Dendritic Triphenylmethylium and Tetraphenylmethane Compounds

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**Abstract:** Stilbenoid dendrimers possessing a methanol or methane core are prepared using Wittig–Horner reactions. The dendritic tris(stilbenyl)carbinols 3a–c are converted into the corresponding methylium salts 3¢a–c on treatment with trifluoroacetic or tetrafluoroboric acid. The extended cross-conjugation in the dendritic methylium ion 3¢c results in a long-wavelength absorption (λ\text{max} = 697 nm) whereas the conjugated model systems 3¢a and 3¢b are red-shifted (λ\text{max} = 772 nm and 748 nm, respectively). Charge delocalization in the cations is evident from the low-field shifts of the 13C NMR signals. In contrast to the dark-blue dyes 3¢a–c, the tris(stilbenyl)carbinols and tetrakis(stilbenyl)methane derivatives 3a–c and 7 exhibit long-wavelength absorption bands in the UV region.

**Key words:** stilbene, charge delocalization, Wittig–Horner reaction, olefination, dendrimers, dyes

From photophysical and photochemical viewpoints, stilbene-containing molecules are a well-studied class of compounds. Therefore, dendrimers possessing stilbenoid building blocks represent an attractive area of research. A number of dendritic structures, in which the dendrons (but not the core) consist of stilbene building blocks, have been described.

We report here on novel stilbenoid dendrimers containing triphenylmethylium or tetraphenylmethane cores. The dendrons of these compounds represent extended π-systems in which full conjugation is blocked by a saturated center (sp3–C) or is ‘opened’ by a carbenium center (sp2–C+). Peripheral alkoxy groups serve as solubilizing groups, and moreover, as electron-donor groups which impart the methylium systems with acceptor–donor character (AD3).

Preparation of the target dendrimers 3a–c and 7 was started from the triphosphonate 1 or the tetraphosphonate 6 (Scheme 1). Wittig–Horner reactions of 1 and aldehyde 2c, and 6 with aldehyde 2d, yielded the desired products 3c (52%) and 7 (68%), respectively. The star-shaped model compounds 3a (70%) and 3b (75%) were prepared via analogous reactions of triphosphonate 1 with aldehydes 2a and 2b, respectively. The substrate aldehydes 2a,2,8 2b,10 2c,11 and 2d contain long, flexible alkoxy chains. Aldehyde 2d was obtained in 82% yield analogously to 2c by reaction of diphosphonate 4, which contains a formyl group protected as a dimethylacetal, with 4-(hexyl-oxo)benzaldehyde (5).

**Scheme 1** Preparation of the dendrimers 3c and 7 and the model compounds 3a and 3b

The Wittig–Horner olefinations gave the expected products in cis/trans ratios of about 5:95. After purification by crystallization, the amount of cis isomers still present was
less than 2%. The detection limit for cis-configured double bonds in our study was 2%, and hence we were unable to detect any cis-configured dendrimers in our products. This was found to be the case for the solid products 3a, 3c, and 7, as well as for the oily product 3b which was purified by column chromatography on silica gel.

Treatment of the carbinols 3a–c with trifluoroacetic acid led to elimination of water and formation of the corresponding triphenylmethylium trifluoroacetates 3¢a–c. In order to shift the equilibrium to favour the salts 3¢a–c, we used a large excess of trifluoroacetic acid (molar ratio of 3/acid = 1:200) (Scheme 2).

Table 1 summarizes the key 13C NMR data for the transformations of 3a–c into salts 3¢a–c. For comparison, we have included the corresponding 13C NMR data for triphenylcarbinol (Ph3COH) and its cation (Ph3C+). The 13C chemical shifts are highly sensitive towards changes in the partial charges. The formation of the triphenylmethylium ions is apparent from the strong low-field shift of the signal due to the central carbon atom (C¼). The Δδ value of Ph3COH/Ph3C+ is 131.7 ppm. The corresponding Δδ values of 3a–c/3¢a–c decrease in the order 3c > 3b > 3a (120.8, 111.1 and 109.2 ppm, respectively). This trend results from the increasing delocalization of the positive charge. The meta-branched in dendrimer 3¢c is less suited to charge delocalization than the linear conjugation present in 3¢a,b. Therefore, dendrimers 3¢c exhibit the highest Δδ value. Charge delocalization occurs over the whole ion, but the major effect is apparent at the ortho-positions (α and β) of the benzene rings adjacent to the central carbon atom (Scheme 2 and Table 1).

Table 1  Selected 13C NMR Data of Carbinols 3a–c in CDCl3 and Their Corresponding Triphenylmethylium Ions 3¢a–c in CDCl3–CF3COOD (7:3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Central C</th>
<th>α-C</th>
<th>β-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>δ</td>
<td>81.8</td>
<td>128.3</td>
</tr>
<tr>
<td>3¢a</td>
<td>δ</td>
<td>191.0</td>
<td>140.3</td>
</tr>
<tr>
<td>3b</td>
<td>δ</td>
<td>81.8</td>
<td>128.3</td>
</tr>
<tr>
<td>3¢b</td>
<td>δ</td>
<td>192.9</td>
<td>140.6</td>
</tr>
<tr>
<td>3c</td>
<td>δ</td>
<td>82.3</td>
<td>128.3</td>
</tr>
<tr>
<td>3¢c</td>
<td>δ</td>
<td>203.1</td>
<td>140.8</td>
</tr>
<tr>
<td>Ph3COH</td>
<td>δ</td>
<td>81.9</td>
<td>127.8</td>
</tr>
<tr>
<td>Ph3C+</td>
<td>δ</td>
<td>213.6</td>
<td>143.6</td>
</tr>
<tr>
<td>Δδ</td>
<td></td>
<td>131.7</td>
<td>15.8</td>
</tr>
</tbody>
</table>

a The positions of C¼, α-C and β-C are shown in Scheme 2.
b The corresponding 13C chemical shifts of Ph3COH and cation Ph3C+ are included for comparison.

and para-positions (α and β) of the benzene rings adjacent to the central carbon atom (Scheme 2 and Table 1).
Apart from small effects due to the medium, the \(^1\)H and \(^{13}\)C NMR data of dendrimer 3 are the same in CDCl\(_3\) and CDCl\(_3\)-CF\(_3\)COOD (7:3).

The tris(styryl)carbinols 3a–c and tetrakis(styryl) methane 7 show long-wavelength electron transitions in the UV region at about 330 nm in CHCl\(_3\). Dendrimer 6 (3a–c) has, for example, a \(\lambda_{\text{max}}\) value of 327 nm (\(\epsilon = 112350 L \text{mol}^{-1} \text{cm}^{-1}\)) and dendrimer 7 has a \(\lambda_{\text{max}}\) value of 327 nm (\(\epsilon = 151950 L \text{mol}^{-1} \text{cm}^{-1}\)).

The saturated sp\(^3\) center in 3a–c and 7 prevents the systems being fully conjugated whilst homoconjugation has a comparably small effect. The obtained \(\epsilon\) values indicate the presence of three and four more or less independent chromophores in 3a–c and 7, respectively.

Formation of the methylium dye 3c \(\rightarrow 3\'c\) shifts the UV band into the visible region (\(\lambda_{\text{max}} = 697 nm\)) because the central sp\(^2\) carbon atom allows cross-conjugation of the dendrons. Interestingly, the bathochromic shift resulting from formation of methylionium 3a is larger (\(\lambda_{\text{max}} = 772 nm\)). Apart from the ‘opened’ conjugation through the center, each ‘arm’ of 3a has push–pull character. In principle, dendrimer 3c represents an AD\(^3\) system,\(^4\) but due to the meta-branching, the intramolecular charge transfer (ICT) is much smaller in 3c since it is reduced to a mere inductive or field effect.

The dark blue dyes 3a–c could be isolated in pure solid state as tetrafluoroborates, but they are very hygroscopic, becoming sticky as they begin to hydrolyze and fade in color. Although the reaction center is sterically shielded in 3c, it did not exhibit higher stability towards hydration in comparison to 3a,b.

Melting points were measured with a Büchi melting point apparatus and are uncorrected. UV/Vis spectra were obtained with a Zeiss MCS 320/340 diode array spectrometer. \(^1\)H and \(^{13}\)C NMR spectra were recorded with a Bruker AMX 400 spectrometer at 400 MHz and 100 MHz, respectively. CDCl\(_3\) served as solvent and TMS as internal standard, unless otherwise noted. Field desorption (FD) mass spectra were obtained with a Finnigan MAT 95 spectrometer.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.87 (t, J = 6.8 Hz, 9 H, \text{CH}_3), 1.21–1.37 (m, 48 H, \text{CH}_2), 1.75–1.83 (m, 12 H, \text{CH}_2), 3.95 (t, J = 6.6 Hz, 6 H, OCH\(_2\)), 6.86 and 7.59 (AA'BB', 12 H, ArH, outer benzene rings), 6.94 and 7.04 (AB, J = 16 Hz, 6 H, alkene H), 7.26 and 7.41 (AA'BB', 12 H, ArH, inner benzene rings).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9 (CH), 68.2 (OCH\(_3\)), 81.8 (central C), 114.9, 125.8, 127.7, 128.3 (ArCH), 126.0, 128.7 (alkene CH), 131.8, 136.9, 145.7, 159.1 (ArC).

MS (FD): \(m/z\) (%) = 1119 (100) [M+].


\(\text{Tris}(4\text{-}(E)-2\text{-}[4\text{-}(dodecyloxy)phenyl]ethyl)phenyl)methanol (3a)\)

Reaction of triphosphonate 1\(^1\)(1.0 g, 1.44 mmol) and aldehyde 2a\(^7\) (1.57 g, 5.41 mmol) gave 3a; yield: 1.13 g (70%); mp 96 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.84–0.95 (m, 27 H, \text{CH}_3), 1.22–1.38 (m, 144 H, \text{CH}_2), 1.69–1.75 (m, 6 H, \text{CH}_3), 1.75–1.83 (m, 12 H, \text{CH}_2), 3.95 (t, J = 6.5 Hz, 6 H, OCH\(_2\)), 6.69 (s, 6 H, ArH, outer benzene rings), 6.94 and 7.00 (AB, J = 16 Hz, 6 H, alkene H), 7.26 and 7.41 (AA'BB', 12 H, ArH, inner benzene rings).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.0 (\text{CH}), 22.6, 26.0, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9 (\text{CH}), 68.2 (OCH\(_3\)), 81.8 (central C), 114.9, 125.8, 127.7, 128.3 (ArCH), 126.0, 128.7 (alkene CH), 131.8, 136.9, 145.7, 159.1 (ArC).

MS (FD): \(m/z\) (%) = 1119 (100) [M+].


\(\text{Tris}(4\text{-}(E)-2\text{-}[3,4,5\text{-}(dodecyloxy)phenyl]ethyl)phenyl)methanol (3b)\)

Reaction of triphosphonate 1\(^1\)(1.0 g, 1.44 mmol) and aldehyde 2b\(^7\) (4.71 g, 7.15 mmol) gave 3b as a yellowish oil; yield: 2.40 g (75%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.84–0.95 (m, 27 H, \text{CH}_3), 1.22–1.38 (m, 144 H, \text{CH}_2), 1.38–1.51 (m, 19 H, \text{CH}_3), 1.69–1.75 (m, 6 H, \text{CH}_3), 1.75–1.83 (m, 12 H, \text{CH}_2), 3.95 (t, J = 6.5 Hz, 6 H, OCH\(_2\)), 6.69 (s, 6 H, ArH, outer benzene rings), 6.94 and 7.00 (AB, J = 16 Hz, 6 H, alkene H), 7.28 and 7.43 (AA'BB', 12 H, ArH, inner benzene rings).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.0 (\text{CH}), 22.7, 26.1, 29.3, 29.4, 29.5, 29.7, 30.4, 31.9 (\text{CH}), 68.2 (OCH\(_3\)), 69.3 (OCH\(_2\)), 73.6 (OCH\(_2\)), 81.8 (central C), 105.6, 126.0, 128.3 (ArCH), 127.1, 129.4 (alkene CH), 132.5, 136.6, 138.8, 145.9, 153.4 (ArC).

MS (FD): \(m/z\) (%) = 2226 (29) [M+], 733 (100).

Anal. Calcld for C\(_{149}\)H\(_{256}\)O\(_{16}\): C, 81.49; H, 11.32. Found: C, 81.38; H, 11.29.
Tris(2,3,5-tris(bis(4-[(E)-2-[(3,4,5-tri(hexyloxy)phenyl]ethynyl]phenyl)methylium trifluoroacetate (3b)

H NMR [400 MHz, CDCl3–CF3COOD (7:3)]: δ = 0.87–0.90 (m, 27 H, CH3), 1.25–1.55 (m, 162 H, CH2), 1.84–1.90 (m, 18 H, CH2), 4.16 (t, J = 6.5 Hz, 6 H, OCH2, m-OC2H5), 4.25 (t, J = 7.0 Hz, 12 H, OCH2, p-OC2H5), 6.97 (s, 6 H, ArH, outer benzene rings), 7.27 and 7.62 (AB, J = 16.2 Hz, 6 H, alkene H, inner benzene rings).

UV/Vis: λmax = 748 nm (measurement of a 13.8 × 10−5 M solution of 3b and a 0.53 M solution of CF3COOH in CHCl3).12

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References