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Photochemical generation of benzene–naphthalene biplanemers

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Abstract—A direct biplanemer synthesis could be achieved by a quantitative $[4\pi+4\pi]$ photocycloaddition of benzyloxy substituted benzene and naphthalene rings (**3d**, $e \neq 4d$, e). Since the products do not show a thermal Cope rearrangement—in contrast to the related longicyclic conjugated 9,10-benzotricyclo[4.2.2.2^{2.5}]dodeca-3,7,9-trienes—but a quantitative reverse reaction, they are interesting systems for an optical switching.

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Biplanemers of aromatic hydrocarbons like the title compounds represent π systems with an interesting topology. The spatial and the through-bond interaction of the π centers conveys these compounds special physical and chemical properties.^{1–9} According to the Goldstein–Hoffmann classification,¹⁰ benzene–naphthalene biplanemers are longicyclic conjugated systems consisting of three olefinic double bonds and a benzene ring. The crucial reaction step for the preparation of these compounds is the [4 π +4 π]photocycloaddition of naphthalene and 1,3-cyclohexadienes.^{1–9} The then still lacking π bond has to be introduced by a subsequent reaction step. A further disadvantage of this strategy is due to the fact that different orientations of the two 4 π components can lead to stereoisomers.⁹

We found now the first direct $[4\pi+4\pi]$ photocycloaddition of benzene and naphthalene rings. Stimulated by the addition of electron-rich benzene rings and anthracene,¹¹ we prepared compounds $3a-e^{12}$ by phase transfer mediated Williamson syntheses of 1 and 2 and irradiated 3a-e in benzene with a mercury middle pressure lamp equipped with a Duran glass filter. A slow stream of Ar purged through the diluted (ca. 10^{-3} M) solution, which were kept at 10 ± 5 °C. Whereas **3b** and **3c** proved to be photostable under these conditions, **3a** showed a slow but not really productive photoreaction; however, a quantitative $[4\pi+4\pi]$ photocycloaddition was observed

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for 3d and 3e to yield the biplanemers $4d^{13}$ and 4e (Scheme 1).¹⁴

The UV spectra of 4d revealed the disappearance of the naphthalene absorption. As a result of the loss of aromaticity in the naphthalene and the benzene ring, which were involved in the photocycloaddition, the ¹H NMR spectrum of 4d showed a typical change relative to that of the starting compound 3d. The methylene groups in the five-membered ring gave AB spin patterns at $\delta = 3.71/3.97$ (²J = -8.8 Hz, 4-H) and 4.60/4.66 $(^{2}J = -10.3 \text{ Hz}, 2\text{-H})$. The methine proton 9-H gave a dd signal at $\delta = 3.46$ because of its coupling with 8-H $({}^{3}J = 10.3 \text{ Hz})$ and 17-H $({}^{3}J = 7.7 \text{ Hz})$. The other methine group (8-H) gave a ddd signal at $\delta = 3.20$ because it coupled with 9-H (${}^{3}J = 10.3 \text{ Hz}$), 6-H $({}^{4}J = 1.8 \text{ Hz})$, and 18-H (${}^{4}J = 2.2 \text{ Hz}$). The olefinic protons on the cyclohexadiene ring resonated at relatively high field, namely at $\delta = 4.31$ (d, ${}^{4}J = 1.8$ Hz, 6-H) and $\delta = 4.95$ (d, ${}^{4}J = 2.2$ Hz, 18-H). Analogous results were obtained for 4e.

In the reverse process, the products **4d** and **4e** could be quantitatively cleaved to **3d** and **3e**, respectively, by heating to 90–100 °C. The Cope rearrangement, often observed for such biplanemers,^{2,4,6,7} could not be found under the conditions used here; there were no hints for one of the two possible [3,3]shift which should lead to **5d,e** or **6d,e**. Presumably the sterically demanding CH₂–O–CH₂ clamp in **4d,e** is the reason for the absence of this rearrangement. On the other hand, the CH₂–O– CH₂ linker is a precondition, that the $[4\pi+4\pi]$ photocycloaddition, which is well-known for anthracenes¹⁴



Scheme 1. Reversible formation of biplanemer 4.

could be realized here for naphthalene–benzene systems. The entirely reversible process $3d, e \rightleftharpoons 4d, e$ represents an interesting molecular basis for optical switching processes or for optical data storage.¹⁵

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- 12. 1-(Benzyloxymethyl)naphthalenes: compound 3a: colorless glass; ¹H NMR (CDCl₃): δ = 4.55 (s, 2H, β -CH₂), 4.97 (s, 2H, α-CH₂), 5.00 (s, 4H, CH₂), 6.54 (t, 1H, aromat. H), 6.62 (d, 2H, aromat. H), 7.28-7.52 (m, 14H, aromat. H), 7.85 (m, 2H, aromat. H), 8.10 (m, 1H, aromat. H); FD MS: m/z (%) = 460 (100, M⁺). Anal. Calcd for C₃₂H₂₈O₃: C, 83.45; H, 6.13. Found: C, 83.39; H, 6.26. Compound **3b**: colorless glass; ¹H NMR (C₆D₆): $\delta = 3.37$ (s, 6H, OCH₃), 3.85 (s, 3H, OCH₃), 4.42 (s, 2H, β-CH₂), 4.89 (s, 2H, α-CH₂), 6.55 (s, 2H, aromat. H), 7.29 (m, 3H, aromat. H), 7.44 (m, 1H, aromat. H), 7.65 (m, 2H, aromat. H), 8.20 (m, 1H, aromat. H); FD MS: m/z (%) = 338 (100, M⁺·). Anal. Calcd for C₂₁H₂₂O₄: C, 74.54; H, 6.55. Found: 74.61; H, 6.65. Compound 3c: colorless crystals, mp C. 79 °C; ¹H NMR (CDCl₃): δ = 3.79 (s, 6H, OCH₃), 3.80 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 4.52 (s, 2H, β-CH₂), 5.06 (s, 2H, α-CH₂), 6.55 (s, 2H, aromat. H), 7.24–7.35 (m, 3H, aromat. H), 7.79 (m, 2H, aromat. H), 8.08 (m, 1H, aromat. H); FD MS: m/z (%) = 368 (100, M⁺). Anal. Calcd for C₂₂H₂₄O₅: C, 71.72; H, 6.57. Found: C, 71.81; H, 6.62. Compound **3d**: colorless crystals, mp 88 °C; ^{1}H NMR (CDCl₃): δ = 3.92 (s, 3H, OCH₃), 4.53 (s, 2H, β -CH2), 4.96 (s, 4H, CH2), 5.06 (s, 2H, α-CH2), 6.51 (m, 1H, aromat. H), 6.61 (m, 2H, aromat. H), 7.27-7.49 (m, 13H, aromat. H), 7.78 (m, 2H, aromat. H), 8.10 (m, 1H, aromat. H); FD MS: m/z (%) = 490 (100, M⁺). Anal. Calcd for C₃₃H₃₀O₄: C, 80.79; H, 6.16. Found: C, 80.69; H, 6.17. Compound **3e**: colorless crystals, mp 102 °C; ¹H NMR (CDCl₃): δ = 3.92 (s, 3H, OCH₃), 4.49 (s, 2H, β -CH₂), 5.01 (s, 6H, OCH₃), 5.05 (s, 2H, α-CH₂), 6.64 (s, 2H, aromat. H), 7.23-7.50 (m, 18H, aromat. H), 7.79 (m, 2H, aromat. H), 8.10 (m, 1H, aromat. H); FD MS: m/z (%) = 597 (100, $[M+H^+]$). Anal. Calcd for $C_{40}H_{36}O_5$: C, 80.51; H, 6.08. Found: C, 80.62; H, 6.05.
- 13. 3-Oxatricyclo[7.6.2.2^{5,8}]nonadeca-6,10,12,14,16,18-hexaenes: Compound 4d: colorless solid, mp 90 °C (dec.); ¹H NMR (C₆D₆): $\delta = 3.12$ (s, 3H, OCH₃), 3.20 (ddd, ³J = 10.3 Hz, ⁴J = 2.2 Hz, ⁴J = 1.8 Hz, 1H, 8-H), 3.46 (dd, ³J = 10.3 Hz, ³J = 7.7 Hz, 1H, 9-H), 3.50/4.01 (AB, ²J = -11.0 Hz, 2H, 7-OCH₂), 3.71/3.97 (AB, ²J = -8.8 Hz, 2H, 4-H), 4.31 (d, ${}^{4}J = 1.8$ Hz, 1H, 6-H), 4.54 ('s', 2H, 19-OCH₂), 4.60/4.66 (AB, ${}^{2}J = -10.3$ Hz, 2H, 2-H), 4.95 (d, ${}^{4}J$ = 2.2 Hz, 1H, 18-H), 5.08 (d, ${}^{3}J$ = 7.7 Hz, 1H, 17-H), 6.92-7.32 (m, 14H, aromat. H); ¹³C NMR (C₆D₆): $\delta = 43.0, 51.3$ (C-8, C-9), 55.0 (OCH₃), 57.1, 66.7 (C-1, C-5), 69.8, 70.2, 70.4, 80.7 (C-2, C-4, OCH₂), 99.5, 104.3, 108.7, 122.5, 124.9, 125.4, 126.4, 127.9, 128.0, 128.1, 128.4, 128.6, 128.7 (aromat. and olefin. CH), 137.6, 137.7, 146.7, 147.6, 164.8, 165.4, 168.5 (aromat. and olefin. C_a); FD MS: m/z (%) = 490 (100, M⁺). Anal. Calcd for C₃₃H₃₀O₄: C, 80.79; H, 6.16. Found: C, 80.45; H, 6.15. Compound 4e: colorless solid, mp 100 °C (dec.); ¹H NMR $(C_6D_6): \delta = 3.08$ (s, 3H, OCH₃), 3.37/4.01 (AB, $^{2}J = -11.0$ Hz, 2H, OCH₂), 3.73/3.98 (AB, $^{2}J = -8.8$ Hz,

2H, 4-H), 3.76 (d, ${}^{3}J$ = 8.1 Hz, 1H, 9-H), 4.34 (s, 1H, 6-H), 4.53–4.65 (m, 4H, 2-H and OCH₂), 4.91 ('s', 2H, OCH₂), 5.02 (s, 1H, 18-H), 5.29 (d, ${}^{3}J$ = 8.1 Hz, 1H, 17-H), 6.83 (m, 1H, aromat. H), 6.95 (m, 1H, aromat. H), 7.05–7.45 (m, 17H, aromat. H); the correlation of the 1 H NMR signals with certain protons is based on 2D measurements; 13 C NMR (C₆D₆): δ = 54.7 (C-9), 55.0 (OCH₃), 55.6, 66.7 (C-1, C-5), 69.4, 70.0, 70.5, 70.5, 80.7 (C-2, C-4, OCH₂), 86.7 (C-8), 100.4, 104.4, 109.0, 122.4, 125.1, 125.4, 127.1, 127.3, 127.9, 128.0, 128.1, 128.2, 128.4, 128.6, 128.7, 128.8

(aromat. and olefin. CH), 137.4, 137.5, 139.9, 146.8, 147.0, 162.7, 163.6, 168.1 (aromat. and olefin. C_q); FD MS: m/z (%) = 597 (100, [M+H⁺]). Anal. Calcd for C₄₀H₃₆O₅: C, 80.51; H, 6.08. Found: C, 80.60; H, 6.05.

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- 15. The direct photolysis leads to the reverse reaction whereas the triplet sensitized process causes the formation of cage compounds by intramolecular $[2\pi+2\pi]$ cycloadditions.