(d), 49.5 (t), 49.7 (t), 52.1 (q), 126.5 (d), 127.6 (d, 2), 128.5 (d, 2), 144.0 (s), 167.4 (s), 201.5 (s); IR 2960, 1755, 1720, 1655, 1625, 1450, 1440, 1410, 1320, 1240, 1195, 700 cm⁻¹; MS, *m/z* (relative intensity) 234 (5), 216 (89), 205 (26), 161 (26), 157 (23), 156 (93), 142 (20), 132 (41), 131 (92), 119 (100), 118 (59), 117 (41), 115 (23), 107 (18), 105 (18), 104 (34), 103 (34), 101 (85); exact mass calcd for $C_{14}H_{18}O_3$ 234.126, obsd 234.126.

Methyl 2-Diazo-3-oxo-5-phenylheptanoate (18b). Following the procedure for **5b**, diazo transfer was performed on **18a** (178 mg, 0.76 mmol). The residual oil was chromatographed on 10 g of silica gel with 5% EtOAc/petroleum ether. The first 40 mL was discarded. The next 30 mL was concentrated in vacuo to give α-diazo β-keto ester **18b** as a yellow oil: 170 mg (86%); R_f (20% EtOAc/hexane) 0.44; ¹H NMR δ 0.78 (t, *J* = 6.5 Hz, 3 H), 1.5–1.8 (m, 3 H), 3.1–3.3 (m, 2 H), 3.78 (s, 3 H), 7.1–7.3 (m, 5 H); ¹³C NMR δ 12.0 (q), 29.3 (t), 43.2 (d), 46.4 (t), 52.1 (q), 126.0 (d), 126.3 (d, 2), 127.8 (d, 2), 144.3 (s), 161.8 (s), 191.5 (s); IR 2960, 2140, 1730, 1655, 1550, 1450, 1310, 1210, 700 cm⁻¹; MS, *m/z* (relative intensity) 203 (15), 200 (51), 176 (18), 173 (47), 172 (23), 171 (100), 132 (18), 129 (30), 119 (46), 118 (22), 117 (49), 116 (18), 115 (47), 105 (18), 104 (34), 101 (24); CH₄ CI exact mass calcd for $C_{14}H_{17}N_2O_3$ 261.124, obsd 261.123.

Methyl (4R*,5S*)-5-Methyl-2-oxo-3-phenylcyclopentanecarboxylate (18c). Following the procedure for **5c** and **5d**, cyclization was effected on **18b** (206 mg, 0.8 mmol). The residual oil was chromatographed on 20 g of silica gel with 4.5% EtOAc/petroleum ether. The first 300 mL was discarded. The next 400mL was concentrated in vacuo to give **18c** as a colorless oil: 141 mg (77%); R_f (20% EtOAc/hexane) 0.33; ¹H NMR δ 1.07 (d, *J* = 6.2 Hz, 3 H), 3.03 (d, *J* = 11.7 Hz, 1 H), 2.5–3.0 (m, 4 H), 3.80 (s, 3 H), 7.2–7.4 (m, 5 H); ¹³C NMR 16.9 (q), 43.3 (d), 47.3 (t), 48.5 (d), 52.5 (q), 127.3 (d), 127.5 (d, 2), 128.9 (d, 2), 140.4 (s), 169.3 (s), 208.9 (s); IR 2965, 1740, 1730, 1500, 1460, 1440, 1330, 1295, 1205, 1145, 1040, 695 cm⁻¹; MS, *m/z* (relative intensity) 232 (43), 214 (17), 201 (11), 200 (13), 173 (11), 172 (19), 132 (15), 131 (17), 105 (14), 104 (100), 101 (28); exact mass calcd for $C_{14}H_{16}O_3$ 232.110, obsd 232.110.

3H-Cyclonona[def]biphenylene: An Example of Neutral Homoantiaromaticity

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Abstract: 3H-Cyclonona[def]biphenylene (**6**), a potentially homoantiaromatic neutral hydrocarbon, was synthesized by a bis-Wittig reaction between 1,8-biphenylenedicarboxaldehyde and the bis-ylide made from 1,3-bis(triphenylphosphino)propane dibromide. An X-ray structure of **6** revealed a bent structure for which C-2 and C-4 of the double bonds are close enough to have a theoretical β_{2-4} of about $0.24\beta_0$ (benzene). The photoelectron spectrum indicated some homoconjugation, which on detailed analysis could be accounted for by assuming a β_{2-4} value of $0.33\beta_0$. The UV/visible spectrum of **6** was red-shifted by 4 nm relative to 1,8-divinylbiphenylene (**8**), which PPP-model calculations indicated was composed of a 5-nm *hyper*conjugative *blue* shift and a 9-nm *homo*conjugative *red* shift when $\beta_{24} = 0.3\beta_0$. The ¹H NMR spectrum of **6** was complex but could be analyzed fully. The endo H at C-3 was found to resonate 2.2 ppm downfield of the exo H, which would be qualitatively consistent with a homoantiaromatic ring. However, reduction of one of the double bonds to give **7** caused this shift difference to decrease only to 0.7 ppm, indicating that another factor must be contributing as well. The pattern and magnitudes of the shifts were quantitatively consistent with a combination of local anisotropy effects and a homoantiaromatic ring current. A least-squares fit of the observed shifts to a dual model yielded a β_{2-4} of $0.39\beta_0$ with about an equal contribution from each source. These three lines of evidence all point to significant neutral homoantiaromaticity in **6**.

Since the early proposal of Winstein[2] for homoconjugative stabilization of cations, there has been considerable effort to uncover examples of neutral homoaromaticity.[3] However, an

uncontested compound of this type has yet to be made. Calculations by Houk and Paquette[4] seem to indicate that neutral

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(2) See: Winstein, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 141–176, and references therein.

(3) (a) Warner, P. M. *Topics in Nonbenzenoid Aromatic Chemistry*; 1977; Hirokawa Publishing Co.: Tokyo, 1977; Vol. II, pp 283–352. (b) Chistoph, G. C.; Muthard, J. L.; Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 7782–7784. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106–117. (d) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106*, 5018–5019.

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homoaromatic conjugation, contrary to intuition, would actually be destabilizing, and Paquette has gone so far as to "rule out the likelihood that neutral homoaromatic character will ever be uncovered" in hydrocarbons.[4,5] Grutzner and Jorgensen have taken the same calculations as support for the possibility of neutral homo*anti*aromaticity in hydrocarbons.[6]

There has been much discussion concerning the definition of homoaromaticity and homoantiaromaticity.[7] As with aromaticity and antiaromaticity the question is the degree to which the classical criteria of stability (instability) and bond-length equalization (alternation) should be supplemented or even supplanted by magnetic and spectroscopic criteria. As will be described below, consideration of only a single criterion could be misleading.[7,8]

The nonbonding destabilizing factors that might overwhelm the weak stabilization of homoaromaticity should work in the same direction as the weak π-*de*stabilization of homo*anti*aromaticity. One might suppose that clear-cut examples of homoantiaromaticity should abound, but in fact very few contenders have been offered. An obvious obstacle to clear-cut examples is that the combined instabilities can be severe enough to lead to molecular rearrangements or, at the least, distortions that destroy the very atomic relationships giving rise to the phenomenon. It seems clear that some geometric rigidity of the molecular skeleton must be present.

Using calorimetric data, Stevenson[9] has calculated that if cyclononatetraene were held in an homoantiaromatic configuration, 1, it would be less stable than *cis*-bicyclo[6.1.0]nona-2,4,6-triene

1   **2**   **3**
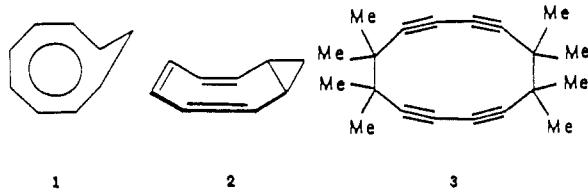
(2) by 32 kcal/mol. In the potentially bishomoantiaromatic octamethylcyclododeca-1,3,7,9-tetrayne[10] (3), photoelectron (PE) spectroscopy revealed small through-space interactions. These are presumably the residue of stronger destabilizing forces that existed before the molecule distorted to minimize them. In more recent work by Houk and Scott,[11] several potentially homoantiaromatic percyclynes were synthesized. Although PE spectroscopy revealed some through-space interactions, no NMR effects due to ring currents were observed. This was attributed to strong bond alternations due to the destabilizing interactions between the nonbonded p orbitals.

We have reported the synthesis of cycloocta[*def*]biphenylene[12] (4), along with a number of related hydrocarbons that exhibit an interesting mixture of olefinic, aromatic, and antiaromatic properties.[13] More recently we made dicyclooctabiphenylene[14]

(4) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797–6802. A referee has noted that the predicted nonexistence of homoaromaticity referred to an energetic criterion rather than the electronic and magnetic criteria employed in the present work.

(5) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991–6996.

(6) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372–1375.

(7) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347–352.

(8) Childs, R. F.; Rogerson, C. V. *J. Am. Chem. Soc.* **1980**, *102*, 4159–4166; **1978**, *100*, 649–651.

(9) Concepcion, R.; Reiter, R. C.; Stevenson, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 1778–1782.

(10) Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 692–696.

(11) (a) Houk, K. N., et al. *J. Am. Chem. Soc.* **1985**, *107*, 6556–6562. (b) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *Ibid.* **1985**, *107*, 6546–6555.

(12) (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohmann, K. G. *J. Am. Chem. Soc.* **1972**, *94*, 2532–2533. (b) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *Ibid.* **1975**, *97*, 1914–1920.

(13) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351–356, and references cited therein.

(14) (a) Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195–7120. (b) Wilcox, C. F., Jr.; Farley, E. N. *Ibid.* **1983**, *105*, 7191–7192.

(5), which was found to display strong antiaromaticity. In a desire to extend these studies to homoantiaromaticity, it was felt that cyclononabiphenylene (6), a homologue of 4, would be an ideal

4   **6**

5

7   **8**
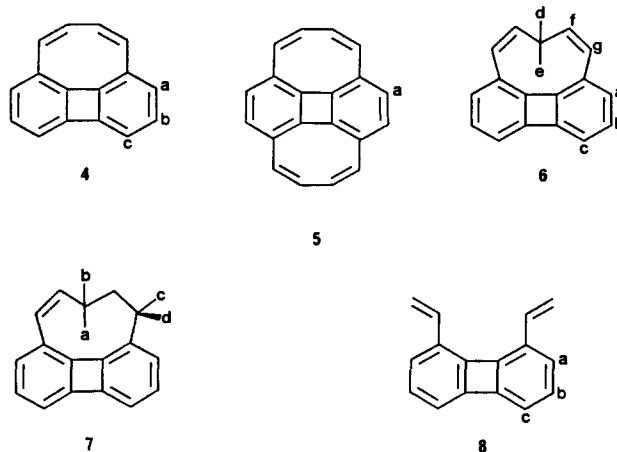
candidate. If the termini of the double bonds were close enough to interact and the system too rigid to allow them to distort, it could exhibit some of the paratropic properties found in 4.

Synthesis. The earlier syntheses of 4 and related hydrocarbons reported from this laboratory involved the bis-Wittig[15] coupling of the bis-ylide derived from 1,8-bis[(triphenylphosphino)-methyl]biphenylene dibromide and the appropriate dicarbonyl compound. The extension to the synthesis of 6 with malonaldehyde[16] was an attractive possibility, but in trial runs it was found that malonaldehyde would not condense with benzyltriphenylphosphonium bromide under our usual conditions (Me₂SO and KO-*t*-Bu). Perhaps malonaldehyde, which exists largely as a pair of equilibrating enol forms,[16] has deactivated carbonyls, or perhaps the phosphonium ylide deprotonates it to give a highly unreactive anion.

The problem was solved by reversing the role of the Wittig partners, that is, by coupling 1,8-biphenylenedicarboxaldehyde with the bis-ylide derived from 1,3-bis(triphenylphosphino)propane dibromide. The dialdehyde was made from a mixture of 1,5-
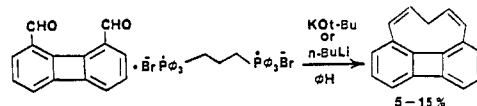
and 1,8-bis(bromomethyl)biphenylene by reaction with silver tosylate and Me₂SO followed by elimination with triethylamine.[17] This procedure is an improvement over the Me₂SO–collidine oxidation employed previously.[18] The 1,8 and 1,5 isomers can be separated by flash chromatography.

Formation of the bis-ylide in dry benzene with excess KO-*t*-Bu followed by dropwise addition of the dialdehyde in benzene gave a black solution, which afforded a 5–15% yield of yellow crystalline 6 after purification by flash chromatography followed by sublimation. The purified compound, which appeared to be spectroscopically pure and gave a good X-ray structure, has a broad melting range (111–117 °C) perhaps due to conformational rearrangements in the crystal upon heating (vide infra).

Our initial attempt to synthesize dihydro-6 (7) involved addition of 1 equiv of Br₂ to 6 followed by reductive debromination. Under most reduction conditions vicinal dibromides eliminate Br₂ to form alkenes, but with NaBH₄ in Me₂SO, 1,2-dibromo-1-phenylethane is cleanly reduced to ethylbenzene.[19] Addition of 1 equiv of Br₂ in CCl₄ at 0 °C in the dark cleanly gave the 1,2-dibromide as an

(15) Vollhardt, K. P. C. *Synthesis* **1975**, 765–780.

(16) George, W. O.; Mansell, V. G. *J. Chem. Soc. B* **1968**, 132–134.

(17) Wilcox, C. F., Jr.; Lassila, K. R., unpublished results.

(18) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889–2895.

(19) Hutchins, R. O.; Hoke, D.; Keough, J.; Koharski, D. *Tetrahedron Lett.* **1969**, 3495–3498.
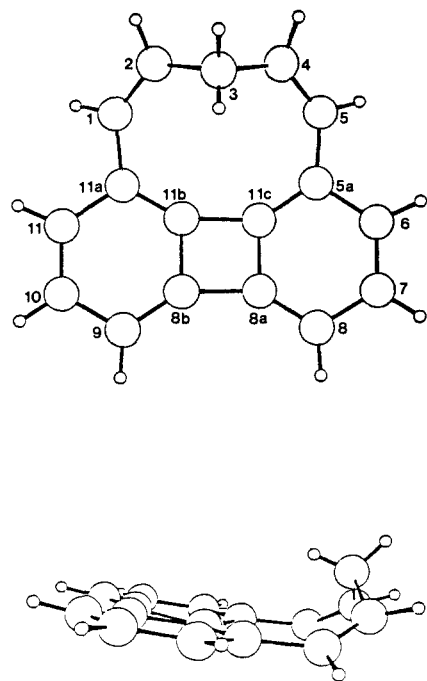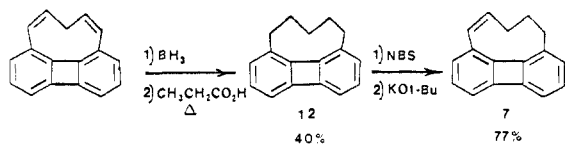
Figure 1. X-ray structure of hydrocarbon 6.

Table I. ^{1}H NMR Data for Hydrocarbons 4, 5, 6, and 8

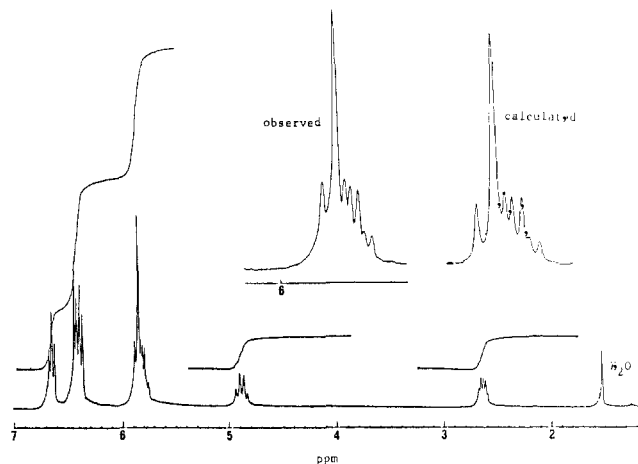| 4		6		5		8	
a	5.83	a	6.38	a	4.55	a	6.92
b	6.21	b	6.64			b	6.75
c	6.05	c	6.43			c	6.54
		d	2.63				
		e	4.88				
		f	5.80				
		f	5.86				

Figure 2. ^{1}H NMR spectrum of hydrocarbon 6. Inset shows observed (left) and calculated (right) plots of region from 5.7 to 6.0 ppm.

oily solid with no 1,2,4,5-tetrabromide being formed. Treatment of 6 with 2.2 equiv of Br₂ under the same conditions gave only 61% dibromide and 27% tetrabromide.[20] Unfortunately, reduction of the dibromide of 6 with these reagents gave only elimination to re-form the starting material, 6.

The synthesis of 7 was achieved by reduction of both double bonds followed by monobromination and elimination. The reduction proved to be more challenging than expected. It was anticipated that hydrogenation with Pd on C would cleave the four-membered ring in biphenylene. However, this unwanted ring opening also occurred with CoCl₂ and LiAlH₄[21] (the structure of this product was confirmed by comparison with the product formed by catalytic hydrogenation of 7H-1,2:3,4-dibenzocyclo-nonatetraene).[22] Attempted reduction of 6 by diimide generated from tosylhydrazide[23] resulted in recovery of starting material.

Tetrahydro-6 (12) was finally synthesized in 40% yield by reaction of 6 with excess BH₃ in refluxing diglyme followed by protonolysis with propionic acid.[24] Reaction of 12 with 1 equiv of N-bromosuccinimide (NBS) in refluxing CCl₄ gave the tetrahydro-6 monobromide as a difficultly purified oily solid. The crude bromide on treatment with excess KO-t-Bu in THF gave 7.

X-ray Structure. The X-ray structure of 6 was determined; a side and top view are shown in Figure 1 (see Experimental Section for details). The most striking feature is that the double bonds are Z-substituted so that the methylene group is held with one of the two hydrogens (H-endo) facing the biphenylene ring and the other (H-exo) pointed away from it. A molecular-mechanics

calculation using the Allinger MMPM force field[25] yielded an energy minimum with a very similar structure.

^{1}H NMR Spectral Analysis. Selected ^{1}H NMR data for 6 and several related compounds are given in Table I. The biphenylenic protons absorb in an ABC pattern. The doublet at 6.43 ppm can be assigned to the a proton next to the four-membered ring by its smaller coupling constant to the central b proton. The smaller coupling constant, due to a smaller bond order resulting from bond fixation induced by the four-membered ring, is characteristic of the biphenylene ring system.[26] This same bond fixation also lowers the diamagnetic ring currents in the benzene rings and produces the upfield shift typical of biphenylenic protons.[13,27]

Annelating paratropic rings onto the biphenylene nucleus introduces remote paramagnetic shifts of the biphenylenic protons and causes a further reduction of the benzenoid diamagnetic ring currents.[13] Both effects produce additional upfield shifts of the biphenylenic protons. An extreme example is 5, for which the benzene rings are calculated to be atropic;[14] the benzene protons are observed upfield at 4.55 ppm. Similarly, protons b and c of 4[12] are shifted upfield by about 0.5 ppm relative to the same protons in 1,8-divinylbiphenylene (8). The shifts of protons b and c of 6 are slightly upfield from those of 8.

The resonances for the ethylenic protons of 6 were unexpectedly complex and could only be analyzed with the aid of LAOCOON III.[28] The calculated and observed spectra are compared in Figure 2. Protons f and g absorb at 5.86 and 5.80 ppm, respectively, a difference of 18 Hz at 300 MHz. The coupling constant between them is only 10.89 Hz, which leads to a more complex second-order spectrum (a quartet with the two inner peaks much taller than the outer ones).[29] The multiplet is made even more complex owing

(20) This difficulty in forming tetrabromides has been seen earlier in similar systems by us and others: Wilcox, C. F., Jr.; Weber, K. A. J. Org. Chem. 1986, 51, 1088-1094.

(21) Ashby, E. G.; Lin, J. J. J. Org. Chem. 1978, 43, 2567-2572.

(22) (a) Garratt, P. J.; Knapp, K. A. J. Chem. Soc., Chem. Commun. 1970, 1215-1216. (b) Rabinowitz, M.; Gazit, A.; Bergman, E. D. J. Chem. Soc., Chem. Commun. 1970, 1430.

(23) van Tamelen, E. E.; Dewey, R. S. J. Am. Chem. Soc. 1961, 83, 3729.

(24) Brown, H. C.; Murray, K. J. Am. Chem. Soc. 1959, 81, 4108-4109.

(25) Allinger, N. L.; Yuh, Y. H. QCPE 1981, 13, 395.

(26) Barton, J. W.; Rowe, O. J. Tetrahedron 1985, 41, 1323-1328.

(27) Figeys, H. P.; Defay, N.; Martin, R. H.; McComie, J. F. W.; Ayres, B. E.; Chadwick, J. B. Tetrahedron 1976, 32, 2571-2578.

(28) Bothner-By, A. A.; Castellano, S. QCPE 1967, 10, 111, LAOCON3. This program calculates least-squares fits of the chemical shifts and coupling constants given the experimental shifts and reasonably good initial assignments. The validity of the fit is revealed both by the quality of fit of the chemical shifts, which are input data, and by the intensity data, which are not part of the input.

(29) Becker, E. D. High Resolution NMR; Academic Press: New York, 1969; p 93.

to the coupling of f to the nonequivalent methylene protons. Because of the rigidity of the system (vide infra), f has different torsional angles from those of d and e and thus different coupling constants. Therefore, the second-order multiplet due to f will be further split into a doublet of doublets by d and e, causing the complex pattern observed.

The 2.25-ppm split between d and e was unexpected, as was their appearance as a pentet and quartet, respectively. With the LAOCOON III program we were able to duplicate the observed spectral values and derive the chemical shifts and coupling constants. The d and e protons have a geminal coupling constant of -11.87 Hz. The doublet for each proton is also split into a triplet by f, so a total of six peaks (triplet of doublets) would be expected for each multiplet. That only a quartet and a pentet are seen is due to a fortuitous overlapping of peaks caused by J_{de} approximately equaling J_{ef}, and J_{de} approximately equaling half of J_{df}. Irradiation of f caused the two multiplets to collapse to doublets as would be expected.

The proton data do not reveal whether the downfield proton absorption at 4.88 ppm is to be associated with H-endo or H-exo. To make this distinction, a $^{13}C-^{1}H$ NOE experiment was performed in which the ^{13}C resonances (at 150.43 and 149.36 ppm) of the two pairs of quaternary carbons in the four-membered ring were recorded under the conditions: (1) proton irradiation off-resonance, (2) selective irradiation of the proton at 2.63 ppm, (3) selective irradiation of the proton at 4.88 ppm. From these data, the NOE enhancements (expressed as a percentage of the theoretical maximum enhancement) of the two ^{13}C resonances were 6 and 6% from irradiation of the upfield proton resonance at 2.63 ppm and 28 and 20% from irradiation of the downfield proton resonance at 4.88 ppm. The background root-mean-square noise introduces an uncertainty into the calculated NOE's corresponding to $s_{NOE} = 10\%$, which means that only the NOE from the interaction of the 4.88-ppm proton with the 150.43-ppm carbon is significantly different (at >95% confidence level) from zero. From the X-ray structure of **6** the distances of the 3H-endo proton to C_{11b}/C_{11c} and C_{8a}/C_{8b} carbons are 2.67 and 5.01 Å, respectively. For the 3H-exo proton the distances are 4.00 and 5.01 Å. It seems reasonable to conclude that the 3H-endo proton, which is by far the closest proton to C_{11b}/C_{11c}, can be associated with the downfield resonance at 4.88 ppm and 3H-exo proton resonates at 2.63 ppm. It also follows that C_{11b}/C_{11c} carbons can be associated with the ^{13}C resonance at 150.43 ppm.

This assignment was confirmed by a 400-MHz proton two-dimensional NOE correlation (2D-NOESY) experiment with a 0.5-s mixing time. Phase cycling was used to supress zero and double quantum coherence,[30] and the two-dimensional transformation was performed by the method of States et al.[31] to show the phase of the cross peaks. The 2-D spectrum was not symmetrized, and the cross-peak intensity data were obtained directly from individual traces in the second dimension. All 2-D cross peaks were negative, consistent with a predominately magnetic dipole origin, rather than chemical exchange.

The X-ray structure reveals that vinyl proton f is 3.00 Å from methylene proton e and 2.03 Å from methylene proton d. It was found that the trace corresponding to the upfield resonance at 2.63 ppm contained negative cross peaks with both the downfield methylene 4.88-ppm resonance and the 5.80-ppm vinyl resonance, with the former being much stronger as would be expected from its closer distance (1.44 Å) and the approximate $1/r^6$ dependence of NOE's. The trace corresponding to the downfield methylene resonance at 4.88 ppm contained the expected negative cross peak with the 2.63-ppm resonance, but no observable cross peak with the vinyl proton f at 5.80 ppm. As expected by symmetry, the trace corresponding to the 5.80-ppm vinyl proton contained a small cross peak with the upfield methylene proton at 2.63 ppm but no observable cross peak with the 4.88-ppm resonance. The absence

of an observable NOE between the vinyl proton and the methylene resonance at 4.88 ppm is consistent with the assignment of the more distant (3.00 Å) inner proton e to the downfield 4.88-ppm resonance and the closer (2.03 Å) outer proton d to the upfield 2.63-ppm resonance. Cross relaxation between protons at a distance of 3.00 Å is predicted to be slower by a factor of 80 than that between the methylene protons at 1.44 Å, while cross relaxation between protons at 2.03 Å is expected to be slower by a factor of only 8 than that between the methylene protons.

Finally, it should be noted that this assignment is consistent with the coupling constants derived from the LAOCOON III analysis and those expected from the empirical Karplus–Conroy[32] relationship: $J_{df} = 6.2$ (calcd), 6.61 (obsd); $J_{ef} = 12.4$ (calcd), 11.62 (obsd) Hz.

To find the barrier for equilibration of the two protons d and e, a series of 80-MHz NMR spectra were run at increasingly higher temperatures. As the temperature increased, the peaks lost their fine structure and broadened. At 165 °C the peaks were only slightly visible, at 180 °C they had disappeared into the baseline, and as the temperature was increased to 195 °C a broad band started to grow in at 3.75 ppm, halfway between the original two peaks. Using an approximation for the rate constant at coalescence[33]

$$k_c = \left(\pi\sqrt{2}/3\right)(\Delta\nu^2 + 6J^2)^{1/2} \tag{1}$$

and the Eyring equation, the barrier to equilibration was found to be 21.5 ± 0.8 kcal/mol. At room temperature this corresponds to a rate constant of 1.0×10^{-3} s^{-1} and a half-life of 11.1 min.

Attempts were also made to study this equilibration by using higher field NMR spectrometers in order to see the coupling in the fully equilibrated spectrum. However, as the field strength increases, the difference in hertz between the chemical shifts also increases and a higher temperature is needed to observe coalescence. At both 400 and 200 MHz a sufficiently high temperature could not be reached.

There are several plausible ways that the two protons could equilibrate at elevated temperatures. The apical carbon could pass through the center of the nine-membered ring (in-conformation) or around the outside. For each of these the transition state could be either planar or twisted. The heats of formation of these structures and for the lowest energy conformation of **6** were calculated by molecular mechanics using the Allinger MMPM force field. The structures of the twist conformations were calculated by imposing C_2 symmetry on the system. The twist-out conformation has the lowest heat of formation of the four calculated transition-state structures with the planar-out having the highest. The calculated ΔG for the equilibration through the twist-out conformation is 20.9 kcal/mol, in very good agreement with the experimental value of 21.5 kcal/mol.

In **7** the biphenylenic absorptions are more complicated. There are two overlapping ABC spin systems, as would be expected for this asymmetric molecule. The upfield region of its NMR spectrum (Figure 3) shows a broad peak for the allylic and benzylic protons and a pentet for the other methylene. The broad peak sharpened upon heating, indicating that at room temperature the sample is above its coalescence temperature. Upon cooling to -80 °C the broad peak split into two multiplets. To simplify the interpretation of these multiplets, the intervening methylene was irradiated to give the partially decoupled spectrum. The chemical shifts and coupling constants for the allylic and benzylic protons were determined with the aid of the LAOCOON III program. The benzylic protons absorb at 2.16 and 2.74 ppm with a coupling constant of -12.0 Hz. The downfield doublet is due to the proton closer to the plane of the biphenylene (Figure 4) and is probably shifted downfield by a combination of ring current and local anisotropy[33,34] effects. The allylic protons absorb at 2.11 and 2.81

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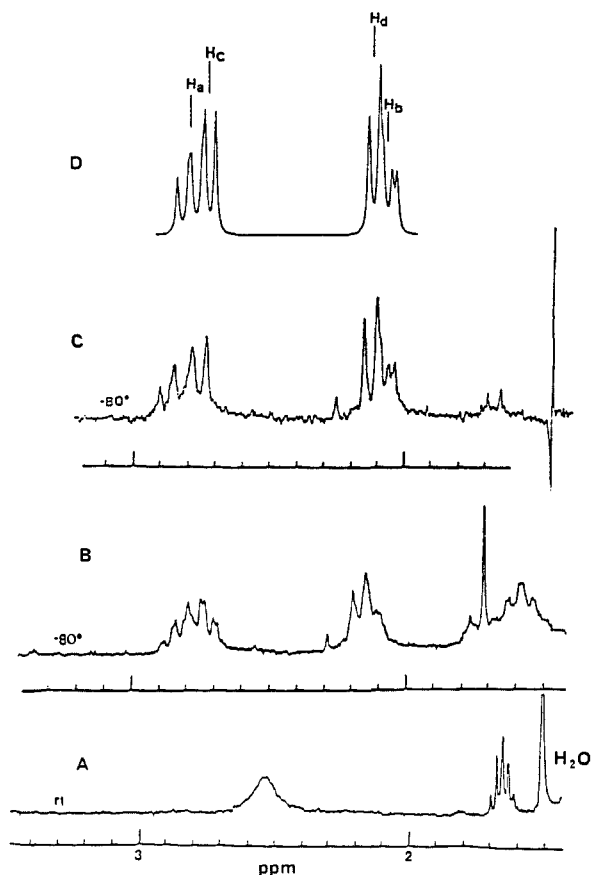
Figure 3. Upfield region of ¹H NMR spectrum of hydrocarbon 7: (A) taken at room temperature; (B) taken at low temperature; (C) partially decoupled at low temperature; (D) simulation of partially decoupled low-temperature spectrum.
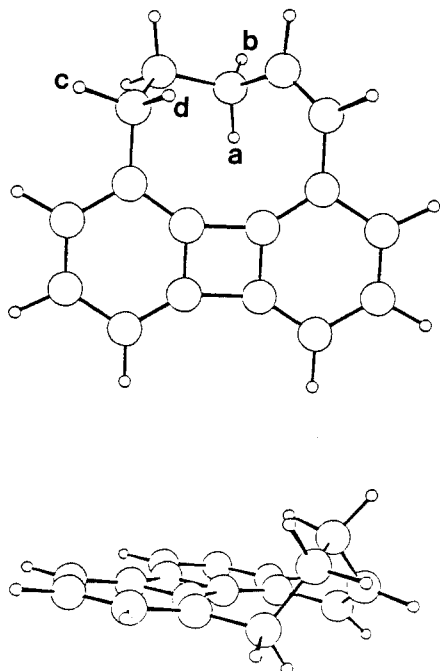

Figure 4. Molecular mechanics generated structure of 7.

ppm and have coupling constants to the adjacent vinyl proton of 4.7 and 11.1 Hz, respectively, and of −13.9 Hz to each other. Because of the low resolution at −80 °C, the doublet of doublets of the downfield allylic proton overlap to give a triplet with one of the peaks obscured. Two peaks of the upfield doublet of doublets are visible. The causes of the differences within the pair of allylic protons will be discussed below.

Table II. Vertical Ionization Energies (eV) of Hydrocarbons 4, 6, 8, and 9

compd	band	$I_{v,j}^{expll}$	assign-ment	$I_{v,j}^{K\,a}$ (MINDO/3)	$I_{v,j}^{c}$ (PPP)[b]
4	1	7.24	4a₂	7.52	7.15
(C₂ᵥ)	2	7.87	3a₂	8.06	8.83
	3	9.19	4b₁	9.53	8.42
	4	9.8	2a₂	10.04	9.70
	5	9.9	3b₁	10.17	9.89
6	1	7.39	18a″	7.69	7.59
(Cₛ)	2	8.00	17a″	8.20	8.00
	3	8.80	22a′	8.62	8.95
	4	9.8	21a′	9.98	9.80
	5	9.9	16a′	10.28	9.87
8	1	7.47	4a₂	7.75	8.64
(C₂ᵥ)	2	8.26	3a₂	8.39	8.21
	3	8.87	4b₁	9.05	8.75
	4	9.86	3b₁	10.09	9.87
	5	10.25	2a₂	10.77	9.88
9	1	7.57	2b₃g	7.73	7.72
(D₂h)	2	8.90	1aᵤ	8.92	8.70
	3	9.66	1b₂g	9.83	9.65
	4	10.06	2b₁ᵤ	10.02	9.90

$^a I_{v,j}^{K} = -\epsilon_j.$ ^{b} See eq 2.

Homoantiaromaticity. If 6 were homoantiaromatic, the paratropic ring current in the nine-membered ring would cause H-endo, sitting over the ring, to be shifted downfield from H-exo as is observed. This is opposite from what is calculated and observed in the homoaromatic homotropylium cation, where H-endo is shifted upfield from H-exo.[35]

As Paquette has discussed in his studies of potentially homoaromatic compounds, the distance R between two p orbitals and their angular orientation determine the overlap integral between them and the amount of conjugation.[36] Among the compounds he looked at, the overlap integral between the formally nonbonded p orbitals varies from 0.042 for cycloheptatriene (R = 2.51 Å, θ = 67.42°) to 0.066 for 1,4,7-cyclononatriene (R = 2.46 Å, θ = 54.18°).[36] None of the compounds studied showed evidence of ring currents so that in spite of the fact that some showed through space interactions (from their PE spectra), none were considered to be homoaromatic.[3b] From the X-ray structure of 6 (Figure 1), it was found that R = 2.50 Å and θ = 57.7°, giving an overlap of 0.056. Although this value lies in the center of the range of the Paquette values and might be taken as an indication that no homoantiaromaticity would be found, this proved not to be so.

Photoelectron Spectroscopy. He (I) photoelectron (PE) spectroscopy is the method of choice to investigate π systems that are suited to show homoconjugation. The investigations on cyclonona-1,4,7-triene,[37] triquinacene,[38] and related species[3b,d] have shown that weak interactions between π fragments can be detected if the fragments have the same basis orbital energies.[37] In 6 these prerequisites are fulfilled.

To elucidate the possibility of homoconjugation between the two ethylenic groups of 6 we have measured its PE spectrum and compared it with those of the related species 4 and 8. We assume that the latter systems represent examples with no (8) and full (4) conjugation between the termini of the ethylenic groups. Since both compounds have the same number of π electrons as does 6, they are ideal models to explore conjugative effects in 6. Together with the PE spectra of 4, 6, and 8 we also need the ionization energies of biphenylene (9) which were recorded some time ago.[39]

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(38) (a) Bünzli, J. C.; Frost, D. C.; Weiler, L. Tetrahedron Lett. 1973, 1159–1162. (b) Bischof, P.; Bosse, D.; Gleiter, R.; Kukla, M. J.; deMeijere, A.; Paquette, L. A. Chem. Ber. 1975, 108, 1218–1223.

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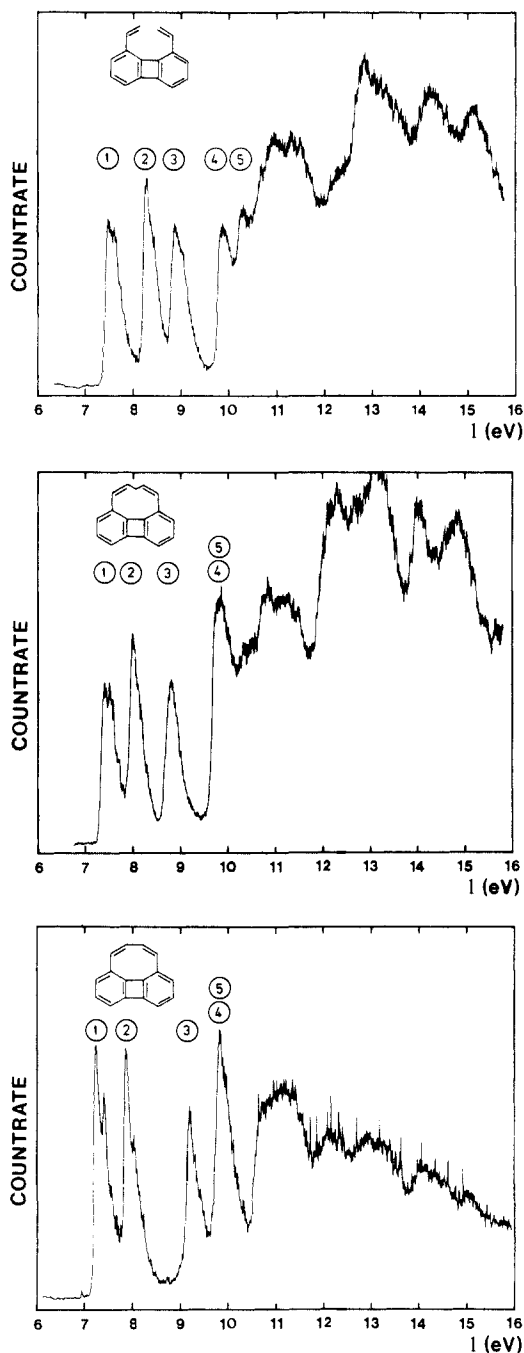Figure 5.　PE spectra of hydrocarbons **4, 6**, and **8**.

Figure 6.　Interaction diagram for formation of **8** from **9** and ethylene.

The PE spectra of **4, 6**, and **8** are shown in Figure 5.　In Table II the corresponding vertical ionization energies, $I_{v,j}$, are collected. All four spectra exhibit four to five bands below 10.5 eV showing a steep onset and a relatively small half-width.　This appearance is typical for ionizations from π electrons of fairly rigid skeletons. To relate these bands to the π molecular orbitals (MO's) of **4, 6, 8**, and **9**, we assume that the measured vertical ionization energies $(I_{v,j})$ can be set equal to the negative values of the calculated orbital energies $(-\epsilon_j)$ (Koopmans' theorem).[40]　This approximation holds quite well for larger π systems as exemplified by numerous investigations.

To calculate the molecular orbital energies of **4, 6, 8**, and **9**, we use the MINDO/3 method[41] and the PPP method.[42]　To
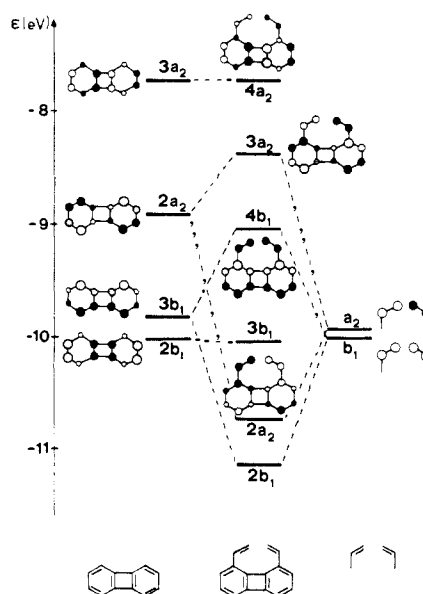
obtain accurate values for the ionization energies from the orbital energies, derived by the latter method, an empirical correction formula has been applied:[43]

$$I_{v,j} = -0.63 - 0.91\epsilon \qquad (2)$$

This formula has been derived by comparing ionization energies with calculated orbital energies of a number of nonbenzenoid aromatic compounds.[43]

To discuss the π MO's of **4, 6**, and **8** we start with the highest occupied π MO's of **9** which are shown on the left of Figure 6. The π MO's of **8** can be derived from those of **9** by interacting two π MO's of two ethylene fragments with those of the biphenylene moiety at positions 1 and 8.　The resulting interaction diagram is shown in Figure 6.　For the basis orbital energies of **9** at left and two vinyl groups at right, we used the result of a MINDO/3 calculation on **9** and propene.　The resulting π MO's of **8** (center of Figure 6) were calculated by the same procedure assuming C_{2v} symmetry.

The interaction diagram leading to **8** shows that the highest occupied MO (HOMO) of **9** will only weakly interact with the two vinyl groups because of large energy difference of the corresponding basis orbital energies and the small AO coefficients at centers 1 and 8 of the biphenylene moiety.　The interaction between $2b_1$ and the vinyl groups is also very minute because of the small AO coefficients at positions 1 and 8 of the biphenylene skeleton.　The main interaction takes place between $2a_2$ and $3b_1$ (see Figure 6) of **9** and the linear combinations of the ethylene fragments.

The resulting interaction pattern for **8** (center of Figure 6) agrees very well with the band pattern of the corresponding PE spectrum (Figure 5).　In both cases we notice three levels nearly equally spaced, separated by about 1 eV from the levels of lower orbital energy.

Starting from the π MO's of **8** we can derive easily the MO's of **4** by allowing the two termini of the vinyl groups to interact with each other.　Using first-order perturbation theory[44] as a guide, we conclude that $4a_2$, $3a_2$, and $2a_2$ will be destabilized while $4b_1$ and $2b_1$ will be stabilized; $3b_1$ should remain constant.　The corresponding correlation diagram, based on the results of a MINDO/3 calculation on **8** and **4**, is given in Figure 7.　A comparison with the MO's predicted for **4** and the PE spectrum

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(42) (a) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466–471, 767–776.　(b) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375–1385.

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(44) (a) Heilbronner, E.; Bock, H. *Das HMO Modell und Seine Anwendung*, Verlag Chemie GmbH: Weinheim, 1968.　(b) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

3H-Cyclonona[def]biphenylene

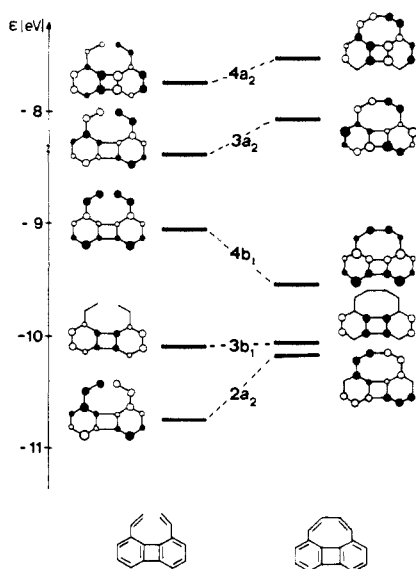*J. Am. Chem. Soc., Vol. 108, No. 24, 1986* 7699

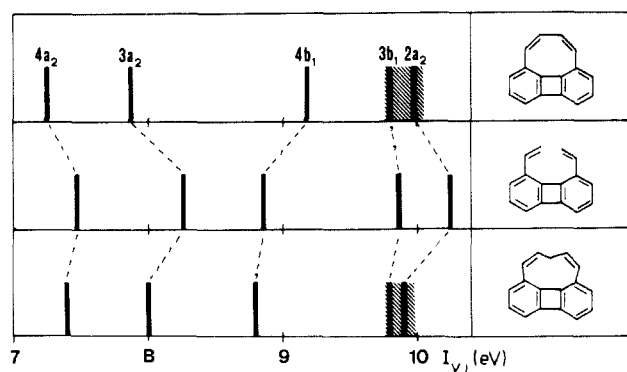Figure 7. Correlation diagram for interconversion of 4 and 8.

Figure 8. Comparison of ionization energies of 4, 6, and 8.

shows a close agreement between experiment and calculation (see also Table II).

If the resonance integral for the homoconjugation between the two termini of the ethylenic groups in 6 is less than the resonance integral between nearest neighbors, the π MO's of 6 should be close to those of 8. A comparison between the ionization energies of the first five bands of 6 and 8 confirms this statement (see Figure 8 and Table II). In going from 8 to 6 we encounter only a small shift of the first, third, and fourth bands (ca. 0.07 eV), while the second (0.26) and the fifth (0.35) are shifted sizably toward lower energy.

To rationalize the difference of both π systems we can discuss four effects: (i) a twist of the two ethylenic groups in 6 and 8 out of the biphenylene plane, (ii) an inductive effect of the CH_2 group in 6, (iii) a hyperconjugative effect of the CH_2 group in 6, (iv) homoconjugation between the two ethylenic groups in 6, separated by 2.5 Å.

To discuss the difference between 6 and 8 with respect to the bending of the vinyl groups, we have to know the structural details of both species. The twist angle of 6 was determined to be about 20° by X-ray investigations. To obtain a reliable value for 8, force field calculations were carried out using a π-SCF force field.[45] It is predicted that both vinyl groups in 8 are twisted by 30°. The resulting minimum geometry can be derived from the exo arrangement of both vinyl groups, coplanar with the biphenylene moiety. A conrotatory rotation of both vinyl groups out of the molecular plane by 30° will give the geometry with the lowest energy. The difference of only 10° in the twist angle of the two

vinyl groups in 8 and 6, respectively, allows us to assume that this difference can be ignored in our qualitative discussion. The inductive effect of the CH_2 group should destabilize all π levels by about the same amount. To judge this we compare the position of the fourth band in the PE spectra of 8 and 6. Both bands are approximately constant. We interpret this by assuming that the inductive effect is smaller than 0.1 eV.

The hyperconjugative effect should only show up in those MO's which are symmetrical with respect to the plane of symmetry, i.e., $4b_1$ (22a'), $3b_1$ (21a'). Because of the different size of the AO coefficients at the termini of 8, we expect a large effect for $4b_1$ but a very small one for $3b_1$. A comparison between the corresponding PE bands of both compounds yields about the same (small) effect for both bands.

The effect of homoconjugation can be directly seen by comparing 6 with 4 (Figure 7). In the latter compound the spatial interaction between both termini is just 1 β. We therefore expect a stabilization of $4b_1$ and a destabilization of all the other π levels up to 10 eV. With the exception of $4b_1$ this is the case.

Assuming that the inductive effect of the CH_2 group and the difference in twist angles between 6 and 8 can be ignored, we can rationalize the difference in the PE spectra of both compounds by assuming that the hyperconjugative effect of the CH_2 group in 6 and the homoconjugation between both ethylenic groups are about the same.

To place this qualitative discussion on a more quantitative basis, we have calculated the ionization energies of 8 and 6 together with those of 9 and 4 by the PPP procedure mentioned above. The results are listed in the last column of Table II. It is seen that the calculated values reproduce the band positions of all four molecules quite well. In the case of 8 we assumed a resonance integral of $\beta' = 0.8\beta_0$ between the biphenylene moiety and the vinyl groups to take care of the twist angle discussed above. For 6 the twist of the ethylenic groups was taken into consideration by $\beta' = 0.9\beta_0$. Varying the resonance integral for the two termini of the ethylenic groups in 6 from $\beta_{2-4} = 0$ to $+0.8\beta_0$ ($\beta_0 = -2.138$ eV), we obtained the results shown in Table II for $\beta_{2-4} = -0.7$ eV. The fairly good agreement between experiment and model calculations on 6 we take as an indication, but not as evidence, that there is a sizable homoconjugation between both termini in 6.

UV/Visible Absorption Spectroscopy. In favorable cases, the longest wavelength UV/visible absorption will reflect the amount of homoconjugation.[46,47] Hydrocarbon 4, which is fully conjugated, has a longest wavelength absorption at 621 nm,[12] whereas the nonconjugated 8 absorbs at 400 nm. If a homointeraction existed in 6, it should absorb somewhere between these two values. The longest wavelength absorption of 6 comes at 404 nm, reminiscent of the typical 5-nm red shift observed for the addition of alkyl groups to the ends of double bonds (Woodward shift). The situation in 6 is, however, more complicated than with simple double bonds. Because of the a symmetry of the HOMO (see Figure 7), the low-lying pseudo p orbital of the CH_2 group will not have its energy raised, whereas the LUMO, which has b symmetry, will mix and have its energy raised. The result is that in 6 the CH_2 group causes a *hyper*conjugative *blue* shift. The *homo*conjugative interaction between the termini of the double bonds has the opposite effect. PPP calculations carried out with a model[48] that reproduces the typical red shifts of alkyl groups in methylated benzenes yields a calculated *blue* shift of 5 nm. The difference of 9 nm between this result and the observed shift is attributed to homoconjugation. Using the same PPP model with varied β_{2-4} values, the observed shift was reproduced for a β value

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(46) Winstein, S.; Kreiter, C. G.; Brauman, J. I. *J. Am. Chem. Soc.* 1966, 88, 2047–2048.

(47) For an example where the UV effects do not reflect the amount of homoconjugation, see ref 10.

(48) The approach described by Pancir, J.; Matousek, I.; Zahradnik, R. *Collect. Czech. Chem. Commun.* 1973, 38, 3039–3066, was used with the CH_2 group represented by a pseudo p orbital contributing two electrons, a Z value of +2.0, an ionization potential of 25.00 eV, and a bond-length increment of 0.15 Å.

Table III. Calculated Chemical Shifts (δ) due to Double-Bond Local Anisotropies

	6		7
	X-ray[a]	MMPM[b]	MMPM[b]
H_{endo}	1.36	1.08	0.57
H_{exo}	0.32	0.26	0.15
$\Delta\delta_{calcd}$	1.04	0.82	0.38
$\Delta\delta_{exptl}$	2.25	2.25	0.70

[a] Using coordinates from X-ray structure. [b] Using coordinates from MMPM structure.

of $0.3\beta_0$. Thus the PE spectrum and the UV spectrum both indicate that there is a small but significant homoconjugative interaction.

Because of small values of the AO coefficients in the LUMO at the termini of the double bonds, the homoconjugative shift is not very sensitive to small values of β, but increases sharply (toward a λ_{max} of 621 nm) as β increases past $0.5\beta_0$ and second-order mixing of the other orbitals increases the coefficients. The combination of this insensitivity and a hyperconjugative blue shift manages to hide a significant homoconjugative interaction.

Homoantiaromatic Ring Currents. The value of $\beta = 0.30–0.33\beta_0$ estimated from the PE and UV/visible measurements is fully consistent with the value theoretically estimated from the X-ray structure. At a separation of 2.50 Å and an interorbital angle of 57.7°, the overlap integral is 0.056[33] which yields a β of $0.24\beta_0$. With this value of β a ring current of -0.22 relative to $+1.00$ for benzene is calculated for the nine-membered ring.[49] Using as a model for the ring current an in-plane-segmented current loop,[50] the endo H is calculated to resonate 1.13 ppm downfield from the exo H.

This estimate is quite different from the observed splitting of 2.25 ppm. An unreasonably large value of β would be required to reproduce the observed splitting and would lead to poor results for the remaining biphenylenic protons. It would appear that some other factor is contributing to the shift difference.

Local Anisotropy Effects. Another possible contributor for the chemical shift difference is the local anisotropy (LA) effect of the double bonds flanking the methylene carbon. Looking at the X-ray structure, it can be seen that the endo H is in the deshielding region of the double bonds[51] and would be shifted downfield. It is not obvious by inspection of models whether the exo H would be shielded or deshielded by the double bonds.

If one of the double bonds were removed and the geometric relationship between these protons and the remaining double bond did not change, the split between the exo and endo protons would decrease. If only local effects were operative, the split would decrease by a factor of 2 to 1.1 ppm. The geometry of 7, calculated by molecular mechanics[25] (Figure 4), was compared with the similarly calculated geometry of 6 and the two were found to be very similar.[52] On cooling, the resonances of the allylic protons of 7 split into two multiplets centered at 2.11 and 2.81 ppm. By virtue of its larger coupling constant to the adjacent ethylenic proton, the downfield multiplet can be assigned to the endo H. The observed split of 0.70 ppm is only a third of that of 6 instead of the expected factor of 2, possibly due to a change in the geometry of the allylic system not mimicked by the molecular-mechanics calculations or possibly due to changes in the double-bond LA contributions or, more probably, due to the presence of a ring current in 6 that is absent in 7. The existence of a significant chemical shift difference in 7 indicates that much of the split in 6 arises from local anisotropy effects.

To firm up the argument, the LA shifts were estimated using the model introduced by Grant et al.[34,53] The magnetic field of

Table IV. Calculated Chemical Shifts (δ) due to Ring Currents and Local Anisotropies for 6

proton	exptl	calcd	(exptl − calcd)
a	6.38	6.44	−0.06
b	6.64	6.52	+0.12
c	6.43	6.43	0.00
Δ(e−d)	2.25	2.11	+0.13
f	5.80	5.53	+0.27
g	5.86	5.72	+0.14

each double-bond carbon was approximated by the fields caused by electrons circulating in three mutually orthogonal current loops centered on each carbon atom with radii 0.47 Å. The magnitudes of the circulating electron density are chosen to reproduce the components of the shielding tensor, which in principle can be measured experimentally. As the experimental shielding tensors for 6 were unknown, the tensors measured by Grant and Michl for ethylene[54] and benzene[55] were used. To convert the tensorial components to absolute values, 205 ppm was added to each value for ethylene and 208 ppm to each for benzene.[34,53] The shielding due to the double bonds calculated for 6 and 7 are in Table III. The calculations for 6 were performed using both X-ray and molecular-mechanics coordinates, while for 7 only the molecular-mechanics coordinates were used.

Before drawing any conclusions from this calculation it is important to consider whether the use of shielding tensors taken from ethylene could be a source of major error. One might worry that the cis disubstitution of the double bonds might affect the shielding tensors. As it happens, however, the shielding tensors of cis-2-butene have been measured and are very similar to those of ethylene.[56] A more significant possible source of error in the shielding tensors could be the bend of the ethylenic hydrogens out of the plane of the double bond formed by the carbon framework. No estimates of this effect are available. Another major uncertainty in the LA calculations arises from the proximity of the methylene protons to the nearer ethylenic carbon (1.96 and 1.94 Å for the exo and endo protons, respectively). The representation of the magnetic fields as the sum of the fields produced by three current loops may break down at this distance. This is a common problem when using both the dipole and double-dipole approximations of local anisotropies. For example, ApSimon has suggested that the McConnell equation, which is widely used to calculate LA shieldings, does not give accurate results when the proton is closer than 3 Å from the dipole.[57] In the present calculations we have attempted to minimize this effect by using three current loops at each of the double-bond carbons rather than a single set at the center of the bond.

In spite of these concerns with the validity of the model, it is instructive to accept it at face value and then inquire as to what value of β is required to fit the NMR spectrum after correcting for the local anisotropy effects. The results of a least-squares fit are given in Table IV. The five chemical shifts for protons attached to sp^2 carbons and the chemical shift difference between the two methylene protons were fit as a function of β_{2-4}. The best value was found to be $\beta_{2-4} = 0.39\beta_0$, which gave a standard deviation in fit of the six experimental shifts of 0.06 ppm. This exceptionally good fit and agreement with the values of β estimated independently seems too good to be fortuitous. It strongly supports the earlier conclusion that 6 has significant homoconjugation and should be classified as homoantiaromatic.

It is worth noting that while fault might be found with any one of the several experimental and theoretical probes reported here,

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(50) Wilcox, C. F., Jr.; Rigos, A. A., manuscript in preparation.
(51) Günther, H.; Jikeli, G. *Chem. Rev.* **1977**, *77*, 599–637.
(52) These calculations uncovered another minimum 5.0 kcal/mol higher in energy than the one shown in Figure 4. This structure may be an intermediate on the pathway that equilibrates the allylic and benzylic protons at room temperature.

(53) Barfield, M.; Grant, D. M.; Ikenberry, J. *J. Am. Chem. Soc.* **1975**, *97*, 6956–6961.
(54) Zilm, K. W.; Conlin, R. T.; grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 8038–8039.
(55) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333–3334.
(56) Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672–6676.
(57) ApSimon, J. W.; Craig, W. G.; Demarco, P. V.; Mathieson, D. W.; Saunder, L.; Whalley, W. B. *Tetrahedron* **1967**, *23*, 2339–2355.

3H-Cyclonona[def]biphenylene

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their combination all pointing to the same conclusion is quite compelling.

3*H*-Cycloocta[*de*]naphthalene (10), a compound similar in geometry to **6**, is reported[58] to show the CH_2 in the NMR as a triplet at 3.08 ppm. At first glance it is surprising that the methylene protons are not split into two multiplets by LA effects. Indeed, the calculated LA shifts based on MMPM coordinates do predict a 0.70-ppm differentiation of the two protons. The endo H is further out of the plane of the double bond than in **6**, so it is not shifted as far downfield. Analogous to the method described above, the activation energy for the equilibration of the methylene protons of **10** was calculated by MMPM to be 8.3 kcal/mol at 25 °C. This barrier is low enough that the two protons will equilibrate rapidly on the NMR time scale, so only an averaged peak is observed.

Conclusion

The 2.25-ppm chemical shift difference of the methylene protons of 3*H*-cyclonona[*def*]biphenylene is due to a combination of a paratropic ring current and local anisotropies. The homointeraction amounts to about $0.3\beta_0$. This degree of interaction is supported by PE spectroscopy, UV/visible spectroscopy, and ¹H NMR. It is concluded that **6** *is* homoantiaromatic.

Experimental Section

General Methods. ¹H NMR spectra were recorded on a Brucker WM-300 (300-MHz) spectrometer in $CDCl_3$. Shifts are relative to the residual $CHCl_3$ peak (δ 7.240). ¹³C NMR spectra were recorded on a JEOL FX-90 (22.49-MHz) spectrometer in $CDCl_3$ with shifts relative to the central peak of the solvent triplet (δ 77.00). Mass spectra were obtained on an AEI MS902 mass spectrometer. UV–visible spectra were recorded in cyclohexane (Fisher Spectroanalyzed) on a Hewlett-Packard 8450A double-beam spectrometer. Infrared spectra were obtained on an IBM IR98 spectrometer. Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Benzene and THF were freshly distilled from sodium/benzophenone. Me_2SO was distilled from CaH_2 and stored over activated 4-Å molecular sieves. *N*-Bromosuccinimide (NBS) was recrystallized from 10 times its weight of water.[59] CCl_4 was stored over activated 4-Å molecular sieves. The silica gel used for column chromatography was ICN 32-63 mesh. *J* values are given in hertz.

1,5- and 1,8-Bis(bromomethyl)biphenylene. To a mixture of a ca. 1:1 mixture of 1,5- and 1,8-dimethylbiphenylene (10.07 g, 55.9 mmol) and NBS (20.30 g, 111.3 mmol), in CCl_4 (500 mL), was added dibenzoyl peroxide (ca. 10 crystals). The mixture was stirred and heated to reflux for 2 h while illuminated by an incandescent floodlight; refluxing was continued until no more NBS was present (4–8 h). The solution was cooled in a freezer and filtered to remove succinimide. The filtrate was evaporated in vacuo and the residual solid was triturated with cold hexane (25 mL). After traces of hexane were removed in vacuo, a tan mixture of 1,5- and 1,8-bis(bromomethyl)biphenylene (15.85 g, 84%) remained: mp 154–175 °C dec (lit.[12] 150–175 °C dec); identical by ¹H NMR with an authentic sample.

1,8-Biphenylenedicarboxaldehyde. To a ca. 1:1 mixture of 1,5- and 1,8-bis(bromomethyl)biphenylene (3.66 g, 11 mmol) in Me_2SO (30 mL) was added silver tosylate (6.80 g, 24.0 mmol). The mixture was stirred for 2 h and then triethylamine (5 mL) was added (the suspension turned from dull green to bright orange). After 15 min a gooey solid was removed by filtration into a separatory funnel. Water was added and the mixture extracted with Et_2O (4 × 50 mL). The combined ether extracts were washed consecutively with 5% H_2SO_4, saturated $NaHCO_3$ (aq), water (2×), and brine. The bright orange ether layer was dried (MgSO₄), filtered, and concentrated in vacuo to afford an orange solid. The desired product was isolated by flash chromatography on a 3 × 35-cm silica gel column with benzene elution. The third long-wave active band off the column yielded 0.25 g (22%) of 1,8-biphenylenedicarboxaldehyde, identical by ¹H NMR with an authentic sample.

(*Z*,*Z*)-3*H*-Cyclonona[*def*]biphenylene (6). In an oven-dried flask under a N_2 purge were placed dry benzene (800 mL) and 1,3-bis(triphenylphosphino)propane (3.52 g, 4.8 mmol); the suspension was stirred for 1 h under N_2. KO-*t*-Bu (2.50 g, 22.0 mmol) was added quickly and the mixture was stirred for 85 min during which time the contents turned bright orange and all the solids dissolved. 1,8-Biphenylenedicarboxaldehyde (1.00 g, 4.8 mmol) in dry benzene (200 mL) was added drop-

wise to the stirring solution of the bis-ylide over 45 min. After stirring overnight under N_2, the black solution was washed with water (2×) and with brine. The combined aqueous layers were back-extracted with benzene, and the benzene extract dried ($MgSO_4$). The resulting yellow solution was filtered and evaporated in vacuo to an orange oil that slowly solidified. This residue was dissolved in a few milliliters of CS_2 and flash chromatographed on a silica gel column with CS_2 elution. The fast yellow band was collected and passed through silica gel in a fritted-glass funnel with CS_2 to remove remaining polar impurities. Removal of solvent yielded a yellow solid (0.205 g) which was further purified by sublimation (100–115 °C, 1 torr) to give **6** (0.156 g, 15%): mp 111–117 °C (pentane); UV λ_{max} (log ϵ) 215 (4.53), 257 (4.38), 268 (4.36), 280 (4.36), 368 (3.65), 388 (3.68), 404 (3.50); ¹H NMR δ 6.64, 6.43, 6.38 (ABC, J_{AB} = 6.85, J_{BC} = 8.26, 6 H), 5.91–5.75 (complex multiplet, 4 H), 4.88 (dt, J = 11.87, 11.62, 1 H), 2.63 (dt, J = –11.87, 6.61, 1 H); ¹³C NMR δ 150.43, 149.36, 132.58, 130.29, 128.68, 127.71, 126.63, 115.66, 30.39; mass spectrum *m/e* (relative intensity) 218 (2.58), 217 (15.93), 216 (100.0 M⁺), 215 (51.84), 214 (9.07), 213 (13.57), 190 (6.34), 189 (35.91), 188 (6.78), 187 (6.71), 95 (5.53), 64 (6.78); mass spectrum *m/e* 216.0940 (calcd 216.0939 for $C_{17}H_{12}$).

(*Z*)-1,2-Dibromo-2,3-dihydro-1*H*-cyclonona[*def*]biphenylene (11). A solution of **6** (7.5 mg, 0.035 mmol) in CCl_4 (5 mL) was cooled to 0 °C, and Br_2 (0.018 mL, 0.035 mmol, 1.95 M) in CCl_4 was added. The reaction flask was covered with aluminum foil and the solution was stirred at 0 °C for 80 min. The pale orange solution in 20 mL of Et_2O was washed with water, aqueous sodium bisulfite (2×), water, and brine, and then dried ($MgSO_4$). Filtration and evaporation of the solvent in vacuo gave a pale yellow oil that was purified by chromatography on a silica-gel-filled pipet, with hexane. Evaporation of the hexane in vacuo yielded **11** as an oily solid (9.2 mg, 70%): ¹H NMR δ 6.80–6.54 (m, 6 H, ArH), 6.19 (d, J = 11.40, 1 H, ArC*H*=CH), 5.82 (dt, 1 H, ArCH=C*H*), 5.10 (d, J = 2.65, 1 H, ArCHBr), 4.79 (dt, J = 12.4, 2.65, 1 H, CH_2C*H*Br), 3.60 (dt, J = 12.4, 13.8, 1 H, CH_2), 2.84 (dt, J = 13.8, 2.65, 1 H, CH_2); ¹³C NMR δ 151.26, 150.43, 130.73, 130.34, 129.51, 129.32, 129.02, 128.49, 127.41, 117.71, 115.91, 50.13, 49.01, 36.00; mass spectrum *m/e* (relative intensity) 379 (2.76), 378 (14.99), 377 (5.34), 376 (28.20), 375 (3.27), 374 (14.42), 297 (14.65), 296 (8.56), 295 (14.07), 294 (7.01), 217 (15.97), 216 (100.0 M⁺ – 2Br), 215 (64.10), 214 (9.76), 213 (23.61), 189 (28.49), 188 (7.18), 187 (9.82); mass spectrum *m/e* 375.9302 (calcd 375.9287 for $C_{17}H_{12}{}^{79}Br^{81}Br$).

Reaction of 11 with $NaBH_4$. In a small flask were placed **11** (8.6 mg, 0.023 mmol), Me_2SO (3 mL), and sodium borohydride (excess), and the mixture was stirred for 2 h under a N_2 purge. The reaction mixture was stirred for an additional 19 h at 85 °C. The yellow reaction mixture was poured into 300 mL of dilute brine and extracted with hexane (3 × 15 mL). The combined hexane extracts were dried ($MgSO_4$) and filtered. Removal of solvent in vacuo gave a yellow solid (3.7 mg, 74%) that was identical with **6** by ¹H NMR.

1,2,4,5-Tetrabromo-2,3,4,5-tetrahydro-1*H*-cyclonona[*def*]biphenylene. A solution of **6** (7.5 mg, 0.035 mmol) in CCl_4 (5 mL) was cooled to 0 °C and Br_2 (0.04 mL, 0.078 mmol, 1.95 M) in CCl_4 added. The reaction flask was covered with aluminum foil and the solution was stirred for 2 h at 0 °C. The solution was diluted with Et_2O and extracted with aqueous sodium bisulfite and brine and then dried ($MgSO_4$). After filtration, the solvent was evaporated in vacuo to yield 13 mg of an orange oil, which was run through a silica-gel-filled pipet with CS_2. The resulting solution was separated into two components by flash chromatography on a 1.5 × 18-cm silica gel column with 1:1 (v/v) CS_2/hexane (21 3-mL fractions were collected). Fractions 3–15 were combined and the solvent was removed in vacuo to give **11** (8.0 mg, 61%), identical by ¹H NMR with an authentic sample. Fractions 16–21 gave the tetrabromide (5.0 mg, 27%): ¹H NMR δ 6.86, 6.61 (m, 6 H, ArH), 5.50 (dd, J = 6.9, 6.6, 2 H, C*H*BrCH₂), 5.21 (d, J = 6.9, 2 H, ArCHBr), 3.22 (dt, J = 15.7, 6.6, 1 H, CH_2), 2.78 (dt, J = 15.7, 7.6, 1 H, CH_2); mass spectrum *m/e* (intensity) 538 (6.47), 536 (9.95), 534 (6.60), 378 (19.00), 376 (36.22), 375 (13.60), 374 (18.71), 297 (15.59), 296 (22.39), 295 (16.88), 294 (20.20), 217 (17.75), 216 (100.00 M⁺ – 4Br), 215 (86.73), 214 (14.79), 213 (29.22), 189 (30.05), 187 (11.01); mass spectrum *m/e* 531.7684 (calcd 531.7675 for $C_{17}H_{12}{}^{79}Br_4$).

2,3,4,5-Tetrahydro-1*H*-cyclonona[*def*]biphenylene (12). In a dried flask under a N_2 purge were placed **6** (9.0 mg, 0.042 mmol) and diglyme (6 mL, dried over activated 4-Å molecular sieves). BH_3-THF (0.2 mL, 0.2 mmol) was added via an oven-dried syringe (some bubbling), and the reaction was stirred for 20 min. Propionic acid (0.1 mL, 1.34 mmol) was added and the reaction mixture was refluxed for 9 h. Et_2O (30 mL) was added and the solution extracted with water (75 mL). The ether layer was washed with water (2×), saturated aqueous $NaHCO_3$ (2×), and water. The colorless ether solution was dried ($MgSO_4$), filtered, and evaporated in vacuo to a yellow oil. The oil was put through a pad of silica gel in a fritted funnel with CS_2 and was further purified by prep-

(58) Nelson, S. F.; Gillespie, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1874–1882.

(59) Recent work from this laboratory (Cornell) shows that unrecrystallized NBS works better for this and similar benzylic brominations.

arative thin layer chromatography (Analtech Silica Gel, 2000 μ) with CS_2. Two bands were scraped off the plate and rinsed with CS_2. The upper band was not identified, but it was not starting material. The lower band was **12** (4.5 mg, 49%, pale yellow): mp 94–96 °C; ^{1}H NMR δ 6.65, 6.51, 6.49 (ABC, J = 9.4, 7.2, 6 H, ArH), 2.61 (t, J = 6.0, 4 H, ArCH_2), 1.77 (pentet, J = 6.3, 4 H, ArCH$_2$CH_2), 1.62 (pentet, J = 6.5, 2 H, ArCH$_2$CH$_2$CH_2); ^{13}C NMR δ 132.10, 131.07, 127.90, 114.59, 30.58, 24.54, 22.69; mass spectrum m/e (relative intensity) 221 (17.71), 220 (100.00 M$^+$), 219 (15.35), 218 (65.88), 217 (12.77), 216 (9.42), 215 (12.99), 205 (8.24), 204 (8.70), 203 (21.28), 202 (32.52), 192 (12.99), 191 (21.81), 190 (11.51), 189 (25.68), 179 (9.35), 178 (14.13); mass spectrum m/e 220.1258 (calcd 220.1252 for $C_{17}H_{16}$).

(Z)-2,3-Dihydro-1H-cyclonona[def]biphenylene (7). A solution of **12** (5.2 mg, 0.023 mmol) and NBS (4.2 mg, 0.024 mmol) in CCl_4 (5 mL) was refluxed for 6 h, the first hour under an incandescent floodlight. The reaction mixture was distributed between water and Et$_2$O, and the ether layer washed with water (2×) and with brine. The yellow ethereal solution was dried ($MgSO_4$), filtered, and evaporated in vacuo to yield a yellow oil. The oil was passed through a silica-gel-filled pipet with CS_2. Removal of solvent gave an oil which was used directly in the next step.

KO-t-Bu (0.03 g, excess) was stirred for 3.6 h with a solution of the oil in THF (5 mL) and then distributed between water and Et$_2$O. The ether layer was washed with water and brine, dried ($MgSO_4$), filtered, and evaporated in vacuo to a colorless oil. The oil was passed through a silica-gel-filled pipet with CS_2 elution and was further purified by flash chromatography on a 1.1 × 25-cm silica gel column with hexane. Removal of solvent in vacuo yielded **7** (4 mg, 77% based on **12**) as on oily pale yellow solid: ^{1}H NMR δ 6.65 (broad t, 2 H, ArH), 6.50 (m, 4 H, ArH), 6.22 (d, J = 10.4, 1 H, ArCH), 5.5 (quartet, 1 H, CHCH$_2$), 2.6–2.5 (m, 4 H, ArCH$_2$ and CHCH_2), 1.7 (broad pentet, 2 H, CH$_2$CH_2CH$_2$); mass spectrum m/e 219 (20.91), 218 (19.30 M$^+$), 217 (34.38), 216 (12.78), 215 (23.08), 213 (7.29), 203 (27.66), 202 (58.15), 191 (7.90), 190 (7.97), 189 (21.86); mass spectrum m/e 218.1084 (calcd 218.1095 for $C_{17}H_{14}$).

Photoelectron Spectroscopy. The He I PE spectra of the pure samples were recorded at 75 (**8**), 100 (**6**), and 90 °C (**4**) on a Perkin-Elmer PS 18 photoelectron spectrometer equipped with a He I light source. The spectra were calibrated with Ar and Xe. An estimated accuracy of ±0.05 eV was achieved for the single bands and of ±0.1 eV for the shoulders.

Single-Crystal X-ray Structure Determination of 6. Crystals of **6** were grown by slow evaporation of pentane solutions. A roughly cubic crystal with edges ca. 0.4 mm was cut from a larger crystal and used in all subsequent experiments. Preliminary X-ray photographs displayed orthorhombic symmetry, and accurate lattice constants of a = 17.020 (1), b = 8.4911 (6), and c = 7.8142 (5) Å were determined from a least-squares fit of 15 diffractometer measured 2θ values. The crystal density, 1.27 g/cm^3, indicated that four molecules of **6** made up the unit cell. The systematic extinctions were consistent with space group $Cmc2_1$. All unique diffraction maxima with 2θ < 114° were collected on a computer-controlled four-circle diffractometer using variable-speed 1° ω scans and graphite monochromated Cu Kα radiation (1.54178 Å). Of the 542 reflections measured in this fashion, 459 (85%) were judged observed (F_o > $3\sigma(F_o)$) after correction for Lorentz, polarization, and

background effects.[60] A phasing model was found without difficulty using a multisolution tangent formula approach.[60] All nonhydrogen atoms were easily located on the initial E synthesis. Hydrogen atoms were located on a ΔF synthesis after partial refinement of the nonhydrogen positions and thermal parameters. Block-diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens have converged to a crystallographic residual of 0.0529 (R_w = 0.0635) for the observed data. Further results of the crystallographic experiments are available and are described in the supplementary material paragraph.

Registry No. 4, 36230-20-3; **6**, 104642-21-9; **7**, 104642-22-0; **8**, 36230-21-4; **9**, 259-79-0; **11**, 104642-25-3; **12**, 104642-23-1; 1,3-bis-(triphenylphosphino)propane dibromide, 7333-67-7; 1,5-dimethylbiphenylene, 55277-56-0; 1,8-dimethylbiphenylene, 36230-17-8; 1,5-bis-(bromomethyl)biphenylene, 104642-24-2; 1,8-bis(bromomethyl)biphenylene, 36396-04-0; 1,8-biphenylenedicarboxaldehyde, 58746-94-4; 1,2,4,5-tetrabromo-2,3,4,5-tetrahydro-1H-cyclonona[def]biphenylene, 104642-26-4.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances and angles, and torsional angles for **6** (5 pages). Ordering information is given on any current masthead page.

(60) All crystallographic calculations were done on a PRIME 9955 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were the following: REDUCE and UNIQUE, data reduction programs by M. E. Leonwicz, Cornell University, 1978; MULTAN 78, MULTAN 80, and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses), written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978 and 1980; DIRDIF, written by P. T. Beurskens et al., University of Nijmegen, Netherlands, 1981; MITHRIL, an automatic solution package written by C. J. Gilmore, University of Glasgow, Scotland, 1983; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables, written by K. Hirotsu, Cornell University, 1978.