An Unusual Bilaterally Flanked Olefin; *X*-Ray Crystal Structure of 5,14;7,12-Bis-(*o*-benzeno)-6,13-ethenylidene-5,5a,6,6a,7,12,12a,-13,13a,14-decahydropentacene

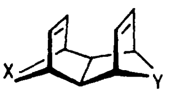
By Douglas N. Butler* and Indranil Gupta
(*Chemistry Department, York University, Toronto, Ontario* M3J 1P3, *Canada*)

and Winnie Wong Ng and Stanley C. Nyburg
(*Chemistry Department, University of Toronto, Toronto, Ontario* M5S 1A1, *Canada*)

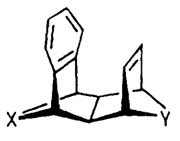
Summary Spectroscopic and chemical evidence reveals the intramolecular π–π orbital proximity in the novel Diels–Alder adducts (**7**) and (**9**); the *X*-ray crystal structure of (**9**) is reported.

The design and synthesis of organic systems contrived to exhibit specific, intramolecular functional group proximities continues, though no systematic approach seems to have been attempted.

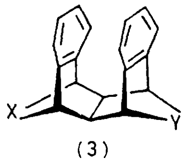
Restricting the functionalities to olefins and benzene rings, the hydrocarbon series (**1a**—**c**) to (**3a**—**c**) may be considered. Of these only (**1a**), (**2a**), and (**3a**) are known;[1] however the carbon frameworks of (**2b**) and (**3c**) are to be found in (**4**)[2] and janusene[3] respectively. As well as the 'parallel' arrangements in these examples, these functionalities could be 'orthogonal' as, for example, in hydrocarbons (**5**) and (**6**).



(1)

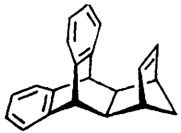


(2)

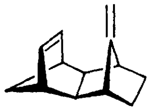


(3)

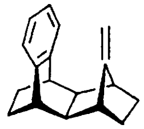
a; X = Y = $-CH_2-$
b; X = $-CH_2CH_2-$, Y = $-CH_2-$
c; X = Y = $-CH_2CH_2-$



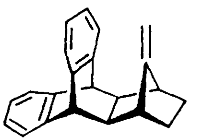
(4)



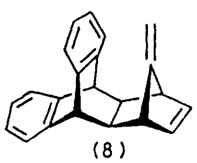
(5)



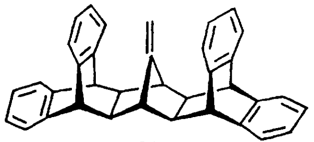
(6)



(7)



(8)



(9)

We report here the synthesis and some of the chemistry of three systems related to (**6**), namely (**7**), (**8**), and (**9**). We report also the *X*-ray structure analysis of (**9**), a decacylic hydrocarbon with a terminal olefin sandwiched between the faces of two benzene rings.

It is not commonly appreciated that anthracene readily forms [$4\pi + 2\pi$] adducts with dienophiles of the norbornene type.[2,4] Thus by heating anthracene and 7-methylenenorbornene[5] (mole ratio 1 : 4) in a sealed tube at 170 °C for 20 h, the adduct (**7**) is obtained [m.p. 144 °C, 72%; ^{1}H n.m.r. ($CDCl_3$): δ 1·1—1·5 (A_2B_2, 4H), 1·98 (s, 2H), 2·08 (m, 2H), 3·62 (s, 2H), 4·18 (m, 2H), and 6·97—7·35 (m, 8H)].

Similarly, a mixture of anthracene and 7-methylenenorbornadiene[5] (mole ratio 1 : 5, sealed tube, 185 °C, 12 h) yielded (**8**) [m.p. 141—2 °C, 15%; ^{1}H n.m.r. ($CDCl_3$): δ 2·17 (m, 2H), 2·73 (t, 2H), 3·43 (s, 2H), 4·17 (m, 2H) 6·30 (t, 2H), and 6·93—7·50 (m, 8H)] and (**9**) [m.p. > 350 °C, 26%; ^{1}H n.m.r. ($CDCl_3$): δ 1·86 (s, 4H), 2·06 (s, 2H), 2·58 (s, 2H), 4·11 (s, 4H), and 6·80—7·12 (m, 16H) separated by chromatography on neutral alumina with hexane. The notable feature of the ^{1}H n.m.r. spectra of the adducts (**7**), (**8**), and (**9**) is the effect of the diamagnetic anisotropy of the proximal aromatic ring(s) on the vinyl $=CH_2$ resonances. These occur respectively at δ 3·62, 3·43, and 2·58 (thus extending to a new high-field limit the range of absorptions of protons bound to sp^2 carbon in hydrocarbons).† No significant long wavelength absorption in the u.v. spectra beyond 280 nm is found in (**7**), (**8**), or (**9**).[1]

The isolated molecule (**9**) (Figure) would be expected to have symmetry *mm*2 (C_{2v}). *X*-Ray structure analysis requires there to be eight molecules in a cell with eight equivalent positions. Thus, *a priori*, there would be no need for the molecules to be symmetric. It happens, however, that four of the eight molecules have one of their *m* planes exactly in the space group mirror and the remaining four have their other *m* plane lying in this mirror. The two independent molecules have thus one each of the two mirror symmetries expected. Deviations from full C_{2v} symmetry are in both cases very slight.

Crystal data: (**9**), $C_{36}H_{28}$, $M = 460·2$, orthorhombic, space group $Pna2_1$ or $Pnma$ (latter confirmed), $a = 21·722(3)$, $b = 17·379(2)$, $c = 12·939(2)$ Å, $Z = 8$, $D_c = 1·25$ g cm^{-3}, μ(Cu-K_α) = 0·766 cm^{-1}. Data were collected on an automated Picker four-circle diffractometer using Ni-filtered Cu-K_α radiation. Of 3929 intensities measured, 3068 were

---

† These δ values may be compared with those of the 1 : 1 adducts of anthracene with norbornene and norbornadiene and the 2 : 1 anthracene–norbornadiene adduct whose bridge methylene *syn*-protons (at highest field) occur respectively at δ −0·41, −0·20, and −1·03 (ref. 2).

considered significant. The structure was solved by direct methods and refined by full matrix least-squares to a final R value of 0·07.‡

The distance d_1 between atom C(2) and the midpoint of C(8)–C(8′) is: molecule (1), 3·70, molecule (2) (mean) 3·69 Å and d_2 between atom C(1) and the midpoint of C(6)–C(6′), molecule (1), 3·01 and molecule (2) (mean) 2·99 Å. The angle C(3)–C(4)–C(5) ranges from 118·1 to 118·5(2)°, larger than might be expected in the absence of strain.

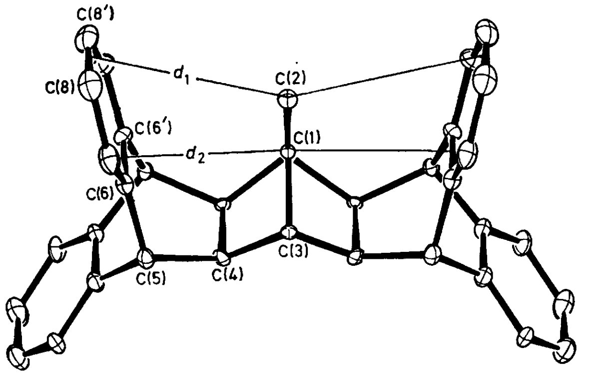
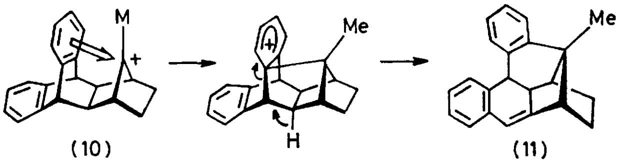


FIGURE. X-Ray structure of (**9**).

Some consequences of the ring–double bond proximity in (**7**) were shown by the following chemistry. Firstly, the methylene protons exchanged in a few minutes for deuterium atoms in the two-phase $CDCl_3$–D_2SO_4 system at 20 °C. This implication of the internally π-stabilized carbonium ion (**10**) was further supported by the complete conversion of (**7**) in $CHCl_3$–H_2SO_4 at 20 °C, 12 h, into the isomeric hydrocarbon (**11**);¶ m.p. 150—151 °C as rationalized in the Scheme.§

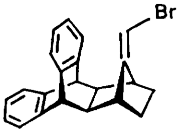


(10) (11)

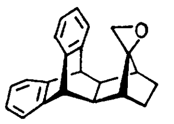
SCHEME

In a second example, mono-bromination of (**7**) in $CHCl_3$ using Br_2 or N-bromoacetamide afforded the substitution product (**12**), m.p. 156 °C, as the immediate and only bromination product.

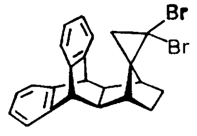
This appears to be a rare, perhaps unique, example of a direct electrophilic bromination of a hydrocarbon olefin[6] and again, an internally π-stabilized ion related to (**10**) is implicated. Further bromination involved proximal ring attack. m-Chloroperbenzoic acid in $CHCl_3$ converted (**7**) into the epoxide (**13**),¶ as did ozone in CH_2Cl_2 at 0 °C.** This epoxide was rearranged to either the *syn*- or *anti*-aldehydes (**15a**)¶ and (**16a**)¶ from which the reduction products (**15b,c**)¶ and (**16b,c**)¶ were readily prepared. Alcohol (**15b**) was more conveniently prepared *via* hydroboration–oxidation; however (**7**) could not be hydrogenated to (**15c**). Reaction of (**7**) with an excess of $PhHgCBr_3$ or $CHBr_3$–$KOBu^t$ gave the adduct (**14**)¶ which has been used to provide the corresponding allene and *spiro*-cyclopropene.



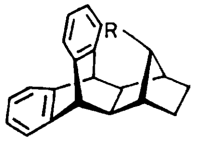
(12)



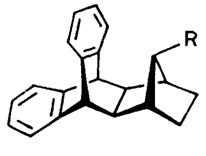
(13)



(14)



(15) a–c



(16) a–c

a; R = CHO
b; CH_2OH
c; R = Me

In contrast with the chemistry of (**7**), the hydrocarbon (**9**) does not react with any of the reagents just mentioned. Thus D_2SO_4, Br_2, O_3, BH_3–tetrahydrofuran, or :CBr_2 all failed to react with (**9**), and to date, we have not observed any reactions at the site of the entombed olefin.

These results support, in a simple and direct way, the commonly held view that a particular geometric approach of electrophilic reagents to the π-electrons of an olefin is necessary for reaction to occur.

(*Received, 7th February* 1980; *Com.* 135.)

---

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ All new compounds are structurally assigned from analytical, spectroscopic, and (in some cases) chemical data.

§ Compound (**7**) was also slowly but clearly isomerized to (**11**) by liquid SO_2 in a sealed tube at 20 °C.

** Epoxide formation from ozone is fairly common in tri- and tetra-substituted olefins. This is the only case of a terminal olefin–epoxide conversion using ozone which we have found.

[1] H. Prinzbach, G. Sedelmeier, C. Kruger, R. Goddard, H. H. Martin, and R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 271.
[2] D. N. Butler, A. Barrette, and R. A. Snow, *Synth. Commun.*, 1975, **5**, 101.
[3] S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, 1967, **89**, 1476; W. H. Macintyre and A. H. Tench, *J. Org. Chem.*, 1973, **38**, 130.
[4] T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *J. Am. Chem. Soc.*, 1977, **99**, 871.
[5] R. W. Hoffmann, H. Kurz, M. T. Reetz, and R. Schüttler, *Chem. Ber.*, 1975, **108**, 109.
[6] Electrophilic bromination of olefins bearing hetero-atoms on the double bond are known: M. Hojo, R. Masuda, Y. Kokuryo, H. Shioda, and S. Matsuo, *Chem. Lett.* (*Jpn.*), 1976, **5**, 499. For a possible hydrocarbon precedent see: S. Hatakeyama, T. Mitsuhashi, and M. Oki, *Chem. Lett.* (*Jpn.*), 1978, **5**, 559.