

In contrast, NSF_3 reacts with HF/AsF_5 to afford the stable and isolable pentafluorosulfanylammonium salt **6**^[12, 14]. The dimethylamino group in **5** reduces the electrophilicity of the central sulfur atom to such an extent that F^\ominus can no longer add to increase the coordination number; in this way, all subsequent steps to a product analogous to **6** are blocked.

The salts **3** are stable, colorless solids (m.p. = 101°C (**3a**), 103°C (**3b**)) that are readily attacked by nucleophiles, e.g. H_2O or X^\ominus of NaCl - and KBr -IR plates. They were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1). Bands at 945 and 910 cm^{-1} in the IR spectrum are assigned to the $\nu_{\text{as}}(\text{SF})$ and $\nu_{\text{sym}}(\text{SF})$ vibrations.

Table 1. NMR data of salts **3** and **5** [a] as well as the neutral S^{IV} derivative $(\text{Me}_2\text{N})_2\text{SF}_2$ [13].

	^{19}F [a] $\delta(\text{SF}_2)$	^1H $\delta(\text{CH}_3)$	^{13}C [b] $\delta(\text{CH}_3)$	$^4J_{\text{HF}}$ [Hz]	$^3J_{\text{FC}}$ [Hz]
3a	38.6 [c]	4.20 (t)	48.19 (t)	4.75	2.1
3b	37.9 [c]	4.22 (t)	48.21 (t)	4.80	2.1
5	54.7 (sept.)	3.16 (t) (N-H 7.37)	—	2.89	—
$(\text{Me}_2\text{N})_2\text{SF}_2$	7.5 (br. s)	2.72 (br. s)	37.71 (s)	—	—

[a] ^{19}F -NMR (**3a**, **3b**: 60 MHz, SO_2 , 301 K; **5**: 75.4 MHz, SO_2 , 253 K), ^{13}C -NMR (20.15 MHz, SO_2 , 309 K), ^1H -NMR (80.13 MHz, SO_2 , 304 K). [b] Proton decoupled. [c] Of the 13 lines expected only 11 were observed.

The NMR data for the cations of salts **3** and **5** as well as the neutral S^{IV} derivative $(\text{Me}_2\text{N})_2\text{SF}_2$ ^[13] are shown in Table 1; nevertheless, a direct comparison of the cations with the neutral compound is not without problems since in this the sulfur atom has trigonal-bipyramidal coordination, but in the cation the sulfur atom is tetrahedral. The nature of the anion in **3** does not influence the spectroscopic data of the dication; no interaction therefore appears to be present in solution.

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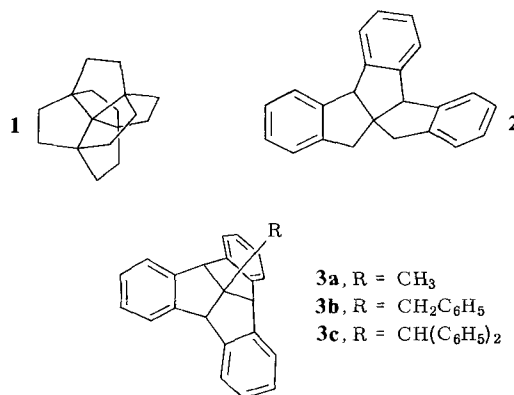
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[10] **4a**: ^{19}F -NMR (60 MHz, SO_2 , stand. CFCl_3): $\delta = 54.75$ (br. s, SF), -33.75 (br. s, AsF); ^1H -NMR (60 MHz, SO_2 , stand. TMS): $\delta = 3.47$ (t, $J(\text{HF}) = 2.7$ Hz, CH_3); **4b**: ^{19}F -NMR (60 MHz, SO_2 , stand. CFCl_3): $\delta = 56.97$ (sept., SF); ^1H -NMR (60 MHz, SO_2 , stand. TMS): $\delta = 3.48$ (t, $J(\text{HF}) = 2.65$ Hz, CH_3) (A. Waterfeld, Diplomarbeit, Universität Göttingen 1977).

- [11] **2a**: ^{19}F -NMR (60 MHz, SO_2 , CFCl_3): $\delta = 54.5$ (SF); ^1H -NMR (60 MHz, SO_2 , TMS): $\delta = 3.60$ ($J(\text{F}-\text{CH}_3) = 7.7$ Hz, CH_3), 3.48 ($J(\text{F}-\text{CH}_3)_2 = 2.5$ Hz, $(\text{CH}_3)_2$) [6c]; **2b**: ^{19}F -NMR (60 MHz, SO_2 , CFCl_3): $\delta = 54.4$ (SF); ^1H -NMR (60 MHz, SO_2 , TMS): $\delta = 3.53$ ($J(\text{F}-\text{CH}_3) = 7.8$ Hz, CH_3), 3.44 ($J(\text{F}-\text{CH}_3)_2 = 2.6$ Hz, $(\text{CH}_3)_2$).
[12] NMR data for **6**: ^{19}F -NMR (235.35 MHz, SO_2 , stand. CFCl_3): $\delta = 76.37$ ($^2J(\text{F}-\text{F}) = 156.5$ Hz, SF_4), 52.43 (SF); ^1H -NMR (60 MHz, SO_2 , stand. TMS): $\delta = 8.8$ (NH). The 1:1 compound $\text{SF}_5\text{NH}_2 \cdot \text{HCl}$ can be obtained at -78°C , but at room temperature decomposes into its components: J. S. Thrasher, K. Seppelt, *Z. Anorg. Allg. Chem.* 507 (1983) 7. Analogous structural and bonding behavior are expected for **6** as for the recently described isoelectronic $\text{F}_5\text{P}-\text{NH}_3$ (W. Storz, D. Schomburg, G.-V. Rösenthaler, R. Schmutzler, *Chem. Ber.* 116 (1983) 367). The $^2J(\text{N}-\text{F}_4)$ coupling observed in $\text{F}_5\text{P}-\text{NH}_3$ is not found in **6**.
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[14] General Procedure: **3**: SO_2 (5–10 mL) is condensed onto 2–3 mmol MF_5 (**a**: $\text{M} = \text{As}$; **b**: $\text{M} = \text{Sb}$) and CH_3F (slight excess); the mixture is warmed slowly to -30°C and held at this temperature for 2–3 h until formation of $(\text{MeOSO})^+\text{MF}_6^-$ is complete. The solution is then cooled again to -196°C and **1** condensed in; the mixture is warmed slowly to room temperature and stirred for 2 d. After removal of the solvent **3a** and **3b** are isolated in quantitative yield as analytically pure solids.—**5** and **6**: 5 mL HF and MeF_5 are condensed into a cold trap (Kel-F) containing 1–2 mmol **1** or NSF_3 (molar ratio $\text{NSF}_3 : \text{AsF}_5 < 1:2$) at -196°C . After removal of the volatile products, **5** and **6** remain as almost analytically pure substances. Purer products can be obtained by dissolving the Lewis acid adducts $\text{F}_3\text{M} \cdot \text{N} = \text{SF}_2(\text{NMe}_2)_2$ or $\text{MF}_5 \cdot \text{NSF}_3$ in HF.

A Facile Route to Benzoannulated Centrotriquinanes

By Dietmar Kuck*

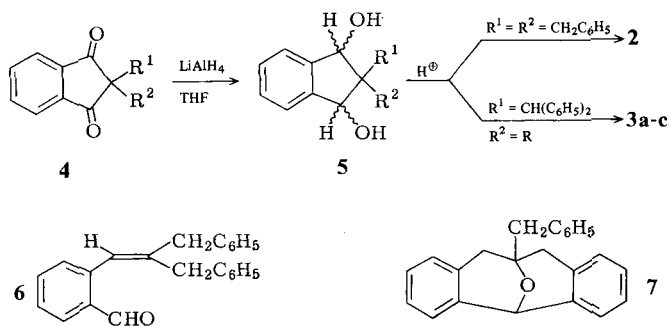
Centropolyquinanes^[1] are a fascinating group of compounds, which, as polycondensed cyclopentane hydrocarbons, have been intensively studied in recent years^[2–4]. They are characterized by a central C atom shared by all cyclopentane rings. The centrohexasquinane (“ C_{17} -hexaquinane”) **1** represents a challenging synthetic target molecule^[5].



We report here a facile synthesis of benzoannulated centrotriquinanes of type **2** and **3**^[6], which can be used as educts for the synthesis of higher centropolyquinanes. Key reaction in the synthesis is the double cyclodehydration of the 2,2-disubstituted 1,3-indanediols **5**, which can readily be prepared by reduction of the corresponding 1,3-indanediones **4**.

Whereas the tribenzotricyclo[6.3.0.0^{1,5}]undecane **2** is obtained in excellent yield^[14], the 10-alkyltriben-

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zo[5.2.1.0^{4,10}]decanes **3** have, up till now, only been accessible in moderate yields (Table 1). We attribute this to the prochirality of the benzhydryl group and, in particular, to the susceptibility of the 1,3-diol system to cleavage under acidic conditions. Moreover, the ring opening is certainly favored by the steric hindrance of the quaternary center. Of greater note therefore is the double cyclization, specifically of **5** ($R^1 = R^2 = \text{CH}(\text{C}_6\text{H}_5)_2$) to **3c**, whose structure, like those of other centrotriquinanes, is consistent with the spectroscopic data (Table 1)^[7].

Table 1. Centrotriquinanes **2** and **3a–3c**. Yields, melting points, and some ¹H- and ¹³C-NMR data (in parentheses) [a].

	Yield [%]	M.p. [°C]	NMR Data			
			C(quart)	C(tert)	C(sec)	C _a (R)
2	92	148	(62.8)	4.44 (62.1)	3.15 [b] (44.5) 3.34 [b]	—
3a	33	239	(60.7)	4.47 (63.7)	—	1.68 (27.6)
3b	18	243	(65.2)	4.80 (61.3)	—	3.33 (45.7)
3c	26	318	(68.7)	5.10 (60.8)	—	4.60 (59.7)

[a] 80 (300) MHz, δ in CDCl_3 . The number of signals from the aromatic groups as well as the integrated intensities and multiplicities reflect the symmetry of the compounds. [b] $^2J = -16.4$ Hz.

Under relatively mild conditions (e.g. $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}/\text{C}_6\text{H}_6$) predominantly products of ring-opening form, e.g. compounds **6** and **7**^[8]. However, under conditions of acid catalysis, **6** is converted into a mixture of **7** and **2**. It can therefore be assumed that the tricycles **2** and **3** are, at least in part, formed via *acyclic* intermediates of type **6**. In the UV spectra^[9] of the tribenzocentrotriquinanes **3**, which have C_{3v} symmetry, the α -bands display a slight bathochromic shift relative to indane^[10] ($\Delta\lambda_{\text{max}} = 2.0\text{--}3.5$ nm) and have a threefold greater molar extinction in each case. In contrast, this effect is absent in **2** ($\Delta\lambda_{\text{max}} < 0.5$ nm). Extensive interactions between the benzene chromophores are therefore—as in other centrotriquinanes of this type^[6]—not present.

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[7] The elemental analyses and mass spectra of all compounds corroborate the compositions given.

- [8] **6**: M.p. = 64–65°C (petroleum ether); ¹H-NMR (80 MHz, CDCl_3/TMS): $\delta = 3.35$ (s, 2H), 3.44 (d, 1.2 Hz, 2H), 6.81 (br. s, 1H), 6.95–7.70 (m, 13H), 7.90 (m, 1H), 10.30 (s, 1H); IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2830 (w), 2730 (w), 1685 (s); MS (70 eV): m/z 312 (M^\ominus , 0.2%), 221 ($M^\ominus - \text{C}_7\text{H}_7$, 100), 115 ($\text{C}_6\text{H}_6^\ominus$, 28), 91 ($\text{C}_7\text{H}_7^\ominus$, 81). — **7**: M.p. = 112–113°C ($\text{C}_2\text{H}_5\text{OH}$); ¹H-NMR (80 MHz, CDCl_3/TMS): $\delta = 2.62$, 3.17 (AB, –16.6 Hz, 4H), 3.10 (s, 2H), 5.79 (s, 1H), 6.9–7.5 (m, 13H); IR (KBr): $\tilde{\nu} = 2840$ (w), 1190 (s), 1080 (s), 1070 (s), 1030 (s); MS (70 eV): m/z 312 (M^\ominus , 59), 221 ($M^\ominus - \text{C}_7\text{H}_7$, 67), 220 ($M^\ominus - \text{C}_7\text{H}_8$, 54), 193 (82), 179 (100), 178 (80), 91 ($\text{C}_7\text{H}_7^\ominus$, 96).
[9] UV spectra (*n*-hexane, $c = 4 \times 10^{-4}$ to 4×10^{-5} mol L⁻¹): **2**: λ [nm] = 274.0 ($\epsilon = 4540$), 267.5 (3840), 261.0 (2310); **3a**: 276.0 (4570), 269.0 (3780), 263.5 (2350); **3b**: 276.3 (4620), 269.2 (4120), 263.0 (2850); **3c**: 276.8 (4410), 269.7 (4080), 263.5 (3010).
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[13] M.p. = 104–105°C (congealed oil); ¹H-NMR (80 MHz, CDCl_3/TMS): $\delta = 1.30$ (d, 5.1 Hz, 2OH), 2.87, 2.99 (AB, –14.1 Hz, 4H), 5.18 (d, 5.1 Hz, 2H), 7.26 (m, 13H); IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3590 (m), 3430 (s).
[14] Procedure: **2**: 2,2-Dibenzyl-1,3-indanedione **4** [11] is obtained in quantitative yield from 1,3-indanedione and benzyl bromide with KF/celite 545 (Fluka) in CH_3CN , by analogy to a procedure described by Bloch and Orvane [12], and reduced with LiAlH_4 in tetrahydrofuran (THF) using standard methods to afford the *trans*-1,3-diol **5** ($R^1 = R^2 = \text{CH}_2\text{C}_6\text{H}_5$) [13] (crude yield quantitative).—A solution of this diol (3.3 g, 10 mmol) in 120 mL xylene is refluxed with 85% H_3PO_4 (1.6 g) for ca. 15 h in a water separator. The reaction solution is then washed with dilute Na_2CO_3 solution and water and dried over Na_2SO_4 . After removal of the solvent an oil is formed from which **2** is obtained as fine, white needles by recrystallization from EtOH.

1,2,3-Benzoxadiazole— Detection in an Argon Matrix and in Solution**

By Reinhard Schulz and Armin Schweig*

The notion that compounds such as **1** with 1,2,3-oxadiazole structures are not capable of existing^[1,2] was refuted for the first time by PE spectroscopic studies on 6-diazo-2,4-cyclohexadienone **2**^[3]. We report here independent experiments in a noble gas matrix and in solution which corroborate the presence of an equilibrium between 1,2,3-benzoxadiazole **1** and 6-diazo-2,4-cyclohexadienone **2**, and remove any doubts^[4] surrounding our previous work^[3].



If—as indicated by the results of PE spectroscopy—the diazoquinone **2** and the oxadiazole **1** both exist in the gas phase, it should be possible to freeze out both components at low temperature. The condensate formed from condensation of diazocyclohexadienone vapor **2** (vaporized at room temperature and ca. 4×10^{-2} mbar) and excess argon in a vacuum flow system at 15 K exhibits intense IR absorptions originating from a compound, which, even during recording of the spectrum, is re-converted into **2**. This retro-isomerization cannot only be followed by IR spectroscopy, but also by the naked eye due to a marked deepening of the color of the originally light yellow matrix (λ_{max} of **2** in hexane: 407 nm). The IR-induced isomerization to **2** at 15.4 K exactly follows first-order kinetics ($\tau_{1/2} = 6.2$ min). By inserting a filter which transmits only

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