peri-Naphthylenediamines
26.* Unexpected formation of naphtho[1,8-*c*,*d*]pyran derivatives in the reaction of 1,8-bis(dimethylamino)naphthalene with trifluoroacetic anhydride. A new type of double naphthalene "proton sponges"

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The reaction of 1,8-bis(dimethylamino)naphthalene ("proton sponge") with trifluoroacetic anhydride afforded new derivatives of naphtho[1,8-*c*,*d*]pyran, *viz*., *trans*- (**4**) and *cis*-1,3-dihydroxy-6,7-bis(dimethylamino)-1,3-bis(trifluoromethyl)-1*H*,3*H*-naphtho[1,8-*c*,*d*]pyran (**5**) and symmetrical 3,4,10,11-tetrakis(dimethylamino)-7,14-bis(trifluoromethyl)-7,14-epoxy-dinaphtho[1,8-*a*,*b*;1′,8′-*e*,*f*]cyclooctane (**3**), which belongs to a new type of double "proton sponges," along with the expected 1,8-bis(dimethylamino)-4-trifluoroacetylnaphthalene. The structures of compounds **3** and **4** were established by spectral studies and X-ray diffraction analysis.

Key words: 1,8-bis(dimethylamino)naphthalene, "proton sponge," naphtho[1,8-*c*,*d*]pyran, *cis*- and *trans*-diols, trifluoroacetic anhydride, C-acylation, covalent hydration, X-ray diffraction analysis, NMR spectra.

In one of the previous publications of this series,[2] it was reported that the reaction of 1,8-bis(dimethylamino)naphthalene (**1**) ("proton sponge") with trifluoroacetic anhydride (TFAA) in CH_2Cl_2 at −30 °C afforded 1,8-bis(dimethylamino)-4-trifluoroacetylnaphthalene (**2**) in 48% yield. Because a demand has arisen for a large amount of ketone **2**, we attempted to modify the reaction conditions with the aim of increasing the yield of **2**. However, we obtained quite unexpected reaction products along with ketone **2**, which revealed new aspects of the reactivity of the "proton sponge." In the present work, we summarize the results of these studies.

Trifluoroacetylation of the "proton sponge." Previously,[2] compound **2** was prepared starting from **1** and TFAA taken in a molar ratio of 1 : 0.6, which was governed by the necessity of trapping trifluoroacetic acid (TFA) that was eliminated with an excess of the highly basic (pK_a = 12.34, in H_2O)[3] "proton sponge."

In the hope of increasing the yield of compound **2** (Scheme 1), we used a one-and-a-half-fold molar excess of TFAA, the temperature being increased to ~20 °C and the duration of the reaction being increased to 48 h. Surprisingly, the reaction performed under these conditions afforded ketone **2** only in trace amounts and produced a very high-melting (m.p. > 330 °C) and chromatographically labile yellow compound, which was soluble both in polar and nonpolar organic solvents, as virtually the only reaction product (the yield was ~53%). This compound gave a simple ^{1}H NMR spectrum, which indicates that it belongs to symmetrical *para*-disubstituted derivatives of the "proton sponge." The NMR spectrum has a singlet (δ 2.74) corresponding to the methyl groups of the equivalent dimethylamino groups as well as two doublets of the aromatic *ortho*-protons (J = 7.9 Hz) at δ 6.82 and 7.61, which were assigned, by analogy with the parent compound **1**, to the *ortho*- and *meta*-protons, respectively.[4] In this case, each peak of the doublet of the *meta*-protons is additionally split into a quartet with a spin-spin coupling constant of 1.1 Hz. This suggests that the molecule under consideration contains two trifluoromethyl groups, at the fluorine atoms of which splitting occurs. Based on the data of elemental analysis and mass spectrometry (a molecular ion peak at m/z 602), as well as in view of the fact that the IR spectra of 1,8-bis(dimethylamino)naphthalene (**1**) and the compound under study are very similar, the structure of double "proton sponge" **3** was assigned to the latter compound. This structure was confirmed by X-ray diffraction analysis (see below).

When $CHCl_3$ was used instead of CH_2Cl_2, the yield of compound **3** decreased to 11%. In addition, 4-tri-

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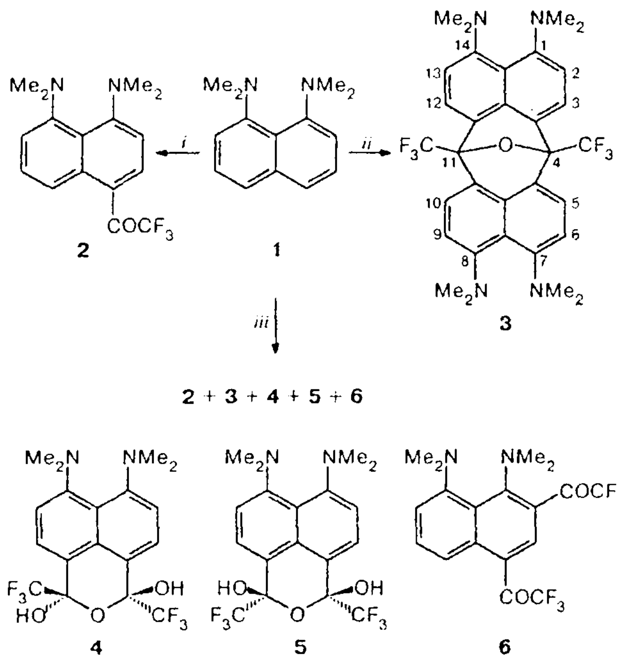
Scheme 1



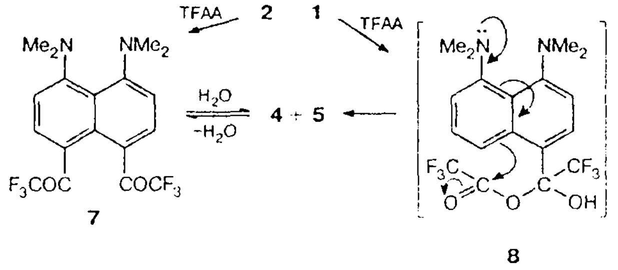
Reagents and conditions: *i*. 0.6 equiv. of TFAA, CH_2Cl_2, −30→0 °C, 30 min. *ii*. 1.5 equiv. of TFAA, CH_2Cl_2, −15 °C, 30 min; ~20 °C, 48 h. *iii*. 1.5 equiv. of TFAA, $ClCH_2CH_2Cl$, ~20 °C, 15 min.

fluoroacetyl- (2) and 2,4-bis(trifluoroacetyl)-substituted derivatives (6) were isolated from the reaction mixture in 19 and 2% yields, respectively. At the same time, storage of the reaction mixture in $ClCH_2CH_2Cl$ at ~20 °C for 48 h led to an increase in the yield of compound 3 to 57%. In the latter case, ketone 2 and diketone 6 were also isolated in small amounts. An important feature of the reaction in dichloroethane is the unexpected formation of *trans*- (4) and *cis*-isomeric (5) 1,3-dihydroxy-6,7-bis(dimethylamino)-1,3-bis(trifluoromethyl)-1*H*,3*H*-naphtho[1,8-*c*,*d*]pyrans. When the duration of the reaction was no more than 30 min, the total yield of 4 and 5 was 11% and the ratio of compounds 4 and 5 was ~2 : 1. We succeeded in separating both diols because *trans*-isomer 4 is less polar and differs somewhat from the *cis* form in solubility. The structures of both isomers were confirmed by the data of IR and NMR spectroscopy and mass spectrometry. The *trans* isomer was also studied by X-ray diffraction analysis (see below). Crystals of the *cis* isomer were changed in the course of X-ray diffraction analysis and we failed to obtain structural data on this compound.

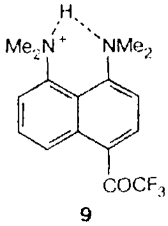
As expected, the ^{1}H NMR spectra of all three naphtho[1,8-*c*,*d*]pyran derivatives 3, 4, and 5 are very similar. The only difference is that the spectra of diols 4 and 5 have an additional two-proton signal of the OH groups observed at δ ~8.2 in DMSO-d$_6$ and at δ ~3.7 in $CDCl_3$ (for the *cis* isomer, this peak is substantially broadened).

The mechanism of formation of naphthopyrans 3—5 is not entirely clear. The most plausible suggestion is that diols 4 and 5 were formed as a result of hydration of intermediate 1,8-bis(dimethylamino)-4,5-bis(trifuoroacetyl)naphthalene (7), by analogy with hydration of *peri*-dialdehydes of the naphthalene series.[5—7] We succeeded in preparing diketone 7 by thermal vacuum dehydration of *cis*-diol 5 (thermolysis of *trans*-diol 4 proceeded with complications). Both isomeric alcohols have no characteristic melting points. When heated above 115 °C, colorless crystals gradually turned orange-red and gave a melt at ~145—165 °C, which solidified upon cooling to form a bright-yellow caramel. According to the ^{1}H NMR spectral data, the latter compound was diketone 7. Actually, this product appeared to be a very hydrophilic compound, which was rapidly converted into an equimolar mixture of diols 4 and 5 upon storage in air and, particularly, in moist solvents in the presence of Al_2O_3.

Scheme 2



Theoretically, the formation of alcohols 4 and 5 can be represented as a result of intramolecular acylation of intermediate 8 that appeared upon addition of a TFAA molecule to the "proton sponge." Indirect evidence in favor of the above mechanism is the following fact. When 1,8-bis(dimethylamino)-4-trifluoroacetylnaphthalene (2) was kept with one equivalent of TFAA in dichloroethane at −15 °C over a short period, the 2,4-bis(trifluoroacetyl)-substituted derivative of "proton sponge" 6, rather than *peri*-diketone 7 or diols 4 and 5, was obtained as the major reaction product (the yield was 22%). In this case, the yield of compound 3 was no higher than 10%. The formation of compound 6 can be explained by the fact that ketone 2 exists in an acidic medium as cation 9 with an essentially asymmetrical intramolecular hydrogen bond.[8] In this compound, the positive charge is localized predominantly on the N(8) atom, as a result of which the benzene ring containing the trifluoroacetic group is deactivated to a lesser degree (an analogous phenomenon



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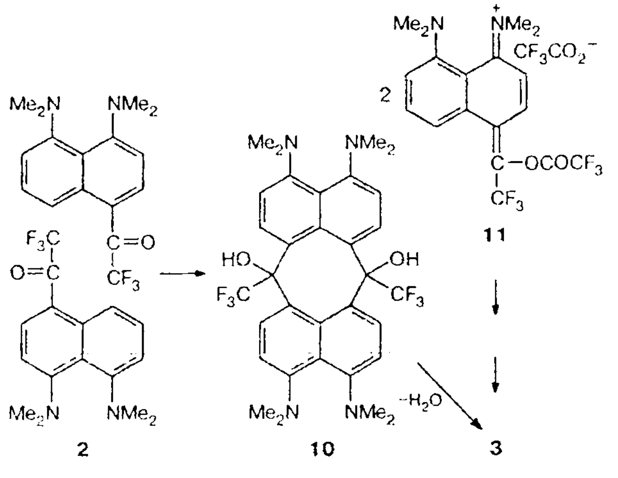
was also observed in the case of nitration of 1,8-bis(dimethylamino)-4-nitronaphthalene).[9] On the whole, it is presently impossible to unambiguously choose between the two above-discussed mechanisms of formation of diols **4** and **5**.

The mechanism of formation of compound **3** is also an intricate question. Formally, it can be represented as a result of nucleophilic addition of two molecules of monoketone **2** to each other through the carbonyl groups (high nucleophilicity of the *ortho* and *para* positions of the "proton sponge" is well known[4]) followed by intramolecular dehydration of a possible intermediate, *viz.*, diol **10** (Scheme 3). Actually, we succeeded in modeling this reaction. It was found that the addition of even a small amount of TFAA to monoketone **2** at −20 °C initiated the formation of compound **3**. This process gradually slowed down as monoketone **2** was converted into cation **9** (due to trapping of the acid that was eliminated). When base **1** was added to salt **9** in the presence of TFAA, the formation of **3** resumed. Interestingly, the action of other Lewis acids ($AlCl_3$, $AlBr_3$, $BF_3 \cdot Et_2O$, or Ac_2O) on ketone **2** in CH_2Cl_2 under various conditions as well as prolonged storage of a melt of ketone **2** in a wide temperature range did not give the desired result. All the aforesaid indicates that the formation of double "sponge" **3** is governed by a fine mechanism that involves the catalytic action of TFAA with a certain template effect. Although the detailed mechanism calls for thorough investigation, the function of TFAA consists presumably in *O*-acylation of monoketone **2** to form equilibrium amounts of cationic intermediate **11**, two molecules of which add to each other to give finally compound **3**.

Scheme 3



An alternative scheme of formation of compound **3** may consist in the nucleophilic addition of "proton sponge" **1** as such to diketone **7** or to diols **4** or **5**. However, attempts to model the latter reactions under conditions of fusion of the reagents or upon heating of these reagents in CH_2Cl_2 in the presence of catalytic amounts of TFA were unsuccessful.

It is worthy of note that trifluoroacetylation of the "proton sponge" essentially depends on the solvent, the temperature, and the reaction time. Thus, the reaction performed at subzero temperature afforded predominantly mono- (**2**) and diketone (**6**). The formation of double "sponge" **3** was favored by an increase in the duration of the reaction, higher temperature (room temperature was optimum), and, apparently, the use of solvents, such as tetrahydrofuran, in which the rate of formation of compound **3** increased substantially and the yield of **3** increased to 66%. It is also interesting that the yields of diols **4** and **5** were decreased to virtually trace amounts when the duration of the process was increased. This suggests that the second acylation of monoketone **2** was reversible, as a result of which the system of equilibriums was gradually shifted to double "proton sponge" **3**, which is characterized by high thermodynamic stability.

X-ray diffraction analysis. The molecular structures of compounds **3** and **4** are shown in Figs. 1 and 2, respectively. The atomic coordinates and the principal geometric characteristics are given in Tables 1—7. As can be seen from Fig. 1, molecule **3** has a butterfly-like conformation whose wings (the naphthalene rings) form an angle of ~106.5°. The central eight-membered ring is folded along the line between the C(1) and C(2) atoms at approximately the same angle (~112°). The geometric parameters of the 1,8-bis(dimethylamino)naphthalene fragments in both compounds differ only slightly from the corresponding characteristics of the parent molecule **1**.[10] Thus, the distances between the *peri*-nitrogen atoms in compounds **1**, **3**, and **4** are 2.79, 2.82 (2.86), and 2.835 Å, respectively. In all three compounds, the *peri*-dimethylamino groups substantially deviate from the mean plane of the naphthalene rings and the rings are distorted due to strong repulsions between the NMe_2 groups. The character of these distortions closely resembles that observed in molecule **1** and is shown in Fig. 3 (solid and empty circles represent atoms located on the opposite sides of the mean plane of the naphthalene ring).

The geometric parameters of the pyran rings in compounds **3** and **4** are substantially different. Thus, the distances between the carbon atoms linked *via* the oxygen bridge (C(1)...C(2) in **3** and C(7)...C(7′) in **4**) are 2.348 and 2.514 Å, respectively. The C(1)—O(1)—C(2) and C(7)—O(1)—C(7′) bond angles are 112.1 and 124.9°, respectively. The O(1) atom deviates from the mean C(5)—C(6)—C(7)—C(8)—C(9)—C(10)—C(11)—C(12)—C(13)—C(14)—C(1)—C(2) plane in **3** by 0.608 Å and from the mean C(1)—C(2)—C(3)—C(4)—C(5)—C(6)—N(1)—C(7) plane in **4** by 0.336 Å. Evidently, the large distortions of the pyran ring in compound **3** are governed by the necessity of reducing strong angular deformations that occur upon fusion of the cyclooctane ring with the *peri* positions of two naphthalene rings. Crystals

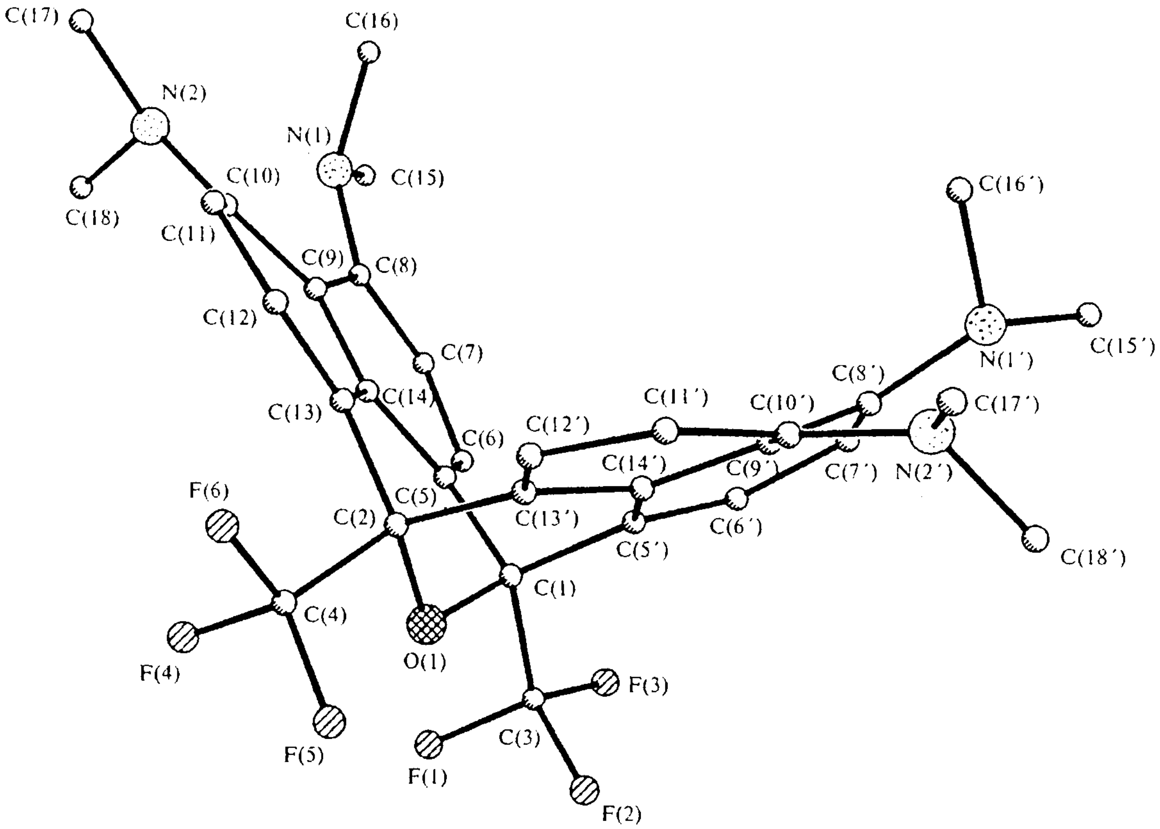


Fig. 1. Molecular structure of compound **3**.

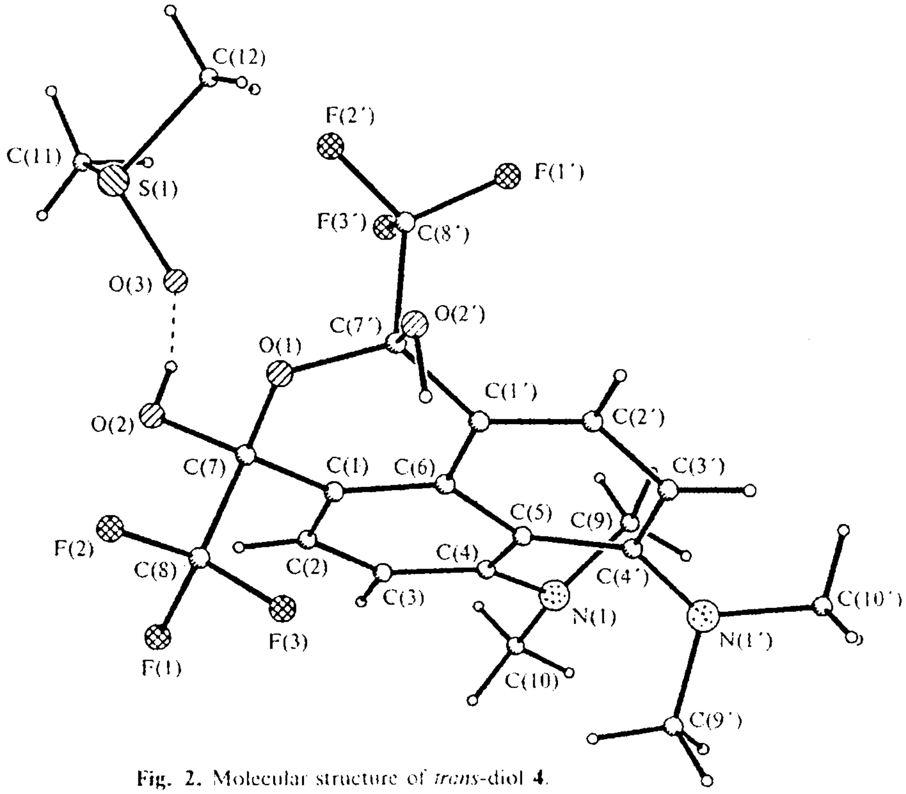


Fig. 2. Molecular structure of *trans*-diol **4**.

of naphthopyran **4** contain two DMSO molecules, which form hydrogen bonds with the protons of both hydroxyl groups of molecule **4**. The O—H...O angle is 167(3)° and the O...O distance is 2.642(2) Å.

Table 1. Atomic coordinates (×10⁴) and isotropic equivalent B_{eq} (isotropic B_{iso} for hydrogen atoms) temperature factors in the structure of **3**

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}/B_{iso}
O(1)	9139(2)	−9(2)	1686(2)	59(1)	C(14′)	8631(3)	1322(3)	664(2)	40(1)
C(1)	8538(4)	−275(3)	994(3)	55(1)	C(15′)	7544(7)	2344(5)	−1991(3)	75(2)
C(2)	8612(4)	734(3)	2037(2)	54(1)	C(16′)	6987(5)	3187(3)	−826(4)	60(1)
C(3)	9383(4)	−1011(3)	695(4)	71(1)	C(17′)	9734(6)	4335(3)	130(3)	66(1)
C(4)	9340(5)	792(4)	2790(3)	75(2)	C(18′)	10211(4)	3210(4)	−808(3)	58(1)
F(1)	9515(3)	−1614(2)	1251(2)	108(1)	H(6)	7240(89)	−1620(63)	350(60)	212(42)
F(2)	10458(3)	−670(2)	565(2)	92(1)	H(7)	5116(57)	−1911(43)	371(41)	131(23)
F(3)	9047(3)	−1394(2)	32(2)	88(1)	H(11)	5321(47)	1170(31)	3169(30)	56(19)
F(4)	9256(3)	79(2)	3224(2)	102(1)	H(12)	7035(41)	1467(29)	2970(27)	53(14)
F(5)	10480(3)	919(2)	2645(2)	92(1)	H(151)	2327(61)	−1806(29)	1190(41)	145(22)
F(6)	9024(3)	1443(2)	3276(2)	90(1)	H(152)	3492(56)	−2341(37)	1310(34)	109(17)
N(1)	3691(4)	−1074(3)	1560(4)	102(2)	H(153)	3347(47)	−1744(41)	563(27)	115(31)
N(2)	3954(4)	−214(4)	3026(3)	104(2)	H(161)	2177(50)	−375(33)	1843(31)	84(16)
C(5)	7324(4)	−638(3)	1218(3)	59(1)	H(162)	3372(51)	345(37)	1800(34)	102(19)
C(6)	6756(5)	−1289(3)	854(4)	78(2)	H(163)	2705(59)	−286(41)	888(40)	109(23)
C(7)	5561(5)	−1462(4)	979(5)	91(2)	H(171)	4009(80)	404(51)	4254(54)	187(32)
C(8)	4922(4)	−985(3)	1514(4)	75(2)	H(172)	2375(77)	−15(51)	3571(43)	158(25)
C(9)	5531(4)	−363(3)	2018(3)	66(1)	H(173)	3229(48)	971(34)	3515(34)	72(19)
C(10)	4995(4)	70(4)	2664(3)	76(2)	H(181)	4583(57)	−1399(35)	3126(33)	86(19)
C(11)	5525(6)	797(6)	2945(4)	81(2)	H(182)	3188(90)	−1376(57)	3280(56)	183(36)
C(12)	6676(5)	1050(5)	2707(3)	71(2)	H(183)	4354(73)	−883(53)	4039(53)	163(30)
C(13)	7296(4)	547(3)	2216(3)	58(1)	H(6′)	7979(54)	−319(43)	−523(37)	123(23)
C(14)	6736(4)	−153(3)	1828(3)	57(1)	H(7′)	7656(44)	807(33)	−1457(32)	85(15)
C(15)	3169(6)	−1805(4)	1117(7)	147(4)	H(11′)	9374(35)	3509(26)	1379(23)	46(12)
C(16)	2966(5)	−288(4)	1470(5)	90(2)	H(12′)	8988(42)	2476(30)	2279(30)	70(14)
C(17)	3318(7)	348(8)	3538(5)	127(3)	H(15A)	6773(49)	1935(36)	−2078(33)	92(17)
C(18)	3946(7)	−1115(8)	3305(7)	161(5)	H(15B)	8201(44)	2027(32)	−2272(29)	68(16)
N(1′)	7813(3)	2547(2)	−1164(2)	50(1)	H(15C)	7542(68)	2887(49)	−2229(46)	145(30)
N(2′)	9434(3)	3478(2)	−177(2)	47(1)	H(16A)	7064(43)	3596(32)	−1175(30)	70(16)
C(5′)	8440(4)	458(3)	398(3)	48(1)	H(16B)	6949(48)	3218(34)	−241(36)	88(18)
C(6′)	8135(4)	326(3)	−384(3)	59(1)	H(16C)	6043(76)	3049(50)	−891(49)	171(30)
C(7′)	7962(4)	1015(3)	−898(3)	55(1)	H(17A)	10489(43)	4258(29)	430(26)	62(13)
C(8′)	8137(3)	1858(3)	−667(2)	44(1)	H(17B)	9010(45)	4596(30)	419(28)	67(14)
C(9′)	8620(3)	2023(2)	111(2)	39(1)	H(17C)	9873(48)	4681(35)	−342(34)	88(17)
C(10′)	9081(3)	2855(2)	375(2)	41(1)	H(18A)	11128(58)	3346(36)	−636(35)	107(20)
C(11′)	9144(4)	3002(3)	1169(2)	48(1)	H(18B)	10001(56)	3497(41)	−1312(40)	115(22)
C(12′)	8952(4)	2337(3)	1726(3)	52(1)	H(18C)	10116(48)	2634(38)	−923(32)	89(19)
C(13′)	8773(3)	1510(3)	1486(2)	47(1)					

Table 2. Bond lengths (*d*) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(1)	1.410(5)	C(4)—F(5)	1.327(6)	C(8)—C(9)	1.455(8)	N(2′)—C(17′)	1.459(6)
O(1)—C(2)	1.421(5)	C(4)—F(6)	1.344(7)	C(9)—C(10)	1.413(8)	C(5′)—C(6′)	1.377(7)
C(1)—C(5′)	1.515(6)	N(1)—C(8)	1.401(6)	C(9)—C(14)	1.438(6)	C(5′)—C(14′)	1.422(6)
C(1)—C(5)	1.531(6)	N(1)—C(16)	1.472(7)	C(10)—C(11)	1.356(10)	C(6′)—C(7′)	1.385(7)
C(1)—C(3)	1.568(7)	N(1)—C(15)	1.475(9)	C(11)—C(12)	1.417(8)	C(7′)—C(8′)	1.371(6)
C(2)—C(4)	1.516(7)	N(2)—C(10)	1.396(7)	C(12)—C(13)	1.334(7)	C(8′)—C(9′)	1.443(6)
C(2)—C(13′)	1.525(6)	N(2)—C(17)	1.418(11)	C(13)—C(14)	1.413(7)	C(9′)—C(14′)	1.427(5)
C(2)—C(13)	1.546(6)	N(2)—C(18)	1.466(11)	N(1′)—C(8′)	1.402(5)	C(9′)—C(10′)	1.454(5)
C(3)—F(3)	1.318(6)	C(5)—C(6)	1.341(7)	N(1′)—C(15′)	1.459(6)	C(10′)—C(11′)	1.359(6)
C(3)—F(1)	1.329(6)	C(5)—C(14)	1.434(7)	N(1′)—C(16′)	1.472(7)	C(11′)—C(12′)	1.406(6)
C(3)—F(2)	1.343(6)	C(6)—C(7)	1.393(8)	N(2′)—C(10′)	1.394(5)	C(12′)—C(13′)	1.353(6)
C(4)—F(4)	1.324(6)	C(7)—C(8)	1.371(8)	N(2′)—C(18′)	1.440(6)	C(13′)—C(14′)	1.424(6)

Table 3. Bond angles (θ) in the structure of **3**

Angle	θ/deg	Angle	θ/deg	Angle	θ/deg
C(1)—O(1)—C(2)	112.1(3)	C(16)—N(1)—C(15)	110.7(5)	C(8′)—N(1′)—C(16′)	116.2(4)
O(1)—C(1)—C(5′)	111.5(4)	C(10)—N(2)—C(17)	120.2(7)	C(15′)—N(1′)—C(16′)	112.4(4)
O(1)—C(1)—C(5)	109.6(4)	C(10)—N(2)—C(18)	116.2(6)	C(10′)—N(2′)—C(18′)	118.0(4)
C(5′)—C(1)—C(5)	111.7(3)	C(17)—N(2)—C(18)	112.4(7)	C(10′)—N(2′)—C(17′)	117.0(4)
O(1)—C(1)—C(3)	100.5(4)	C(6)—C(5)—C(14)	119.7(5)	C(18′)—N(2′)—C(17′)	112.3(4)
C(5′)—C(1)—C(3)	111.8(4)	C(6)—C(5)—C(1)	126.3(5)	C(6′)—C(5′)—C(14′)	118.5(4)
C(5)—C(1)—C(3)	111.2(4)	C(14)—C(5)—C(1)	113.7(4)	C(6′)—C(5′)—C(1)	122.9(4)
O(1)—C(2)—C(4)	99.7(4)	C(5)—C(6)—C(7)	122.6(6)	C(14′)—C(5′)—C(1)	118.6(4)
O(1)—C(2)—C(13′)	109.2(3)	C(8)—C(7)—C(6)	120.6(6)	C(5′)—C(6′)—C(7′)	121.4(5)
C(4)—C(2)—C(13′)	113.5(4)	C(7)—C(8)—N(1)	120.5(6)	C(8′)—C(7′)—C(6′)	121.9(4)
O(1)—C(2)—C(13)	109.6(4)	C(7)—C(8)—C(9)	119.2(5)	C(7′)—C(8′)—N(1′)	120.7(4)
C(4)—C(2)—C(13)	111.8(4)	N(1)—C(8)—C(9)	120.2(6)	C(7′)—C(8′)—C(9′)	118.6(4)
C(13′)—C(2)—C(13)	112.3(3)	C(10)—C(9)—C(14)	118.2(5)	N(1′)—C(8′)—C(9′)	120.6(4)
F(3)—C(3)—F(1)	108.5(4)	C(10)—C(9)—C(8)	123.9(5)	C(14′)—C(9′)—C(8′)	117.6(3)
F(3)—C(3)—F(2)	107.3(4)	C(14)—C(9)—C(8)	117.9(5)	C(14′)—C(9′)—C(10′)	117.7(3)
F(1)—C(3)—F(2)	106.7(4)	C(11)—C(10)—N(2)	118.6(6)	C(8′)—C(9′)—C(10′)	124.7(4)
F(3)—C(3)—C(1)	114.9(4)	C(11)—C(10)—C(9)	118.0(5)	C(11′)—C(10′)—N(2′)	121.8(4)
F(1)—C(3)—C(1)	110.3(4)	N(2)—C(10)—C(9)	123.4(6)	C(11′)—C(10′)—C(9′)	117.8(4)
F(2)—C(3)—C(1)	108.7(4)	C(10)—C(11)—C(12)	122.4(7)	N(2′)—C(10′)—C(9′)	120.4(4)
F(4)—C(4)—F(5)	107.1(4)	C(13)—C(12)—C(11)	119.9(7)	C(10′)—C(11′)—C(12′)	121.9(4)
F(4)—C(4)—F(6)	105.3(4)	C(12)—C(13)—C(14)	119.7(5)	C(13′)—C(12′)—C(11′)	120.7(4)
F(5)—C(4)—F(6)	105.2(5)	C(12)—C(13)—C(2)	121.3(5)	C(12′)—C(13′)—C(14′)	120.0(4)
F(4)—C(4)—C(2)	112.0(5)	C(14)—C(13)—C(2)	119.0(4)	C(12′)—C(13′)—C(2)	125.1(4)
F(5)—C(4)—C(2)	112.5(4)	C(13)—C(14)—C(5)	121.5(4)	C(14′)—C(13′)—C(2)	114.8(4)
F(6)—C(4)—C(2)	114.1(4)	C(13)—C(14)—C(9)	119.6(5)	C(5′)—C(14′)—C(13′)	120.9(3)
C(8)—N(1)—C(16)	117.9(5)	C(5)—C(14)—C(9)	118.8(5)	C(5′)—C(14′)—C(9′)	120.1(3)
C(8)—N(1)—C(15)	116.4(6)	C(8′)—N(1′)—C(15′)	117.5(4)	C(13′)—C(14′)—C(9′)	118.8

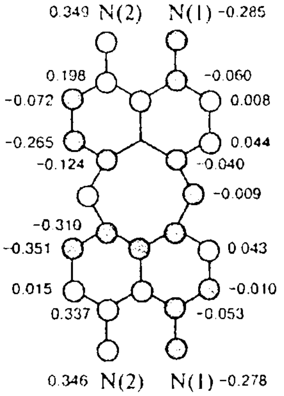


Fig. 3. Deviations (Å) of selected nonhydrogen atoms in molecule **3** from the mean plane of the corresponding naphthalene ring.

Selected properties of double "proton sponge" 3. In the ^{1}H NMR spectrum of compound **3** (Fig. 4) at room temperature, as in the spectrum of the parent compound **1**, the methyl groups of all dimethylamino fragments appear as a singlet, *i.e.*, these groups are magnetically equivalent. However, this signal splits into two singlets upon cooling. In the case of compound **1**, this splitting occurs at −120 °C,[11] while in the case of double "sponge" **3**, coalescence is observed even at 10 °C. It is believed that cooling of "proton sponges" results in "freezing" of the molecules in the conformation containing two magnetically nonequivalent Me groups, *viz.*, the external groups, which are located approximately in the plane of the ring, and the internal groups, which deviate substantially from the ring. It was suggested[11] that the interconversion of the methyl groups has a "narcissistic character" and proceeds through an intermediate planar state with the symmetry C_{2v}. We calculated the $\Delta G^{\#}$ value for compound **3** (61.9 kJ mol^{-1}), which appeared to be twice as large as that for "proton sponge" **1** (31.4 kJ mol^{-1}).[11] The fact that the interconversion in the case of double "proton sponge" **3** is more hindered can be explained as follows. Apparently, the transition to the planar state should also be accompanied by flattening of the naphthalene ring. In the case of compound **1**, flattening occurs without substantial internal hindrances, while this flattening in molecule **3** is, apparently, hindered due to the fixing effect of the central

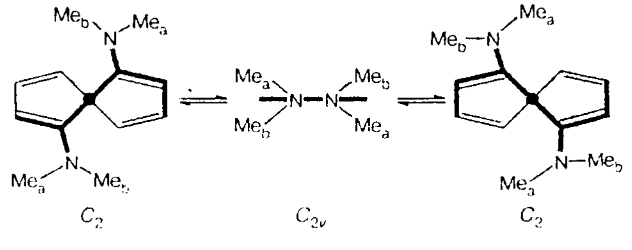


Table 4. Atomic coordinates ($\times 10^4$) and isotropic equivalent B_{eq} (isotropic B_{iso} for hydrogen atoms) temperature factors in the structure of **4**

Atom	x	y	z	B_{eq}/B_{iso}
S(1)	2502(1)	4675(1)	448(1)	40(1)
N(1)	−844(1)	2888(2)	2295(1)	32(1)
F(1)	−832(1)	8050(2)	4331(1)	52(1)
F(2)	−253(1)	9751(1)	4058(1)	41(1)
F(3)	384(1)	7987(2)	4223(1)	62(1)
O(1)	0	8873(2)	25	51(1)
O(2)	−1296(1)	8904(2)	2618(1)	37(1)
O(3)	2753(1)	3525(2)	1024(1)	42(1)
C(1)	−653(1)	6845(2)	2689(1)	23(1)
C(2)	−1315(1)	6198(2)	2797(1)	29(1)
C(3)	−1377(1)	4886(2)	2663(2)	30(1)
C(4)	−750(1)	4178(2)	2486(1)	24(1)
C(5)	0	4809(2)	25	21(1)
C(6)	0	6164(2)	25	21(1)
C(7)	−584(1)	8252(2)	2866(1)	25(1)
C(8)	−320(1)	8511(2)	3878(1)	31(1)
C(9)	−672(2)	2421(2)	1465(2)	42(1)
C(10)	−1530(2)	2257(3)	25(3)	50(1)
C(11)	1503(2)	4360(4)	−140(2)	56(1)
C(12)	2957(2)	4504(4)	−485(2)	57(1)
H(1)	−1565(20)	8702(32)	2051(24)	57(9)
H(2)	−1731(15)	6625(24)	2948(17)	30(6)
H(3)	−1863(16)	4449(25)	2731(17)	33(6)
H(91)	−265(15)	2950(25)	1229(17)	30(6)
H(92)	−500(20)	1571(34)	1527(23)	57(9)
H(93)	−1222(20)	2431(33)	936(23)	61(9)
H(101)	−1432(19)	1372(35)	2501(22)	59(9)
H(102)	−1593(19)	2489(31)	3099(23)	53(9)
H(103)	−2028(23)	2451(33)	2109(24)	60(9)
H(111)	1498(22)	3516(39)	−489(26)	73(11)
H(112)	1193(26)	4283(40)	280(30)	84(13)
H(113)	1356(22)	5067(37)	−608(26)	67(10)
H(121)	2712(19)	5165(30)	−930(22)	48(8)
H(122)	3523(27)	4569(41)	−234(29)	86(13)
H(123)	2758(23)	3682(38)	−783(25)	70(11)

eight-membered ring (*cf.* analogous data on the double binaphthyl "proton sponge"[12]). The signals of the aromatic protons in molecule **3** are virtually insensitive to a change in the temperature.

The electronic absorption spectrum of compound **3** is of interest. The maximum of its long-wavelength absorption band, which is responsible for the yellow color, is observed at 389 nm (lgε 4.09), the character of absorption remaining virtually unchanged on going to the corresponding dication **12**. Compound **3** differs sharply in this property from colorless "proton sponge" **1** (λ_{max} 341 nm, lgε 4.09),[13] in which the transition to the protonated form is accompanied by a substantial hypsochromic shift of the long-wavelength absorption band (λ_{max} 288 nm, lgε 3.85).[4] This suggests that the latter band in the two compounds differs in nature. It is believed that in the case of "proton sponge" **1**, this band is associated with the transfer of the electron density from the n-orbital of the nitrogen atoms to the π-antibonding orbital of the naphthalene ring. Since the NMe_2 groups in compound **3** contribute insignificantly to absorption, the presence of a particular π-interaction between the naphthalene rings can confidently be assumed. Taking into account the strongly bent conformation of molecule **3** (Fig. 1), this interaction occurs, most likely, directly through space rather than *via* the saturated bridges that link both rings.

Table 5. Bond lengths (d) in the structure of **4**

Bond	d/Å
S(1)—O(3)	1.505(2)
S(1)—C(12)	1.784(3)
S(1)—C(11)	1.785(3)
N(1)—C(4)	1.395(3)
N(1)—C(9)	1.454(3)
N(1)—C(10)	1.452(3)
F(1)—C(8)	1.331(3)
F(2)—C(8)	1.338(2)
F(3)—C(8)	1.329(3)
O(1)—C(7)	1.417(2)
O(2)—C(7)	1.384(2)
C(1)—C(2)	1.372(3)
C(1)—C(6)	1.420(2)
C(1)—C(7)	1.511(3)
C(2)—C(3)	1.400(3)
C(3)—C(4)	1.391(3)
C(4)—C(5)	1.450(2)
C(5)—C(6)	1.431(4)
C(7)—C(8)	1.535(3)

Table 6. Bond angles (θ) in the structure of **4**

Angle	θ/deg
O(3)—S(1)—C(12)	105.47(14)
O(3)—S(1)—C(11)	105.11(14)
C(12)—S(1)—C(11)	97.3(2)
C(4)—N(1)—C(9)	118.6(2)
C(4)—N(1)—C(10)	117.7(2)
C(9)—N(1)—C(10)	111.7(2)
C(7)—O(1)—C(7)*	124.9(2)
C(2)—C(1)—C(6)	119.4(2)
C(2)—C(1)—C(7)	120.2(2)
C(6)—C(1)—C(7)	120.0(2)
C(1)—C(2)—C(3)	120.9(2)
C(4)—C(3)—C(2)	121.6(2)
C(3)—C(4)—N(1)	120.5(2)
C(3)—C(4)—C(5)*	118.7(2)
N(1)—C(4)—C(5)*	120.9(2)
C(3)—C(4)—C(5)	118.7(2)
N(1)—C(4)—C(5)	120.9(2)
C(6)—C(5)—C(4)	117.35(12)
C(4)—C(5)—C(4)*	125.3(2)
C(1)*—C(6)—C(1)	119.1(2)
C(1)—C(6)—C(5)	120.44(12)
O(2)—C(7)—O(1)	109.1(2)
O(2)—C(7)—C(1)	114.3(2)
O(1)—C(7)—C(1)	114.8(2)
O(2)—C(7)—C(8)	103.2(2)
O(1)—C(7)—C(8)	104.0(2)
C(1)—C(7)—C(8)	110.4(2)
F(3)—C(8)—F(1)	107.1(2)
F(3)—C(8)—F(2)	107.3(2)
F(1)—C(8)—F(2)	106.7(2)
F(3)—C(8)—C(7)	111.2(2)
F(1)—C(8)—C(7)	112.3(2)
F(2)—C(8)—C(7)	112.0(2)

Note. Atoms generated from the basis atoms by the symmetry operation $-x$, y, $1/2 - z$ are marked with asterisks.

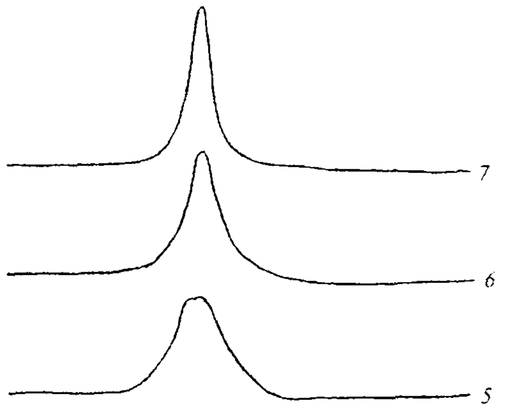
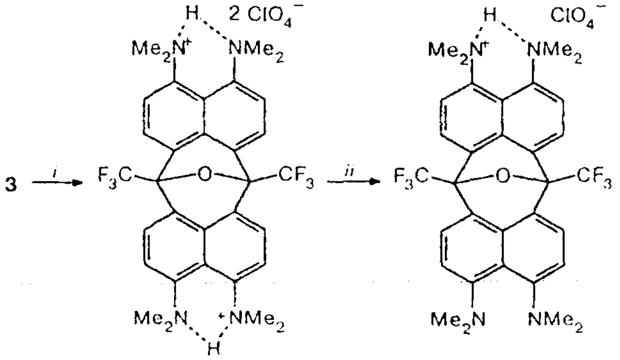


Fig. 4. Signals of the *N*-methyl groups of compound **3** in the ^{1}H NMR spectrum (in CDCl$_3$) depending on the temperature/°C: −60 (*1*), −40 (*2*), −20 (*3*), 0 (*4*), 10 (*5*), 20 (*6*), and 40 (*7*).

We prepared diperchlorate **12** by the reaction of base **3** with an excess of HClO$_4$. The ^{1}H NMR spectrum of **12**, like that of the cation **1** · H$^+$,[3,4] has the signal of the protons of the NH group as a broadened singlet at low field (δNH 18.43 in DMSO-d$_6$ and 18.61 in CD$_3$CN) due to the formation of a strong intramolecular hydrogen bond. However, it is most interesting that the methyl groups in dication **12** (unlike those in the cation **1** · H$^+$, which give one signal that splits into a doublet with the spin-spin coupling constant $J_{\mathrm{NH-Me}}$ = 2.3—2.5 Hz) give two different signals (at δ 3.08 and 3.14 in CD$_3$CN) with smaller and nonequivalent (judging form the peak heights) spin-spin coupling constants ($J_{\mathrm{NH-Me}} < 2$ Hz). This unambiguously indicates that the hydrogen bridges in dication **12** are asymmetrical, which results in the appearance of two types of NMe$_2$ groups. Apparently, this asymmetry provides more substantial spatial separation and, consequently, weaker electrostatic repulsion between the two positive charges. It seems likely that this phenomenon has a general character for dications of double "proton sponges" (*cf.* Refs. 12 and 14).

Although we failed to obtain monoperchlorate **13** preparatively, its ^{1}H NMR spectrum was recorded when an equimolar amount of base **3** was added to a solution of diperchlorate **12** in DMSO-d$_6$. In the NMR spectrum, the signals of the protonated and nonprotonated portions of molecule **13** are clearly distinguished. These signals are very similar to those of dication **12** and base **3**, respectively. For example, the signal of the NH group is observed at δ 18.52. It is particularly remarkable that the hydrogen bridge in monocation **13** is asymmetrical. This is evidenced by the fact that the ^{1}H NMR spectrum has two signals of the nonequivalent NMe$_2$ groups at δ 3.05 and 3.10, each being split into a doublet with spin-spin coupling constants of 1.98 and 1.87 Hz, respectively. It can be seen that the degree of asymmetry of the hydrogen bond is low, and the relatively small spin-spin coupling constants indicate that the proton of the NH group is at a larger distance from the nitrogen atoms compared to that observed in the cation **1** · H$^+$ (*cf.* Ref. 8). It is worthy of note that when equimolar amounts of diperchlorate **12** and base **3** were mixed to form monosalt **13**, 25% of the initial compounds remained in the solution. The latter fact indicates that the first and second ionization constants of compound **3** have relatively close values. The difference ΔpK_a between these constants in a DMSO-d$_6$ solution was ~1.9. The ionization constants of compound **3** in MeCN, which were determined potentiometrically, are as follows: p$K_a{}^1$ = 16.6 and p$K_a{}^2$ = 14.0. Therefore, the basicity of **3** is approximately one-and-a-half orders of magnitude lower than that of the parent compound **1** (pK_a = 18.18, MeCN),[13] which is attributable to the −*I* effect of the CF$_3$ groups.



12 **13**

i. 2 HClO$_4$. *ii*. 1 equiv. of **3**.

Experimental

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Unity-300 instrument (300, 75.4, and 282.211 MHz, respectively) with Me$_4$Si as the internal standard for the ^{1}H and

^{13}C NMR spectra and with $C_6H_5CF_3$ as the internal standard for the ^{19}F NMR spectrum. The UV spectra were measured on a Specord M40 spectrophotometer. The IR spectra were recorded on a UR-20 spectrometer. The mass spectra were obtained on an MX-1321A instrument with direct introduction of the sample into the ion source; the temperature of the ionization chamber was 50—100 °C; the ionizing voltage was 70 eV. The melting points were determined in sealed glass capillaries on a PTP instrument and were not corrected. Chromatography was performed with the use of Al_2O_3 (Brockmann II).

The barrier to rotation of the dimethylamino groups in compound 3 was determined by Eq. (1)[15]

$$\Delta G^{\neq} = 19.14T_c(9.97 + \log(T_c/\Delta\nu)),\ \text{kJ mol}^{-1}, \quad (1)$$

where $\Delta\nu$ is the difference between the chemical shifts of the internal and external methyl groups and T_c is the temperature of coalescence.

The data for compound 3 are as follows: $\Delta\nu$ = 15.2 Hz, T_c = 283 K.

Crystals of compounds 3 and 4 suitable for X-ray diffraction study were grown by isothermal evaporation from solutions in acetone and dimethyl sulfoxide, respectively. The crystallographic characteristics and the principal details of X-ray diffraction studies are given in Table 7. Both structures were solved by direct methods and refined by the least-squares method based on F^2_{hkl} with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically. All calculations were carried out with the use of the SHELXTL PLUS 5 program package (gamma version).[16]

Table 7. Crystallographic characteristics and details of X-ray diffraction studies of compounds 3 and **4**

Parameter	3	4
Molecular formula	$C_{32}H_{32}F_6N_4O$	$C_{22}H_{30}F_6N_2O_5S_2$
Molecular weight	602.62	580.60
Space group	$P2_12_12_1$	$C2/c$
a/Å	11.314(2)	17.240(5)
b/Å	15.414(3)	10.563(3)
c/Å	16.851(3)	15.289(6)
α/deg	90.0	90.0
β/deg	90.0	103.07(3)
γ/deg	90.0	90.0
V/Å^3	2939(1)	2712(2)
Z	4	4
d_{calc}/g cm^{-3}	1.362	1.422
$F(000)$	1256	1208
μ/cm^{-1}	1.10	2.72
Diffractometer	CAD4	Siemens P3/PC
Temperature/K	293	151
Scanning mode	$\theta/(5/3)\theta$	$\theta/2\theta$
θ_{max}/deg	26.0	28.1
Number of reflections	3382	3333
Number of independent reflections	3235	3230
Number of reflections with $I \geq 2\sigma(I)$	1959	2787
R_1 (based on F for reflections with $I \geq 2\sigma(I)$)	0.0421	0.0412
wR_2 (based on F^2 for all N_{conc} reflections)	0.1326	0.2139
N_{conc}	3210	3212
Number of refinable parameters	505	229
GOOF	1.058	1.092

3,4,10,11-Tetrakis(dimethylamino)-7,14-bis(trifluoromethyl)-7,14-epoxydinaphtho[1,8-*a*,*b*;1′,8′-*e*,*f*]cyclooctane (3).* ***A.*** A solution of TFAA (1.5 g, 7 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to a vigorously stirred solution of compound **1** (1 g, 4.7 mmol) in anhydrous CH_2Cl_2 (30 mL) cooled to −15 °C. The reaction mixture turned red-orange and was stirred at −15 °C for 30 min. Then the flask containing the reaction mixture was closed with a stopper and kept at −20 °C for 48 h. The white precipitate that formed (~1 g), which was virtually pure trifluoroacetate of compound **3**, was filtered off, washed with CH_2Cl_2 and hexane, and dried. Then the precipitate was suspended in EtOH (25 mL) and base **3** was precipitated with stirring by adding a 20% KOH solution (~1 mL) to pH 12. The yellow suspension that formed was diluted with water (50 mL) and kept for 2—3 h to obtain crystals. The precipitate was filtered off, washed with water, and dried in air. Yellow crystals were obtained in a yield of 0.72 g (51%), m.p. 338—339 °C (from octane), R_f = 0.82 (Al_2O_3, $CHCl_3$), 0.17 (Al_2O_3, hexane). Found (%): C, 63.3; H, 5.25; N, 9.61. $C_{32}H_{32}F_6N_4O$. Calculated (%): C, 63.79; H, 5.35; N, 9.30. UV (MeOH), λ_{max}/nm (lgε): 350 sh. (4.43), 390 (4.54). IR (Nujol mulls), ν/cm^{-1}: 2780 s (C—H); 1573 v.s, 1513 m (ring). ^{1}H NMR (30 °C, $CDCl_3$), δ: 2.72 (s, 24 H, 4 NMe_2); 6.81 (d, 4 H, H(2), H(6), H(9), H(13), J_o = 8.20 Hz); 7.59 (dq, 4 H, H(3), H(5), H(10), H(12), J_o = 8.20 Hz, $^5J_{H-F}$ = 1.10 Hz). ^{13}C NMR (20 °C, $CDCl_3$), δ: 43.8 (Me, $^1J_{C-H}$ = 133.3 Hz); 111.7 (C(2), C(6), C(9), C(13), $^1J_{C-H}$ =157.4 Hz); 119.8 (C(7a), C(14a)); 120.9 (C(3), C(5), C(10), C(12), $^1J_{C-H}$ = 158.9 Hz); 123.2 (CF_3); 123.9 (C(4), C(11)); 127.6 (C(7b), C(14b)); 130.2 (C(3a), C(4a), C(10a), C(11a)); 150.6 (C(1), C(7), C(8), C(14)). ^{19}F NMR (25 °C, $CDCl_3$), δ: −69.5 (2 CF_3). MS, *m/z* (I_{rel} (%)): 602 $[M]^+$ (100), 587 $[M - Me]^+$ (5), 558 $[M - NMe_2]^+$ (3), 533 $[M - CF_3]^+$ (9).

The filtrate, which was obtained after isolation of the trifluoroacetate of compound **3**, was concentrated to dryness *in vacuo*, suspended in a minimum amount of $CHCl_3$, and made basic with a 10% KOH solution (to pH 12). The chloroform layer was separated, dried over $CaCl_2$, and filtered through a column with Al_2O_3 (*h* = 20 cm, *d* = 2 cm) using $CHCl_3$ as the eluent. First, 4-trifluoroacetyl derivative **2** was collected (R_f 0.95, the yield was 0.15 g, 10.4%) as a viscous oil, which slowly solidified in a refrigerator to form orange-red crystals, m.p. 74—75 °C (from hexane). ^{19}F NMR (25 °C, $CDCl_3$), δ: −68.97 (q, CF_3CO, $^5J_{F-H}$ = 2.1 Hz, $^6J_{F-H}$ = 1.2 Hz). The spectral characteristics of the resulting compound are identical with those of the known sample.[2] Then unconsumed compound **1** was eluted (R_f 0.47, the yield was 0.20 g, 20%).

B. TFAA (0.037 g, 0.176 mmol) was added portionwise (0.0075 g) at 10-h intervals with stirring to a solution of compound **2** (0.10 g, 0.33 mmol) in anhydrous CH_2Cl_2 (3 mL). Within 10 h after the addition of the last portion of TFAA, the precipitate that formed was filtered off, washed with CH_2Cl_2 (1 mL), dried, suspended in EtOH (1 mL), and made basic with a 10% KOH solution (0.5 mL). The yellow precipitate of

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* The arbitrary numbering scheme shown in Scheme 1 was used for the description of the NMR spectra of compound **3**.

compound **3** that formed was washed with water and dried in air. The yield was 0.057 g (57.3%).

The initial ketone **2** was isolated from the filtrate that remained after isolation of the trifluoroacetate of compound **3** as described for procedure *A*, in a yield of 0.032 g (32%).

C. TFAA (0.085 mL, 0.6 mmol) was added dropwise to a stirred solution of compound **1** (0.100 g, 0.047 mmol) in anhydrous THF (2 mL). Then the flask containing the reaction mixture was sealed with a stopper and kept at ~20 °C for 96 h. The white precipitate of the trifluoroacetate of compound **3** that formed was separated, washed on a filter with THF (2 mL), suspended in EtOH (2 mL), and treated with a 20% KOH solution (0.5 mL). Yellow crystals of base **3** were filtered off, washed with water (2 mL), and dried in air. The virtually pure product was obtained in a yield of 0.086 g (61%). The tetrahydrofuran mother liquor was diluted with water (5 mL) and made basic with a 20% aqueous NaOH solution (to pH 14). The emulsion that formed was extracted with $CHCl_3$ (2×3 mL) and the extract was chromatographed on a column with Al_2O_3 (h = 25 cm, d = 2 cm); $CHCl_3$ was used as the eluent. Monoketone **2** (R_f 0.95), double "proton sponge" **3** (R_f 0.82), and the initial compound **1** (R_f 0.47) were successively isolated in yields of 9 mg (6.2%), 8 mg (5.7%), and 14 mg (14%), respectively. The total yield of compound **3** was 0.094 g (66.7%).

Diperchlorate 12.* A 72% perchloric acid solution (0.3 mL, 3.7 mmol) was added dropwise with stirring to a solution of base **3** (0.1 g, 0.17 mmol) in $CHCl_3$ (20 mL). The yellow solution was rapidly decolorized and yielded a white flocculent precipitate. The precipitate was separated, washed on a filter with $CHCl_3$ and hexane, and dried in air. The yield was 0.1 g (75%), m.p. 276—278 °C (from MeCN). Found (%): C, 47.49; H, 4.52; Cl, 8.55; N, 6.69. $C_{32}H_{34}Cl_2F_6N_4O_9$. Calculated (%): C, 47.83; H, 4.26; Cl, 8.82; N, 6.97. UV (MeCN), λ_{max}/nm (lgε): 346 (4.53), 389 (4.53). IR (Nujol mulls), ν/cm^{-1}: 3437 (N—H), 2713 (C—H), 1600 (ring). ^{1}H NMR (25 °C, CD_3CN), δ: 3.08 (s, 12 H, 2 NMe_2); 3.14 (s, 12 H, 2 NMe_2); 8.09 (d, 4 H, H(3), H(5), H(10), H(12), J_o = 6.81 Hz); 8.24 (d, 4 H, H(2), H(6), H(9), H(13), J_o = 6.20 Hz); 18.61 (s, 2 H, 2 NH). ^{1}H NMR (25 °C, DMSO-d_6), δ: 3.05 (s, 12 H, 2 NMe_2); 3.12 (s, 12 H, 2 NMe_2); 8.23 (d, 4 H, H(3), H(5), H(10), H(12), J_o = 8.13 Hz); 8.31 (d, 4 H, H(2), H(6), H(9), H(13), J_o = 7.90 Hz); 18.45 (s, 2 H, 2 NH).

Monoperchlorate 13 was prepared in a solution by adding an equimolar amount of base **3** to a solution of diperchlorate **12** in DMSO-d_6. ^{1}H NMR (30 °C, DMSO-d_6), δ: 1) the protonated portion of the cation: 3.05 (d, 6 H, NMe_2, J_{NH-Me} = 2.0 Hz); 3.10 (d, 6 H, NMe_2, J_{NH-Me} = 1.9 Hz); 8.10 (d, 2 H, *m*-H, J_o = 8.1 Hz); 8.15 (d, 2 H, *o*-H, J_o = 8.2 Hz); 18.52 (br.s, 1 H, NH); 2) the nonprotonated portion: 2.69 (br.s, 12 H, 2 NMe_2); 6.93 (d, 2 H, *o*-H, J_o = 8.4 Hz); 7.72 (br.d, 2 H, *m*-H, J_o = 8.1 Hz).

Trifluoroacetylation of compound 1 in dichloroethane. *A.* A solution of TFAA (0.85 mL, 6 mmol) in $ClCH_2CH_2Cl$ (2 mL) was added dropwise to a solution of compound **1** (1.07 g, 5 mmol) in $ClCH_2CH_2Cl$ (10 mL). The mixture was stirred at ~20 °C for 15 min. Then the mixture was concentrated to dryness in air in a porcelain dish. The residue was triturated with water (20 mL), filtered off, and washed on a filter with water (~40 mL). The aqueous solution and the water-insoluble residue were worked up separately.

The aqueous solution was made basic with a 10% KOH solution (to pH 14). The yellow precipitate that formed was extracted with $CHCl_3$ (2×20 mL) and the chloroform extract was concentrated to ~15 mL and chromatographed on a column with Al_2O_3 (h = 20 cm, d = 2.5 cm); $CHCl_3$ was used as the eluent. Ketone **2** (R_f 0.95), double "sponge" **3** (R_f 0.82), and the initial compound **1** (R_f 0.47) were isolated in yields of 0.10 g (6%), 0.21 g (14%), and 0.42 g (41%), respectively.

The water-insoluble precipitate was stirred in acetone (30 mL) for ~1 h. Then the heavy white precipitate, insoluble in acetone, was filtered off, washed on a filter with acetone (2×5 mL), dried, and recrystallized from MeCN. The mixture was suspended in water (3 mL) and treated with concentrated aqueous ammonia (2 mL). The reaction mixture was extracted with $CHCl_3$ (3×20 mL), the solvent was evaporated, and *trans*-diol **4** was obtained in a yield of 0.16 g (7.5%) as slightly yellowish needle-like crystals, R_f 0.05 (Al_2O_3, $CHCl_3$), which can be recrystallized from DMSO or toluene. Upon heating, the crystals turned yellow (beginning from 75 °C). At 130 °C; the habitus of the crystals changed and orange inclusions appeared. Fusion afforded a transparent red melt in the temperature range of 156—162 °C. IR (Nujol mulls), ν/cm^{-1}: 3550—3350 (associated OH); 2780, 2715, 2653 (C—H); 1580, 1560 (ring). Found (%): C, 51.05; H, 4.70; N, 6.49. $C_{18}H_{18}F_6N_2O_3$. Calculated (%): C, 50.95; H, 4.28; N, 6.60. ^{1}H NMR (30 °C, DMSO-d_6), δ: 2.78 (s, 12 H, 2 NMe_2); 6.98 (d, 2 H, H(5), H(8), $J_{5,4}$ = $J_{8,9}$ = 8.3 Hz); 7.52 (dq, 2 H, H(4), H(9), $J_{4,6}$ = $J_{9,8}$ = 8.20 Hz, $^5J_{H-F}$ = 1.1 Hz); 8.06 (br.s, 2 H, OH).

The acetone extracts were concentrated and a yellow powder was obtained. The powder was washed with a 6 : 1 mixture of hexane and $CHCl_3$ (17 mL). After concentration of the organic extract, 1,8-bis(dimethylamino)-2,4-bis(trifluoroacetyl)naphthalene (**6**) was obtained in a yield of 0.028 g (1.4%) as yellow crystals, m.p. 180—182 °C (from octane). Found (%): C, 53.01; H, 4.22; N, 6.59. $C_{18}H_{16}F_6N_2O_2$. Calculated (%): C, 53.21; H, 3.94; N, 6.89. ^{1}H NMR (30 °C, $CDCl_3$), δ: 2.78 (s, 6 H, C(8)NMe_2); 3.30 (s, 6 H, C(1)NMe_2); 6.95 (d, 1 H, H(7), $J_{7,6}$ = 7.9 Hz); 7.52 (dd, 1 H, H(6), $J_{6,7}$ = 7.9 Hz, $J_{6,5}$ = 8.3 Hz); 8.43 (d, 1 H, H(5), $J_{5,6}$ = 8.3 Hz); 8.48 (br.s, 1 H, H(3)).

The pale-yellow precipitate, which was obtained after washing with a hexane—$CHCl_3$ mixture, was treated with a 10% KOH solution (2 mL) and extracted with $CHCl_3$ (3×10 mL). The solvent was evaporated to dryness and *cis*-diol **5** was obtained in a yield of 0.08 g (3.75%). Pale-yellow crystals with R_f 0.01 (Al_2O_3, $CHCl_3$) can be recrystallized from DMSO. When heated above 148 °C, the crystals gradually turned yellow and melted with decomposition in the temperature range of 150—153 °C. Found (%): C, 51.17; H, 4.55; N, 6.37. $C_{18}H_{18}F_6N_2O_3$. Calculated (%): C, 50.95; H, 4.28; N, 6.60. IR (Nujol mulls), ν/cm^{-1}: 3455, 3310 (OH); 2770 (C—H); 1575, 1550 (ring). ^{1}H NMR (30 °C, $CDCl_3$), δ: 2.84 (br.s, 12 H, 2 NMe_2); 3.75 (s, 2 H, OH); 6.93 (d, 2 H, H(5), H(8), $J_{5,4}$ = $J_{8,9}$ = 8.1 Hz); 7.67 (dq, 2 H, H(4), H(9), $J_{4,5}$ = $J_{9,8}$ = 8.1 Hz, $^5J_{H-F}$ = 1.2 Hz). ^{1}H NMR (30 °C, DMSO-d_6), δ: 2.78 (br.s, 12 H, 2 NMe_2); 7.01 (d, 2 H, H(5), H(8), $J_{5,4}$ = $J_{8,9}$ = 8.1 Hz); 7.56 (dq, 2 H, H(4), H(9), $J_{4,5}$ = $J_{9,8}$ = 8.1 Hz, J_{H-F} = 1.1 Hz); 8.26 (s, 2 H, OH).

B. When the reaction mixture was kept at ~20 °C for 48 h after the addition of the total amount of TFAA, double "proton sponge" **3**, diketone **6**, and the initial compound **1** were obtained in yields of 55%, 2%, and 40%, respectively. The total yield of *cis*- (**4**) and *trans*-diols (**5**) was lower than 1%. Ketone **2** was not detected in the reaction mixture.

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* The arbitrary numbering scheme shown in Scheme 1 was used for the description of the NMR spectra of compound **12**.

C. When the reaction mixture was kept for 7 days, the yields of the reaction products were as follows: 10% (**2**), 57% (**3**), and 19% (the initial "proton sponge" **1**).

Trifluoroacetylation of compound 1 in chloroform. A solution of TFAA (0.31 g, 1.5 mmol) in $CHCl_3$ (5 mL) was added dropwise to a vigorously stirred solution of compound **1** (0.21 g, 1.1 mmol) in freshly distilled $CHCl_3$ (15 mL) cooled to −15 °C. Then the mixture was stirred at −15 °C for 30 min, the reactor flask was sealed with a stopper, and the reaction mixture was kept at ~20 °C for 48 h. The solvent was evaporated to dryness and the residue was suspended in water (10 mL) and made basic with a 10% aqueous solution of KOH (to pH ~13). The suspension that formed was extracted with $CHCl_3$ (3×15 mL). The compounds, which were present in the chloroform extract, were separated by preparative TLC (Al_2O_3, $CHCl_3$). Monoketone **2** (R_f 0.95), double "proton sponge" **3** (R_f 0.82), diketone **6** (R_f 0.80), and the initial compound **1** (R_f 0.47) were isolated in yields of 0.06 g (19.4%), 0.033 g (10.8%), 0.009 g (2.1%), and 0.083 g (39.4%), respectively.

Trifluoroacetylation of compound 2. A solution of TFAA (0.14 mL, 10 mmol) in CH_2Cl_2 (5 mL) was added dropwise with stirring to a solution of ketone **2** (0.3 g, 10 mmol) in dry CH_2Cl_2 (10 mL) cooled to −15 °C. Then the mixture was stirred at ~20 °C for 15 min, poured into a porcelain dish, and concentrated to dryness. The dry residue was washed with water (4×10 mL) and the aqueous extracts were combined, treated with a 10% KOH solution to pH ~13, and extracted with $CHCl_3$ (3×10 mL). The chloroform extracts were combined and concentrated in air and the residue was separated by preparative TLC (Al_2O_3, $CHCl_3$). The initial ketone **2** (R_f 0.95), double "proton sponge" **3** (R_f 0.82), diketone **6** (R_f 0.80), and diol **5** (R_f 0.01) were isolated in yields of 0.172 g (55.5%), 0.029 g (9.7%), 0.092 g (22.4%), and 0.002 g (0.5%), respectively.

The water-insoluble rose-tinted crystalline compound that formed was stirred with acetone (30 mL) during 30 min and white crystals of the trifluoroacetate of diol **4**, which were not dissolved in acetone, were filtered off. The yield was 0.003 g (0.7%).

1,8-Bis(dimethylamino)-4,5-bis(trifluoroacetyl)naphthalene (7). Compound **5** (0.2 g, 0.47 mmol) was heated on an oil bath to 150 °C during 10–15 min, the pressure in the reaction tube being gradually reduced to 2 Torr. The orange melt was kept at 150 °C and 2 Torr for 15 min. After cooling, diketone **7** was obtained as a solid orange-red amorphous product in a yield of 0.19 g (~100%). ^{1}H NMR (30 °C, $CDCl_3$), δ: 2.96 (s, 12 H, 2 NMe_2); 6.75 (dt, 2 H, H(2), H(7), $J_{2,3} = J_{7,6} = 8.7$ Hz); 7.86 (dq, 2 H, H(3), H(6), $J_{3,2} = J_{6,7} = 8.7$ Hz, $^5J_{\mathrm{H-F}} = 1.9$ Hz).

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