

The Synthesis of Norbornadienes Conjugatively Linked to Tetraphenylporphyrin and Anthracene: Towards a Norbornadiene-derived Molecular Electronic Device

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A facile synthesis of 2,3-disubstituted norbornadienes linked to *meso*-5,10,15,20-tetraphenylporphyrin and anthracene by ethene or butadiene bridging groups is described and the potential of the derivatives to transport energy, a requirement for their action as molecular electronic devices, is discussed.

Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)[†] **1** can be considered a 'molecular switch' as it readily undergoes a reversible photoinduced valence-isomerization to quadricyclane (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane) **2** (Scheme 1). This system fulfils at least three of the four requirements for an operational molecular switch, as proposed by Haddon and Lamola;¹ these are bistability, controllable switching and detection of the switched state. The control of an individual molecule, the fourth requirement, will not be readily achieved for any molecular electronic device (MED). Extensive investigations into the use of 2,3-disubstituted norbornadienes/quadricyclanes for solar energy storage have demonstrated the efficiency and switching potential of this reversible system both in solution and when bound to a polymer.²

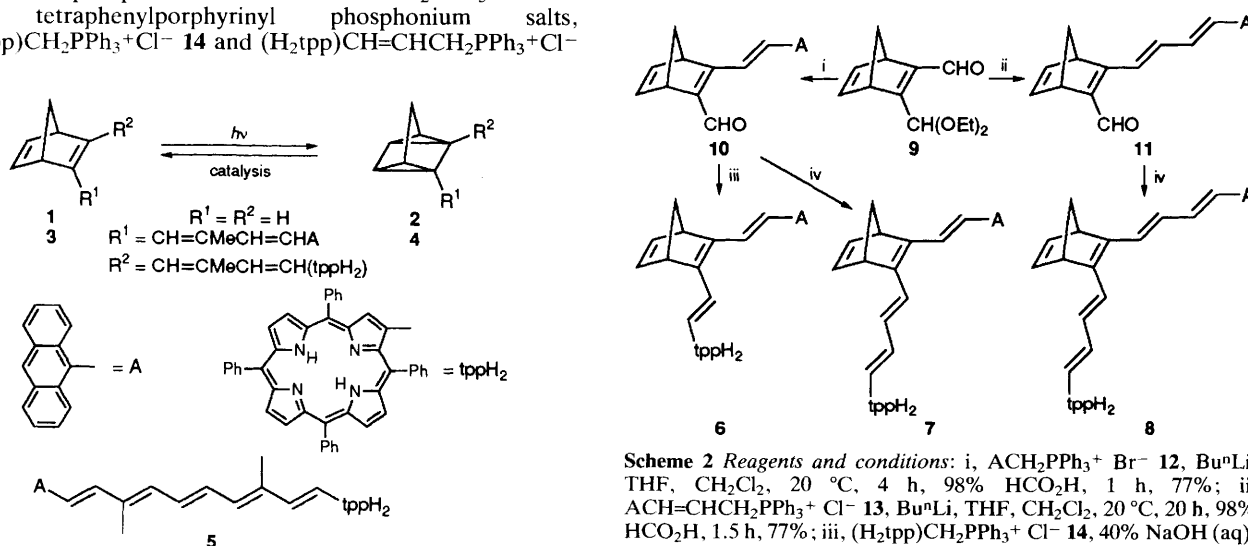
Effenberger *et al.*^{3,4} provided the impetus for the present work when they showed that selective irradiation of polyenes such as **5** led to intramolecular energy transport through the polyene chain; 257 nm irradiation (anthracene excitation) resulted in enhanced porphyrin emissions at 665 and 725 nm. Incorporation of norbornadiene into **5** (see **3**, Scheme 1) could allow controlled switching of this energy transport since formation of the resulting quadricyclane **4** would lead to disruption of the polyene conjugation, diminishing or preventing the energy transport. A molecule such as **3** could then be considered a molecular logic device since 'output' (porphyrin emission) would be controlled by two 'inputs' (anthracene and norbornadiene irradiation). Here we describe the synthesis of three such 2,3-disubstituted norbornadienes **6–8** (Scheme 2) and we examine their absorption spectra with a view to their potential to transport energy, the first stage of a project to develop a molecular logic device.

The most direct route to the synthesis of 2,3-disubstituted norbornadienes such as **6–8** was to utilise the protected dial⁵ **9** in a double Wittig procedure (Scheme 2). A single bis-Wittig reaction of **9** has been reported.⁶ The anthracene aldehyde **10** can be prepared from the known 9-anthryl phosphonium salt, ACH₂PPh₃⁺Br⁻ **12**.⁷ However, the extended-chain anthracene phosphonium salt ACH=CHCH₂PPh₃⁺Cl⁻ **13** and tetraphenylporphyrinyl phosphonium salts, (H₂tpp)CH₂PPh₃⁺Cl⁻ **14** and (H₂tpp)CH=CHCH₂PPh₃⁺Cl⁻

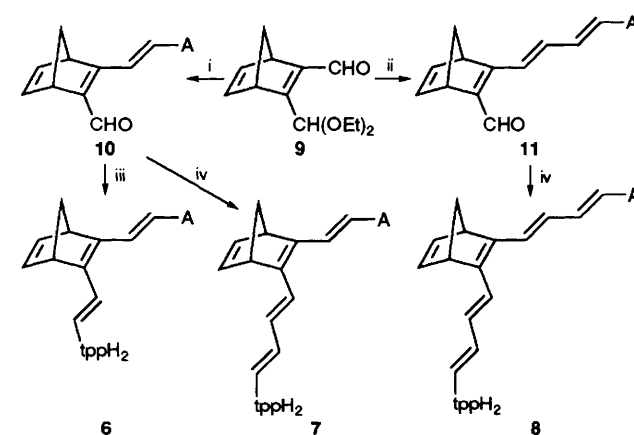
15, required for the syntheses of **11** and **6–8** respectively, had not been reported.[‡] We have now prepared these salts, the syntheses of two of which, **13** and **15**, will be reported in due course. We recently described⁸ the synthesis of tetraphenylporphyrinylmethyltriphenylphosphonium chloride **14** and demonstrated its utility for the syntheses of vinyl-substituted porphyrin derivatives and dimers.

The syntheses of the norbornadienes A1NB1tpp **6**, A1NB2tpp **7** and A2NB2tpp **8**§ were successfully carried out using the double Wittig approach.[¶] Although the aldehyde products **10** and **11** were initially obtained as isomeric mixtures (**10**, *trans*:*cis* 92:8; **11**, *trans*:*cis* 85:15), in both cases the pure *trans*-isomer was isolated after crystallisation. The formations of the porphyrinyl products **6–8** in the second Wittig reaction appeared stereospecific as determined by 270 MHz ¹H NMR spectroscopy. However, the 600 MHz NMR spectra revealed in each case the presence of a small amount of a second porphyrinyl product which appears to be the stereoisomer. In the case of **6**, 2-methyltetraphenylporphyrin initially contaminated the product; chromatography removed this byproduct which may have arisen from base attack on the phosphonium salt **12**.⁹

The formations of **6–8** were readily confirmed from their ¹H NMR spectra which reflected their individual norbornadiene, polyene, anthryl and porphyrinyl components. This was exemplified by the 600 MHz ¹H NMR spectrum of **7**|| for which a DQF COSY spectrum was obtained. The norbornadienyl resonances were typical of a substituted derivative as were the anthryl and porphyrinyl resonances. The most revealing aspect of the spectrum, the vinylic proton resonances, could be fully assigned using the COSY data as well as by comparison to known anthryl and porphyrinyl vinylic derivatives.¹⁰ The *trans* nature of the double bonds in **7** were evident from the large vinylic coupling constants (15–16 Hz). A comparison of this data with that of **6** confirmed the side chain *trans*-configurations of **6** and supported its structural assign-



Scheme 1



Scheme 2 Reagents and conditions: i, ACH₂PPh₃⁺Br⁻ **12**, BuⁿLi, THF, CH₂Cl₂, 20 °C, 4 h, 98% HCO₂H, 1 h, 77%; ii, ACH=CHCH₂PPh₃⁺Cl⁻ **13**, BuⁿLi, THF, CH₂Cl₂, 20 °C, 20 h, 98% HCO₂H, 1.5 h, 77%; iii, (H₂tpp)CH₂PPh₃⁺Cl⁻ **14**, 40% NaOH (aq), CH₂Cl₂; iv, (H₂tpp)CH=CHCH₂PPh₃⁺Cl⁻ **15**, 40–45% NaOH (aq), CH₂Cl₂, 2 h, 49% (**7**) and 46% (**8**)

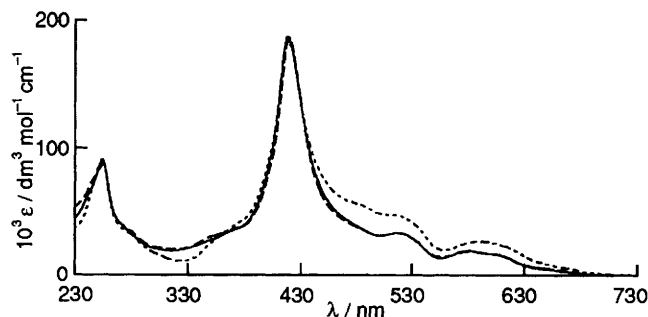


Fig. 1 Electronic absorption spectra of A1NB1tpp **6** (—), A1NB2tpp **7** (---) and A2NB2tpp **8** (....)

ment. While the overall structural characteristics of **8** could be readily seen in its 600 MHz ^1H NMR spectrum, the configuration of the butadiene chains were not as easy to determine since there was significant vinylic and aromatic proton resonance overlap and the signals of the anthryl butadiene moiety appeared to be second order. Again a comparison to the spectrum of **7** allowed at least three of the four porphyrinyl butadiene proton resonances to be assigned. Given that the butadiene moiety of the anthracene aldehyde **11** exhibited second-order characteristics, the all-*trans* structure of A2NB2tpp **9** was consistent with the data.

In order that the norbornadiene derivatives **6–8** function as molecular devices, they must exhibit intramolecular energy transport analogous to **5**. The electronic absorption spectra of **6–8** (Fig. 1) provide good evidence that the energy transport phenomenon should indeed occur. The spectra are almost identical which is not surprising given that the only structural difference between them is the polyene chain length. All compounds show discreet absorptions for the anthryl (257 nm) and tpp (400–600 nm) moieties as observed for **5**.³ All the spectra exhibit a shoulder at 280 nm as well as two others at 355 and 380 nm, the latter of which appears to be an enhanced porphyrinyl N band¹¹ and is observed in a variety of other porphyrinyl materials.¹⁰ All of these absorptions are observed to varying degrees in the spectra of the polyenes synthesised by Effenberger *et al.*^{3,4}

The effect of lengthening the polyene chain is most noticeable in the spectrum of **8** with a diminished absorption at 320 nm and increased absorption from 380–500 nm leading to a broadened base of the porphyrinyl Soret band as is evident for **5**. Indeed, the absorption spectra of **8** and **5** are remarkably similar. This supports the notion that the norbornadiene moiety is a fully conjugated part of the polyene chain.

What is clear from the positions of the anthryl and porphyrinyl absorptions and the lack of splitting of the Soret band in all the norbornadienes **6–8** is that both the terminal groups are not conjugated to the polyene chain. As a result, a complete amalgamation of the component electronic energy levels should not occur and selective excitation and emission from the different groups should take place as for **5**.

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Footnotes

† In order to simplify compound names and aid understanding, we have chosen to use the older nomenclature throughout this paper.

‡ In correspondence with Professor F. Effenberger, University of Stuttgart, we learnt that he had prepared the phosphonium bromide, $(\text{H}_2\text{tpp})\text{CH}=\text{CHCH}_2\text{PPh}_3^+ \text{Br}^-$.

§ The IUPAC name for the norbornadiene **6** is 2-{1'-[2'-(9''-anthryl)ethenyl]}-3-{1''-[2''-(2'''-meso-5''', 10''', 15''', 20'''-tetraphenylporphyrinyl)ethyl]}bicyclo[2.2.1]hepta-2,5-diene. The names for **7** and **8** are just as complex. In order to simplify the reference to these compounds, we have devised a simple code AmNBntpp in which the 9-anthryl (A) and the 2-tetraphenylporphyrinyl (tpp) groups are linked to norbornadiene (NB)(2,3-disubstitution) by m and n conjugated double bonds, respectively.

¶ All new compounds gave satisfactory NMR, UV-VIS and analytical or high resolution MS data.

|| ^1H NMR data for **7**: (600 MHz, CDCl_3) δ_{H} : 8.82 (s, 1 H), 8.79 (s, 2 H), 8.75 (d, 1 H, 3J 4.7 Hz), 8.74 (d, 1 H, 3J 4.8 Hz), 8.71 (d, 2 H, 3J 4.7 Hz, $\text{H}_{\text{pyrroles}}$); 8.35 (s, 1 H, anthryl 10-H); 8.32–8.37 (m, 2 H, anthryl 1-H and 8-H); 8.08–8.23 (3 \times m, 8 H, H_{Ph}); 7.97–8.02 (m, 2 H, anthryl 4-H and 5-H); 7.64–7.82 (3 \times m, 12 H, $\text{H}_{m,\text{Ph}}$); 7.52 (d, 1 H, 3J 15.8 Hz, ethenyl 2-H); 7.45–7.50 (m, 4 H, anthryl 2-H, 3-H, 6-H, 7-H); 7.15 (d, 1 H, 3J 15.9 Hz, ethenyl 1-H); 7.04 (dd, 1 H, 3J 10.8 and 14.9 Hz, butadienyl 3-H); 7.01 (app dd, 1 H, 3J 10.8 and 14.9 Hz), 6.93 (app dd, 1 H, 3J 10.8 and 14.9 Hz, NB 5-H and 6-H); 6.79 (d, 1 H, 3J 14.9 Hz, butadienyl 1-H); 6.24 (dd, 1 H, 3J 10.9 and 14.9 Hz, butadienyl 2-H); 6.21 (d, 1 H, 3J 14.5 Hz, butadienyl 4-H); 4.26 (s, 1 H), 3.98 (s, 1 H, NB 1-H and 4-H); 2.23 (d, 1 H, 3J 6.6 Hz), 2.19 (d, 1 H, 3J 6.6 Hz, NB 7a-H and 7b-H); -2.57 (bd s, 2H, pyrrolic NH).

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