In contrast, NSF₃ reacts with HF/AsF₅ to afford the stable and isolable pentafluorosulfanylammomium salt 6[^12][^14]. The dimethylamino grouping in 5 reduces the electrophilicity of the central sulfur atom to such an extent that F²⁺ 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. H₂O or X⁻ 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 ν₁(SF) and νₚ(SF) vibrations.

### Table 1. NMR data of salts 3 and 5 [a] as well as the neutral SF⁺ derivative (Me₂N)₂SF₂[^13]

<table>
<thead>
<tr>
<th>SF⁺</th>
<th>H</th>
<th>C</th>
<th>J_HF [Hz]</th>
<th>J_FB [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>38.6 [c] 42.10 (t) 48.19 (t)</td>
<td>6.75</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>37.9 [c] 42.22 (t) 48.21 (t)</td>
<td>4.89</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>54.7 (sept.) 3.16 (t)</td>
<td>2.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] SO₂, TMS): δ = 3.48 (J(F-CH₃)=7.7 Hz, CH₃), 3.44 (J(F-(CH₃)_2)=2.5 Hz, (CH₃)₂) [6c]; 2b: SF⁺-NMR (60 MHz, SO₂, CFCI₃): δ = 54.4 (SF); SO₂, TMS): δ = 5.35 (J(F-F)=7.8 Hz, CH₃), 3.44 (J(F-(CH₃))=2.5 Hz, (CH₃)₂).

NMR data for 6: SF⁺-NMR (253.35 MHz, SO₂, stand. CFCI₃): δ = 76.37 (J(F-F)=156.5 Hz, SF₂), 52.43 (SF); SO₂, TMS): δ = 8.8 (NH) The 1:1 compound SF₂-HCl can be obtained at -78°C, but at room temperature decomposes into its components: J. S. Thrasher, K. Seppelt, Z. Anorg. Allg. Chem. 307 (1973) 7. Analogous structural and bonding behavior are expected for 6 as for the recently described iso-electronic F₂P-NH₃ (W. Storzer, D. Schomburg, G.-V. Röschenthaler, R. Schmutzler, Chem. Ber. 116 (1983) 867). The 2N(F₂) coupling observed in Fe₂P-NH₃ is not found in 6.

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### A Facile Route to Benzoannelated Centrotriquinanes

**By Dietmar Kuck**[^3]

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 centrohexaquinane ("C₆-hexaquinnane") 1 represents a challenging synthetic target molecule[^5].

![C₆-hexaquinnane](image)

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

Whereas the tribenzocyclooctatriene(6,3,0)°[5] undecane 2 is obtained in excellent yield[^14], the 10-alkyltriben-
oxidation of 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' = CH(CH3)2) to 3c, whose structure, like those of other centrotriquinanes, is consistent with the spectroscopic data (Table 1)\[7].

<table>
<thead>
<tr>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
<th>(\delta_{(\text{proton})})</th>
<th>(\delta_{(\text{carbon})})</th>
<th>NMR Data</th>
<th>C(_\alpha)(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>92</td>
<td>148 (62.8)</td>
<td>4.44 (62.1)</td>
<td>3.15 [b]</td>
<td>(44.5)</td>
</tr>
<tr>
<td>3a</td>
<td>33</td>
<td>239 (60.7)</td>
<td>4.47 (63.7)</td>
<td>—</td>
<td>(33.6)</td>
</tr>
<tr>
<td>3b</td>
<td>18</td>
<td>243 (65.2)</td>
<td>4.80 (61.3)</td>
<td>—</td>
<td>(65.7)</td>
</tr>
<tr>
<td>3c</td>
<td>26</td>
<td>318 (68.7)</td>
<td>5.10 (60.8)</td>
<td>—</td>
<td>(59.7)</td>
</tr>
</tbody>
</table>

[a] \(\delta_{(\text{proton})}\) = 80 (300) MHz, \(\delta_{(\text{carbon})}\) in CDC\(_3\). The number of signals from the aromatic groups as well as the integrated intensities and multiplicities reflect the symmetry of the compounds. [b] \(\delta_{(\text{proton})}\) = 6.14 Hz.

Under relatively mild conditions (e.g. p-CH\(_3\)C\(_6\)H\(_4\)SO\(_3\)H/C\(_6\)H\(_4\)SO\(_3\)H) 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 spectral\[9] of the tribenzocentrotriquinanes 3, which have \(C_3\)\(_v\) symmetry, the \(\alpha\)-bands display a slight bathochromic shift relative to indane\[10] \(\lambda_{\text{max}} = 2.0-3.5\) nm and have a threefold greater molar extinction in each case. In contrast, this effect is absent in 2 \(\lambda_{\text{max}} < 0.5\) nm. Extensive interactions between the benzene chromophores are therefore—as in other centrotriquinanes of this type\[11]—not present.

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

By Reinhard Schulz and Armin Schweig

The notion that compounds such as 1,2,3-oxadiazole structures are not capable of existing\[12,13] was refuted for the first time by PE spectroscopic studies on 6-diazocyclohexadienone 2\[14]. 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-diazocyclohexadienone 2, and remove any doubts\[15] surrounding our previous work\[16].

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 \(\times 10^{-2}\) 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 \(\lambda_{\text{max}} = 407\) nm. The IR-induced isomerization to 2 at 15.4 K exactly follows first-order kinetics \(r_1 = 6.2\) min. By inserting a filter which transmits only

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

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