 14.4 m (1F, 3″-F), 15.8 m (1F, 5″-F), 16.2 m (2F, 2-F, 4-F); in acetone-d_6: **3a**: 1.4 t (1F, 5-F), 8.7 m (4F, 2′-F, 2″-F, 6′-F, 6″-F), 11.2 d (2F, 4-F, 6-F), 14.6 s (1F, 2-F), 16.9 m (4F, 3′-F, 3″-F, 5′-F, 5″-F′); the ^{19}F NMR spectrum of **3a** was consistent with that reported in [23]. Mass spectrum: *m*/*z*: 568 $[M]^+$.

4,5,17,18,26,28-Hexafluoro-6,16-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (4a) and 4,5,16,17,26,28-hexafluoro-6,18-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (4b). A solution of 0.30 g (2,7 mmol) of resorcinol and 1.48 g (~3 mmol) of isomer mixture **1a**/**1b** (86:14) in 150 mL of acetonitrile was heated to the boiling point, and a solution of 1.0 g (10 mmol) of triethylamine in 5 mL of acetonitrile was added with stirring. The mixture was refluxed for 16 h, the solvent was distilled off under reduced pressure (~20 mm Hg), and the residue was subjected to silica gel column chromatography using carbon tetrachloride–chloroform (~5:1 by volume) as eluent to isolate 1.04 g (62%) of a product containing tetraoxacalixarenes **4a** and **4b** at a ratio of 86:14. Double recrystallization of the product from carbon tetrachloride gave 0.39 g of **4a** with mp > 200°C. IR spectrum (KBr), ν, cm^{-1}: 1601, 1485 s (C=C$_{arom}$), 1552 s (NO_2), 1365 m (NO_2), 1244 s (C–O), 1166 s, 1115–1014 m (C–F). ^{19}F NMR spectrum of **4a** (CCl_4–$CDCl_3$), δ_F, ppm: 11.4 d (2F, 4-F, 18-F, *J* = 23.0 Hz), 16.8 d.d (2F, 5-F, 17-F, *J* = 23.0, 10.0 Hz), 24.8 d (2F, 26-F, 28-F, *J* = 10.0 Hz). ^{1}H NMR spectrum of **4a** (CCl_4–$CDCl_3$), δ, ppm: 5.84 s (1H, 25-H), 5.93 s (1H, 27-H), 6.96 d.d (2H, 22-H, 24-H, *J* = 8.3, 2.3 Hz), 7.03 d.d (2H, 10-H, 12-H, *J* = 8.3, 2.3 Hz), 7.35 t (1H, 23-H, *J* = 8.3 Hz), 7.41 t (1H, 11-H, *J* = 8.3 Hz). Found, %: C 50.59; H 1.69; F 20.09. *m*/*z* 568 $[M]^+$. $C_{24}H_8F_6N_2O_8$. Calculated, %: C 50.90; H 1.42; F 20.13; N 4.95. *M* 566. ^{19}F NMR spectrum of **4b** (CCl_4–$CDCl_3$), δ_F, ppm (from the spectrum of mixture **4a**/**4b**): 11.8 d (2F, 4-F, 16-F, *J* = 23.0 Hz), 16.9 d.d (2F, 5-F, 17-F, *J* = 23.0, 10.0 Hz), 25.0 d (2F, 26-F, 28-F, *J* = 10.0 Hz).

4,5,10,11,12,17,18,26,27,28-Decafluoro-6,16-dinitro-2,8,14,20-tetraoxapentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (5a), 4,5,10,11,12,16,17,26,27,28-decafluoro-6,18-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (5b), and 5,6,10,11,12,16,17,26,27,28-decafluoro-4,18-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (8a). *a*. The reaction was carried out as described above for the synthesis of **4a** and **4b** using 0.36 g (2 mmol) of tetrafluororesorcinol, 0.94 g (2 mmol) of isomer mixture **1a**/**1b** (86:14), and 1.0 g (10 mmol) of triethylamine in 20 mL of acetonitrile (reflux, 10 h). By silica gel column chromatography we isolated 0.59 g (46%) of mixture **5a**/**5b** at a ratio of 86:14 (GC/MS), and double recrystallization of that mixture from carbon tetrachloride gave 0.29 g of **5a** with mp > 200°C.

Compound **5a**. IR spectrum (KBr), ν, cm^{-1}: 1593, 1502 s (C=C$_{arom}$), 1554 s (NO_2), 1362 m (NO_2), 1246 s (C–O), 1167 s, 1146 s, 1107–1032 m (C–F). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$: 2.6 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 7.1 m (1F, 27-F), 8.7 d.d (2F, 10-F, 12-F, *J* = 22.0, 2.0 Hz), 11.4 d (2F, 4-F, 18-F, *J* = 22.0 Hz), 17.2 d.d (2F, 5-F, 17-F, *J* = 22.0, 8.0 Hz), 18.1 d (2F, 26-F, 28-F, *J* = 8.0 Hz); in acetone-d_6: 2.5 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 8.5 d.d (2F, 10-F, 12-F, *J* = 22.0, 2.0 Hz), 11.1 d (2F, 4-F, 18-F, *J* = 22.0 Hz), 11.5 m (1F, 27-F), 16.0 d.d (2F, 5-F, 17-F, *J* = 22.0, 8.0 Hz), 18.8 d (2F, 26-F, 28-F, *J* = 8.0 Hz). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 5.90 m (1H, 25-H), 7.07 d.d (2H, 22-H, 24-H, *J* = 8.3, 2.2 Hz), 7.44 t (1H, 23-H, *J* = 8.3 Hz); in acetone-d_6): 6.86 m (1H, 25-H), 7.22 d.d (2H, 22-H, 24-H, *J* = 8.3, 2.2 Hz), 7.59 t (1H, 23-H, *J* = 8.3 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 101.31 (C^{25}), 114.81 (C^{22}, C^{24}), 130.43 d.d (C^6, C^{16}, $^2J_{CF}$ = 12.9, J_{CF} = 3.5 Hz), 132.19 t (C^3, C^{19} or C^9, C^{13}, $^2J_{CF}$ = 13.6 Hz), 133.03 (C^{23}), 135.75 d (C^7, C^{15}, $^2J_{CF}$ = 11.7 Hz), 137.22 t.d (C^9, C^{13} or C^3, C^{19}, $^2J_{CF}$ = 12.8, J_{CF} = 3.7 Hz), 139.60 d.t.d (C^{11}, $^1J_{CF}$ = 250.5, $^2J_{CF}$ = 13.7, J_{CF} = 4.3 Hz), 141.69 d.d (C^{10}, C^{12}, $^1J_{CF}$ = 252.9, $^2J_{CF}$ = 13.9 Hz), 142.54 d.d.d (C^4, C^{18}, $^1J_{CF}$ = 258.2, $^2J_{CF}$ = 14.9, J_{CF} = 4.0 Hz), 142.91 d (C^{27}, $^1J_{CF}$ =

251.8 Hz), 143.41 d.d.d (C^5, C^{17}, $^1J_{CF}$ = 253.6, $^2J_{CF}$ = 13.8, J_{CF} = 4.8 Hz), 144.27 d (C^{26}, C^{28}, $^1J_{CF}$ = 252.9 Hz), 158.69 (C^1, C^{21}). Found, %: C 45.02; H 0.85; F 30.10; N 4.39. *m*/*z* 634 $[M]^+$. $C_{24}H_4F_{10}N_2O_8$. Calculated, %: C 45.16; H 0.63; F 29.76; N 4.39. 638.

Compound **5b**. ^{19}F NMR spectrum (CCl_4–$CDCl_3$), δ_F, ppm (from the spectrum of mixture **5a**/**5b**): 2.8 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 7.2 m (1F, 27-F), 8.4 d.d and 9.2 d.d (2F, 10-F, 12-F, *J* = 22.0 Hz), 11.2 d and 11.7 d (2F, 4-F, 16-F, *J* = 23.0 Hz), 16.9 d.d and 17.0 d.d (2F, 5-F, 17-F, *J* = 23.0, 9.0 Hz), 17.5 d and 17.9 d (2F, 26-F, 28-F, *J* = 9.0 Hz).

b. Likewise, the reaction of 0.12 g (1.1 mmol) of resorcinol with 0.65 g (1.1 mmol) of mixture **3a**/**3b** (96:4) in the presence of 0.7 g (7 mmol) of triethylamine in 60 mL of acetonitrile under reflux for 13 h, followed by appropriate treatment, gave 0.27 g (38%) of a product containing 85% of **8a** and 6% of **5b** (GC/MS). Recrystallization of the product from carbon tetrachloride afforded 0.21 g of **8a**. IR spectrum (KBr), ν, cm^{-1}: 1608 m, 1508 v.s, 1490 v.s (C=C_{arom}), 1556 v.s (NO_2), 1365 m (NO_2), 1246 m (C–O), 1173 m, 1162 m, 1091–987 s (C–F). ^{19}F NMR spectrum (CCl_4–$CDCl_3$), δ_F, ppm: 3.2 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 7.6 s (1F, 27-F), 9.0 d.d (2F, 10-F, 12-F, *J* = 22.0, 2.0 Hz), 10.6 d (2F, 6-F, 16-F, *J* = 22.0 Hz), 17.1 d.d (2F, 5-F, 17-F, *J* = 22.0, 9.0 Hz), 17.5 d (2F, 26-F, 28-F, *J* = 9.0 Hz). ^{1}H NMR spectrum (CCl_4–$CDCl_3$), δ, ppm: 5.86 s (1H, 25-H), 6.98 d.d (2H, 22-H, 24-H, *J* = 8.3, 2.3 Hz), 7.38 t (1H, 23-H, *J* = 8.3 Hz). Found: *m*/*z*: 637.9808 $[M]^+$. $C_{24}H_4O_8N_2F_{10}$. Calculated: *M* 637.9803.

4,5,17,18,26,28-Hexafluoro-11,23-dimethyl-6,16-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (6a) and 4,5,16,17,26,28-hexafluoro-11,23-dimethyl-6,18-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (6b). A solution of 2.0 g (20 mmol) of triethylamine in 10 mL of acetonitrile was added with stirring to a solution of 0.29 g (2 mmol) of orcinol and 0.85 g (4 mmol) of pentafluoronitrobenzene in 30 mL of acetonitrile, cooled to 0°C. The mixture was stirred for 1 h at 0°C and for 1 h at room temperature, 110 mL of acetonitrile and 0.29 g (2 mmol) of orcinol were added, and the mixture was refluxed for 33 h. The solvent was distilled off, and the residue was subjected to chromatography to isolate 0.73 g (61%) of a mixture of **6a** and **6b** (84:16, GC/MS). Double recrystallization of the product from carbon tetrachloride gave 0.44 g of **6a**. IR spectrum (KBr), ν, cm^{-1}: 1618 s, 1591 s, 1495 v.s (C=C_{arom}), 1550 v.s (NO_2), 1359 s (NO_2), 1292 s (C–O), 1151 s, 1113–1007 s (C–F). ^{19}F NMR spectrum of **6a**, δ_F, ppm: in CCl_4–$CDCl_3$: 11.1 d (2F, 4-F, 18-F, *J* = 23 Hz); 16.6 d.d (2F, 5-F, 17-F, *J* = 23.0, 10.0 Hz), 24.8 d (2F, 26-F, 28-F, *J* = 10.0 Hz); in acetone-d_6 (from the spectrum of mixture **6a**/**6b**): 9.9 d (2F, 4-F, 18-F, *J* = 23.0 Hz), 14.7 d.d (2F, 5-F, 17-F, *J* = 23.0, 10.0 Hz), 24.9 d (2F, 26-F, 28-F, *J* = 10 Hz). ^{1}H NMR spectrum of **6a**, δ, ppm: in CCl_4–$CDCl_3$: 2.34 s (3H, 23-CH_3), 2.38 s (3H, 11-CH_3), 5.64 s (1H, 25-H), 5.74 s (1H, 27-H), 6.80 d.d (2H, 22-H, 24-H, *J* = 2.0, 1.0 Hz), 6.88 d.d (2H, 10-H, 12-H, *J* = 2.0, 1.0 Hz); in acetone-d_6 (from the spectrum of mixture **6a**/**6b**): 2.37 s (3H, 23-CH_3), 2.41 s (3H, 11-CH_3), 6.63 s (1H, 25-H), 6.73 s (1H, 27-H), 6.91 d (2H, 22-H, 24-H, *J* = 2.0 Hz), 7.00 d (2H, 10-H, 12-H, *J* = 2.0 Hz). ^{19}F NMR spectrum of **6b** (acetone-d_6), δ_F, ppm (from the spectrum of mixture **6a**/**6b**): 10.0 d (2F, 4-F, 18-F, *J* = 23.0 Hz), 14.7 m (2F, 5-F, 17-F), 25.0 d (2F, 26-F, 28-F, *J* = 10.0 Hz). ^{1}H NMR spectrum of **6b** (acetone-d_6), δ, ppm (from the spectrum of mixture **6a**/**6b**): 2.39 s (6H, 11-CH_3, 23-CH_3), 6.73 s (2H, 25-H, 27-H), 6.91 m (2H, 12-H, 24-H), 7.00 m (2H, 10-H, 22-H). Found for **6a**, %: C 51.84; H 1.94; F 19.93; N 4.60. *m*/*z* 594 $[M]^+$. $C_{26}H_{12}F_6N_2O_8$. Calculated, %: C 52.54; H 2.04; F 19.18; N 4.71. *M* 594.

4,5,10,11,12,17,18,26,27,28-Decafluoro-23-methyl-6,16-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (7a) and 4,5,10,11,12,16,17,26,27,28-decafluoro-23-methyl-6,18-dinitro-2,8,14,20-tetraoxapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene (7b) were synthesized as described above for **6a**/**6b** from 0.29 g (2 mmol) of orcinol, 0.85 g (4 mmol) of pentafluoronitrobenzene, and 0.46 g (2.5 mmol) tetrafluororesorcinol using 2.0 g (20 mmol) of triethylamine and 30 mL of acetonitrile; the mixture was refluxed for 14 h. By silica gel column chromatography we isolated 0.58 g (44%) of mixture **7a**/**7b** (80:20, GC/MS). Double recrystallization of that mixture from carbon tetrachloride–light petroleum gave 0.30 g of **7a**.

Compound **7a**. IR spectrum (KBr), ν, cm^{-1}: 1618 m, 1583 m, 1510 v.s, 1491 v.s (C=C_{arom}), 1552 s (NO_2), 1361 s (NO_2), 1292 s (C–O), 1151 s, 1107 m, 1022 v.s (C–F). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 2.4 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 7.1 s (1F, 27-F), 8.7 d.d (2F, 10-F, 12-F, *J* = 22.0, 2.0 Hz), 11.2 d (2F, 4-F, 18-F, *J* = 23.0 Hz), 17.1 d.d (2F, 5-F, 17-F, *J* = 23.0, 8.0 Hz), 18.1 d (2F, 26-F, 28-F, *J* = 8.0 Hz). ^{1}H NMR spectrum

($CDCl_3$), δ, ppm: 2.38 s (3H, 23-CH_3), 5.69 s (1H, 25-H), 6.88 m (2H, 22-H, 24-H). Found: *m*/*z* 651.9955 $[M]^+$. $C_{25}H_6O_8N_2F_{10}$. Calculated: *M* 651.9959.

Compound **7b**. ^{19}F NMR spectrum (CCl_4–$CDCl_3$), δ_F, ppm (from the spectrum of mixture **7a**/**7b**): 2.6 t.d (1F, 11-F, *J* = 22.0, 5.0 Hz), 7.6 s (1F, 27-F), 8.5 d.d (1F, *J* = 22.0, 2.0 Hz), 9.2 d.d (1F, *J* = 22.0, 2.0 Hz) (10-F, 12-F), 11.0 d and 11.6 d (1F each, 4-F, 18-F, *J* = 23.0 Hz), 16.8 d.d (2F, 5-F, 17-F, *J* = 23.0, 9.0 Hz), 17.8 d and 18.1 d (1F each, 26-F, 28-F, *J* = 9.0 Hz).

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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