Cyclooctannelated Biphenylenes. Diagnosis of an Anomalous Bond Length by Analysis of Ring Current Geometric Factors[1]

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The syntheses and properties of the benzocyclobutene- and naphtho[b]cyclobutene-fused dicyclooctabiphenylenes **8** and **9** are described. These π systems show paratropic ^{1}H NMR effects with magnitudes between those of the parent hydrocarbon dicycloocta[def,jkl]biphenylene (**7**) and the cycloocta[def]biphenylenes **1**, **2**, and **3**. A complete ^{1}H NMR spectral analysis was performed on a series of 14 polycyclic hydrocarbons related to biphenylene (**10**) including **1–3** and **7–9**. A self-consistent Hückel–McWeeny ring current model provided an excellent description of the ^{1}H NMR spectra observed for these polycycles. Correlation of biphenylenic ^{1}H NMR chemical shifts with calculated ring currents for the polycycles **1**, **2**, **3**, **7**, **8**, **9**, and **10** afforded a semiempirical determination of ring current geometric factors for these systems. Deviations of certain observed geometric factors from theoretical "Biot–Savart" values were found to be diagnostic for an unusually long bond in the cyclobutene ring of the higher annelates **2**, **3**, **8**, and **9**.

One of the most noteworthy characteristics of conjugated π systems is the marked effect of topology upon magnetic behavior, and particularly upon NMR chemical shifts.[2] While there is little doubt that the chemical shift variation seen in conjugated systems is due in part[3] to differences in localized contributions to shielding/deshielding ("local anisotropies"),[4] the major part of this chemical shift variability is generally thought to result from changes in the delocalized electronic circulations ("ring currents").[5] The ring current model has been applied rather successfully to the ^{1}H NMR shifts of a multitude of conjugated systems, including benzenoid polycycles,[6] annulenes,[7] dehydroannulenes,[3] and porphyrins.[8] While there have been some ring current treatments of paratropic ("antiaromatic") polycycles,[9] these have been rather limited in scope due to the relative scarcity of experimental data.

A number of polycyclic hydrocarbons related to biphenylene (**10**) have been synthesized in this laboratory[10] and elsewhere.[11] These include the paratropic cyclo-

Chart I
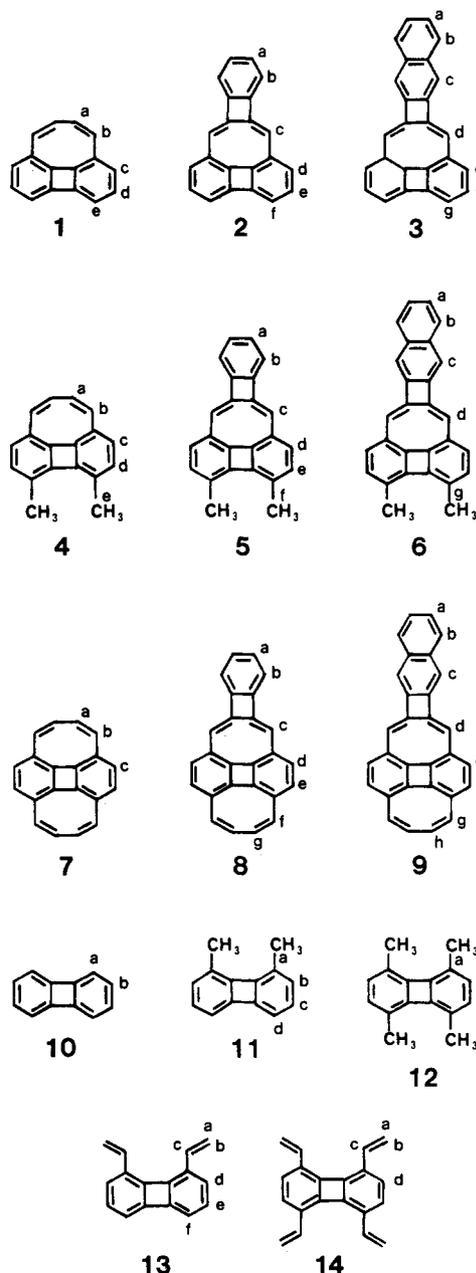
(1) Taken in part from the Ph.D. thesis of ENF, Cornell University, 1984.

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octa[def]biphenylene (**1**),[10a,b] the higher annelates **2**[10c,d] and **3**,[10e] and the strongly paratropic dicycloocta[def,jkl]bi-

phenylene (7).[10f,g] We have now prepared the annelated dicyclooctabiphenylenes 8 and 9, as well as the dimethyl polycycles 4,[10g] 5, and 6; we have also performed a complete ¹H NMR analysis of the entire hydrocarbon series 1–14 (Chart I). We wish to report these synthetic and spectroscopic results, and to present an examination of the resulting ¹H NMR data base by using the Hückel–McWeeny ring current model.[12]

Experimental Section

General Methods. ¹H NMR spectra were recorded on a Bruker WM-300 spectrometer with Me₄Si as an internal reference in CDCl₃. Mass spectra were obtained on an AEI MS902 mass spectrometer. UV–visible spectra were taken with Cary 219 and Cary 15 spectrophotometers. Melting points were determined with either a MEL-TEMP or Thomas-Hoover capillary apparatus. Melting and boiling points are uncorrected. THF was freshly distilled from sodium/benzophenone, and Me₂SO was dried over 4-Å molecular sieves. The following synthetic materials were prepared according to the references cited: glyoxal monomer,[10b,g] 1,4,5,8-tetrakis[(triphenylphosphonio)methyl]biphenylene tetrabromide (15),[10f,g] benzocyclobutenedione,[10c,13a] and naphtho-[b]cyclobutenedione.[10e,13b,c]

Benzo[3′,4′]cyclobuta[1′,2′:6,7]dicycloocta[1,2,3,4-def:1′,2′,3′,4′-jkl]biphenylene (8). A 500-mL three-necked flask, equipped with a 125-mL addition funnel and magnetic stirrer, was charged with 2.00 g (1.27 mmol) of tetraphosphonium salt (15) and 200 mL of Me₂SO, and then the mixture stirred for 2 h while flushing with argon. Benzocyclobutenedione (0.18 g, 1.36 mmol) was dissolved in 50 mL of THF and placed in the addition funnel, and KOt-Bu (0.62 g, 5.52 mmol) was added to the flask. The solution of dione was then added dropwise over 0.5 h and the mixture allowed to stir for 1 h. The addition funnel was charged with 40 mL of glyoxal solution in THF (vide supra) and slow dropwise addition was begun, finally yielding a clear reddish-orange solution with suspended orange polymers. The reaction was allowed to stir for 0.5 h after completion of the addition, and was then poured into a separatory funnel with water (1 L) and CH₂Cl₂ (300 mL). The emulsified organic layer was drained, the aqueous layer was washed with CH₂Cl₂ (2 × 300 mL), and the combined organic layers were washed with water (5 × 1 L). The organic emulsion was bulk dried with Na₂SO₄, then rinsed free (CH₂Cl₂) and dried over MgSO₄. The solution was filtered and evaporated to a red oily solid. The residue was extracted by grinding well with CS₂ (4 mL), and the deep red extracts were chromatographed on a 2.5 × 30 cm silica gel column (Woelm, 32–63 μm), eluting with CS₂. The fast hydrocarbon fraction, consisting of overlapped red and green bands, was collected as a single fraction and evaporated to a dark red oily wax, 6.8 mg. NMR showed the product to consist of 4, 3.1 mg (1%), 5, 1.1 mg (¹/₃%), and 8, 2.6 mg (²/₃%). The product, dissolved in CS₂ (2 mL), was further purified by flash chromatography on silica gel (1.1 × 30 cm) with hexane elution. A faster red band yielded, upon evaporation, 4 as a red oil. A slower green band yielded light green needles upon evaporation, which proved to be a mixture of 5 and 8 in unchanged proportions.

5: ¹H NMR (300 MHz, CDCl₃) δ 7.45–7.29 (4 H, m, AA′BB′) centered 7.37, 6.4114 (4 H, s) resolved as AB doublets (J = 8.37 Hz) in CS₂, 6.1032 (2 H, s), 2.1064 (6 H, s).

8: ¹H NMR (300 MHz, CDCl₃) δ 7.49–7.41 (4 H, m, AA′BB′) centered 7.45, 5.8276–5.8002 (2 H, d, J = 8.235) centered 5.8193, 5.8078 (2 H, s), 5.5763–5.5485 (2 H, d, J = 8.351) centered 5.5624, 4.58–4.36 (4 H, m, AA′BB′) centered 4.47; mass spectrum, m/e (relative intensity) 328 (1.78), 327 (1.91), 326 (4.55), 317 (2.43),

316 (6.93), 313 (1.52); mass spectrum, m/e 326.1090, calcd 326.1095 for C₂₆H₁₄.

While none of these compounds showed the extreme instability of 7, it was found that all compounds related to 1 remain pure for longer periods of time when stored as dilute solutions in the freezer.

3,4-Dimethylbenzo[3′,4′]cyclobuta[1′,2′:6,7]cyclooocta-[1,2,3,4-def]biphenylene (5). The Wittig condensation of benzocyclobutenedione with the ylide of 15 was set up exactly as for 8. The solution of dione was added slowly dropwise over 3.5 h and the reaction was stirred for 22 h; it was then quenched by the addition of water (10 mL) and stirred for a further 1.5 h. The mixture was poured into a separatory funnel with 50% saturated brine (500 mL) and CH₂Cl₂ (200 mL). The organic layer was drained and the aqueous layer washed with CH₂Cl₂ (2 × 100 mL). The combined organic layers were washed with water (4 × 250 mL) and 25% saturated brine (1 L). The orange solution was dried over MgSO₄, filtered, and evaporated to a dark red oily solid. The residue was ground well with CS₂ (4 × 1 mL) to extract the product, and the extracts were placed atop a 2.5 × 30 cm silica gel column (Woelm, 32–63 μm). Elution with CS₂ produced a fast orange band, which was collected in a single 75-mL fraction. The product solution was evaporated to give red-orange powdery scales of solid, which were shown by TLC to consist of the dimethyl hydrocarbon (5) and tetramethylbiphenylene (12). The solid was dissolved in CS₂ (0.5 mL) and flash chromatographed on a 1.1 × 30 cm silica gel column with hexane under 10 psi of air. The slow orange product band was collected in a single fraction of 75 mL. Evaporation yielded 5 as fine red-orange needles: 15.4 mg (4%); mp 213–215 °C (as red scales from CCl₄); mass spectrum, m/e (relative intensity) 306 (3.78), 305 (26.95), 304 (100.00), 302 (8.21), 300 (10.66), 289 (5.86), 287 (6.85), 152 (11.59), 150 (9.17), 144 (6.82), 143 (7.41), 138 (4.34), 137 (4.13), 58 (4.16), 43 (9.20); mass spectrum, m/e 304.1242, calcd 304.1252 for C₂₄H₁₆.

Naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:6,7]dicyclooocta[1,2,3,4-def:1′,2′,3′,4′-jkl]biphenylene (9). A Wittig condensation was set up as described for 8 with 0.24 g (1.32 mmol) of naphtho-[b]cyclobutenedione in THF (55 mL). The solution of dione was then added dropwise over 1.5 h to give a slightly reddened mixture. A 40-mL portion of glyoxal monomer in THF (vide supra) was placed in the addition funnel and added dropwise to the reaction mixture over 0.75 h. The reaction slowly clarified to give a red solution and was stirred for an additional 0.25 h. The solution was poured into a separatory funnel with water (1 L) and CH₂Cl₂ (300 mL), producing a large quantity of fine red-orange polymers and an emulsified organic layer. The organic layer was drained and the aqueous layer washed with CH₂Cl₂ (2 × 100 mL). The combined organic layers were washed with water (2 × 1 L) to disperse the emulsion, and the polymer-containing aqueous layer was discarded. The organic layers were washed again with water (2 × 1 L) and saturated brine (500 mL) and then dried over MgSO₄. The solution was filtered and evaporated to yield a very dark red oil. The oil was treated with CS₂ (6 × 1 mL); the extracts were placed on a 2.5 × 30 cm silica gel column (Woelm, 32–63 μm) and eluted with CS₂. Two fast, colored bands emerged (faint red and deep olive green), which separated completely and were collected as two fractions. The first fraction was evaporated to give a waxy red crystalline solid, 2.5 mg (1%), identified as dimethyl compound 4: mp 114–117 °C.

The second (green) fraction gave upon evaporation a powdery green-brown solid, which appeared to be a mixture of green and red-brown components, 4.3 mg. NMR showed the product to be composed to the hydrocarbon 9, 2.6 mg (¹/₂%), and the dimethyl hydrocarbon 6, 1.7 mg (¹/₃%).

9: ¹H NMR (300 MHz, CDCl₃) δ 7.93–7.87 and 7.53–7.47 (4 H, m, AA′BB′), 7.7101 (2 H, s), 5.5653–5.5351 (2 H, d, J = 9.054) centered 5.5502 (distorted by superimposition of singlet), 5.5351 (2 H, s), 5.3385–5.3109 (2 H, d, J = 8.294) centered 5.3247, 4.34–4.16 (4 H, m, AA′BB′) centered 4.25; mass spectrum (high temperature only, obscured relative to CO₂), m/e 376 (2.42); mass spectrum, m/e 376.1229, calcd 376.1252 for C₃₀H₁₆.

6: ¹H NMR (300 MHz, CDCl₃) δ 7.89–7.83 and 7.49–7.43 (4 H, m, AA′BB′), 7.071 (2 H, s), 6.3848–6.3070 (4 H, d/d, AB, J = 8.399), 6.0598 (2 H, s), 2.0791 (6 H, s); mass spectrum, m/e (relative intensity) 356 (6.78), 355 (30.41), 354 (100.00), 353 (5.89), 352 (10.17), 351 (5.06), 350 (9.23), 339 (6.05), 337 (5.69), 177 (12.21),

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176 (5.84), 175 (9.02), 169 (6.16), 168 (7.36), 44 (28.38), 43 (16.01); mass spectrum, m/e 354.1398, calcd 354.1408 for $C_{28}H_{18}$.

3,4-Dimethylnaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:6,7]cyclo-octa[1,2,3,4-*def*]biphenylene (6). A Wittig condensation reaction was set up as for 8 with 0.89 g (0.57 mmol) of the tetraphosphonium salt 15, 0.30 g (2.7 mmol) of KO*t*-Bu, and 102.9 mg (0.57 mmol) of naphtho[*b*]cyclobutenedione in 65 mL of THF. The dione solution was added slowly dropwise to the ylide over 4 h. The reaction mixture was stirred overnight and then quenched with water (10 mL). The mixture was stirred for a further 1.5 h and was then poured into a separatory funnel containing CH_2Cl_2 (200 mL) and 20% saturated brine (500 mL). The mixture was shaken well, the red-orange organic layer was drawn off, and the aqueous layer extracted with CH_2Cl_2 (200 mL). The combined organic layers were washed with water (3 × 500 mL) and saturated brine (250 mL) and then dried over $MgSO_4$. The solution was filtered and evaporated to give an oily red solid, which was treated with CS_2 (4 × 1 mL) and ground well to extract the product. The dark red extracts were placed atop a 2.5 × 30 cm silica gel column (Woelm, 32–63 μm) and eluted with CS_2. The fast orange-red product band was collected as a single 40-mL fraction. Evaporation gave a light reddish-tan solid weighing 3.8 mg. The product was observed by NMR to be composed of the product dimethyl compound 6, 3.0 mg (1.5%), and some of the tetramethylbiphenylene 12, 0.8 mg. Flash chromatography of the product on a 1.5 × 25 cm silica gel column (Woelm, 32–63 μm), eluting with hexane/ether, gave pure 6 as a dark red-brown powdery solid: mp 252–254 °C dec.

Results and Discussion

Synthesis and Properties. Earlier syntheses[10a-e] of the polycycles 1, 2, and 3 employed a "bis-Wittig" technique[14] in which the cyclooctene ring was formed by condensation of 1,8-bis[(triphenylphosphonio)methyl]biphenylene dibromide with the appropriate 1,2-dicarbonyl component. This procedure was extended to the preparation of 7 in a "double bis-Wittig" reaction of glyoxal with the tetrakis(phosphonium) salt 15 (Scheme I). However, analogous attempts to prepare the fused polycycle 17 gave only traces of the dimethyl hydrocarbon 5. Concurrent studies in this laboratory[15] had shown the biphenylenoid ylides to be kinetically quite sensitive to the nature and degree of substitution in the carbonyl component. It was thus presumed that the second cyclization of 16 with benzocyclobutenedione was competing ineffectually with hydrolysis to 5. This raised the interesting possibility of a "mixed double bis-Wittig" reaction, whereby quenching of the intermediate bis(ylide) with the more reactive glyoxal would yield polycycle 8, which was predicted to exhibit greater paratropicity than 17. Indeed, the sequential addition of dicarbonyl components to ylide 16 produced the polycycles 8 and 9 in yields of $2/3$% and $1/2$%, which were comparable to yields obtained for 7 (1%). These reactions also produced the dimethyl hydrocarbon 4, and either 5 (with 8) or 6 (with 9) as well. While 4 was readily separable from 8 and 9 by flash chromatography, we were unable to separate the hydrolysis products 5 and 6 from 8 and 9. The identities of the contaminating dimethyl compounds were thus confirmed by independent hydrolytic syntheses from the intermediate bis(ylide), in yields of 4% and 1.5%, respectively.

The dimethyl polycycles 4, 5, and 6 proved to be virtually identical to the parent hydrocarbons 1, 2, and 3 in all respects. In particular, the UV–visible spectra of the methylated compounds were found to be almost unchanged from those of the unsubstituted hydrocarbons (spectral data available as Supplementary Material, vide infra). This would seem to indicate band polarizations parallel to the long biphenylene axis,[16] which is in accord

Scheme I
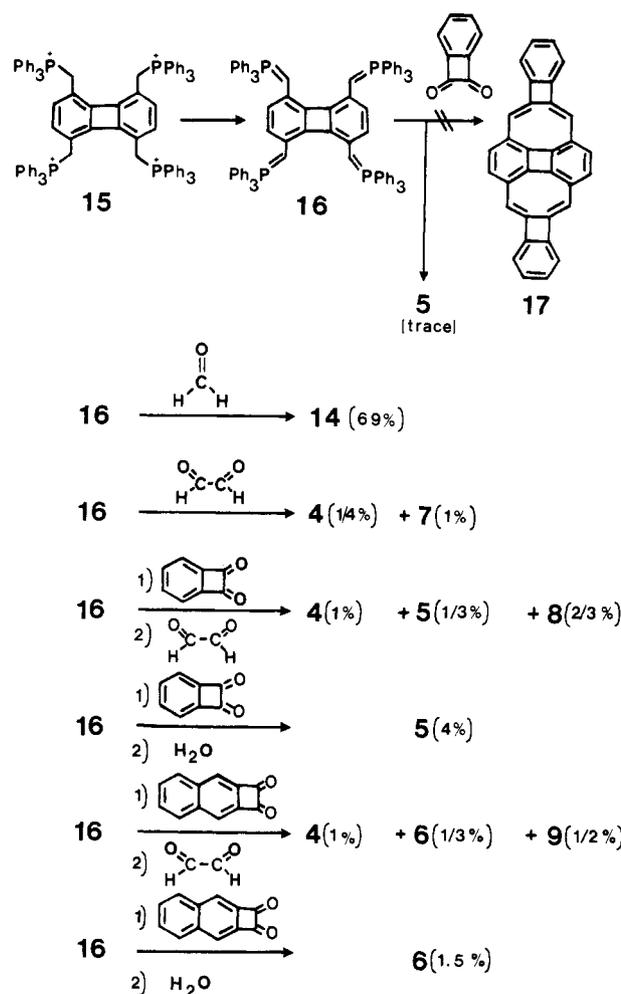
with calculations by Favini, Gamba, and Pitea[17] for 1, and with the long-wavelength transition moments predicted even by simple Hückel theory.

The dicyclooctabiphenylenes 8 and 9 were found to be less stable than 1, but somewhat more stable than 7, and could thus be kept as solids for short periods of time. Solutions of 8 and 9 were intensely green ("lime" and "olive", respectively), and gave UV–visible spectra that were clearly similar to 1 despite contamination with 5 and 6. The ^1H NMR spectra of 8 and 9 showed paratropic effects ranging between those of 1, 2, and 3 and those of 7. To the first approximation, shifts for the dicyclooctene systems appear exactly as might be expected by the superposition or annelation of 1 with either 1, 2, or 3. These NMR effects are discussed more fully in the following sections.

^1H **NMR Spectral Analysis.** The ^1H NMR chemical shift data for polycycles 1–14 (Table I) were obtained in a manner similar to that of Haigh and Mallion[6c] for benzenoid polycycles, though with some notable differences. Like the previous authors, we obtained spectra under standardized conditions, performed computer-assisted analysis of complex spin systems (LAOCOON III),[18] and

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Table I. ¹H NMR Chemical Shift Data[a]

proton δ	proton δ	proton δ
1	**6**	**11**
a 4.606	a 7.461	a 2.184
b 4.735	b 7.862	b 6.530
c 5.827	c 7.707	c 6.632
d 6.214	d 6.060	d 6.457
e 6.049	e 6.325	
	f 6.367	**12**
2	g 2.079	a 2.139
a 7.377		b 6.425
b 7.442	**7**	
c 6.154	a 3.626	**13**
d 6.511	b 3.587	a 5.335
e 6.630	c 4.549	b 5.644
f 6.427		c 6.739
	8	d 6.917
3	a 7.435	e 6.748
a 7.481	b 7.460	f 6.539
b 7.881	c 5.808	
c 7.749	d 5.813	**14**
d 6.096	e 5.563	a 5.341
e 6.419	f 4.524	b 5.655
f 6.571	g 4.412	c 6.762
g 6.371		d 6.955
	9	
4	a 7.502	
a 4.563	b 7.898	
b 4.715	c 7.710	
c 5.741	d 5.535	
d 6.012	e 5.551	
e 1.862	f 5.326	
	g 4.285	
5	h 4.212	
a 7.336		
b 7.398	**10**	
c 6.103	a 6.623	
d 6.411	b 6.728	
e 6.411		
f 2.107		

[a] The precision of these measurements was ±0.0006 ppm; deviations from infinite dilution are estimated to be about ±0.005 ppm. See text for further discussion of method.

made final comparisons by graphical inspection of calculated (CALCOMP) and observed spectra. However, the present spectra were all taken at 300 MHz in CDCl₃ solutions (<¹/₁₀% Me₄Si internal reference), as opposed to 60–220 MHz in CCl₄, and our data are not extrapolated to infinite dilution. The latter point is probably of less concern, since all samples were quite dilute (<10 mg/mL), and any deviations should be even less significant in comparison to the larger range of chemical shifts in the present study (~4 ppm). The use of CDCl₃ solvent, though, deserves some comment. While the CCl₄ solvent system is advantageous due to higher isotropicity[6c] and less π-dipolar interaction[19] than CDCl₃, we have found the latter solvent to give improved FT NMR spectral resolution and lock stability.[20] Though the use of CDCl₃ induced only a small shift compared to CCl₄, the mixing of our CDCl₃ data with

those from CCl₄ solutions is inadvisable for highly quantitative work.

Ring Currents. The relative paratropicities of both the mono- and dicyclooctabiphenylenes are well described by an iterative McWeeny ring current model.[10b,f,g,12] Ring current values (Table II) are in accord with the observed ordering of general paratropicity (**7 > 9 > 8 > 1 > 3 > 2 > 10**). Particularly notable in both the calculated ring currents and the observed chemical shifts is the marked reduction of paratropicity due to cyclobutannelation in the higher polycycles **2**, **3**, **8**, and **9**. Furthermore, the paratropicity of the unfused cyclooctene rings in **8** and **9** is only partially diminished relative to **7** by fusion of the opposite cyclooctene ring. These facts are readily rationalized by the conjugated circuit theory,[21] which predicts the [4]/[8] ring fusion to produce several [10]π circuits analogous to the periphery of the weakly diatropic bicyclo[6.2.0]decapentaene.[22] The effects of these additional circuits should become weaker with increasing distance within the molecular framework, as is observed. The effects of fusion are also explained by Kruszewski's rule,[23] which predicts cyclobutannelation at an edge of low bond order to produce a relatively stabilizing effect, and presumably greater diatropicity. As the increased opposing bond order of the benzo edge relative to the naphtho[b] edge should produce a greater retention of the pure cyclobutene fusion stabilization, one would expect the naphthannelates **3** and **9** to exhibit lower "stability" and diatropicity, which is indeed observed.

The order of the methyl proton shifts for hydrocarbons **4**, **5**, **6**, and **11** is also reflected by the magnitude of the biphenylenic B ring current in the respective unsubstituted hydrocarbons **1**, **2**, **3**, and **10**. The observed shifts are spread between those of toluene (δ 2.35, J = +1.0) and 1-methylcyclohexene (δ 1.65, J = 0.0); a simple interpolation considering only the B ring current gives "observed" ring current values of +0.303, +0.652, +0.613, and +0.763 for systems **4** (**1**), **5** (**2**), **6** (**3**), and **11** (**10**), respectively. Calculated values for the last three systems are thus indicated to be a bit too paratropic, which is not unreasonable due to both the nature of the calculations[10g,24] and to the presence of anomalously long bonds not accounted for by the model (vide infra). Hydrocarbon **4** appears to be slightly more paratropic than calculated; this is probably due to the cyclooctene ring current neglected in this interpolation.

A more quantitative correlation of calculated ring currents with the chemical shift calculations was also performed and is discussed in the following section.

Ring Current Geometric Factors. Most ring current models describe the ¹H NMR chemical shift δ_r as a function of relative ring currents J_i and relative geometric factors K_{ri} for the ith ring and the rth proton:[5,6h]

$$\delta_r = \delta_0 + \sum_{i=1}^{n} J_i K_{ri} \tag{1}$$

where δ_0 is the hypothetical shift of an atropic sp²-bound

(19) The π-dipolar interaction affects primarily the dipolar proton shift (due to geometric factors), and thus the use of CHCl₃ as a *reference*; it is most notable at high concentrations of the π component: (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High-resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959; pp 428–431. (b) Jackman, L. M. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: New York, 1959; pp 45–46. This effect has been used as an empirical criterion of aromaticity: Anet, F. A. L.; Schenck, G. E. *J. Am. Chem. Soc.* **1971**, *93*, 556–557. The effect is undoubtedly operative in our spectral samples, but any induced shifts of hydrocarbon resonances should be quite small and relatively uniform.

(20) Our spectra exhibited a considerable degradation of resolution when external capillary or remote locking techniques were employed, or when the locking procedure was omitted. The vastly superior resolution of the CDCl₃-locked spectra was judged to outweigh the potential for undesirable solvent effects.

(21) (a) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68–70. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444–450. (c) Randić, M. *Tetrahedron* **1977**, *33*, 1905–1920. (d) Randić, M. *Pure Appl. Chem.* **1980**, *52*, 1587–1596. (e) Randić, M. *Pure Appl. Chem.* **1983**, *55*, 347–354. (f) Gomes, J. A. N. F. D. Phil. Thesis, Oxford, 1976. (g) Gomes, J. A. N. F.; Mallion, R. B. *Rev. Port. Quim.* **1979**, *21*, 82–89. (h) Gomes, J. A. N. F. *Theor. Chim. Acta* **1981**, *59*, 333–356.

(22) (a) Kabuto, C.; Oda, M. *Tetrahedron Lett.* **1980**, *21*, 103–106. (b) Oda, M.; Oikawa, H. *Tetrahedron Lett.* **1980**, *21*, 107–110.

(23) Kruszewski, J. *Pure Appl. Chem.* **1980**, *52*, 1525–1540.

(24) (a) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598. (b) Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1981**, *46*, 719–727. (c) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–1548.

Table II. Iterative McWeeny Ring Currents[a]
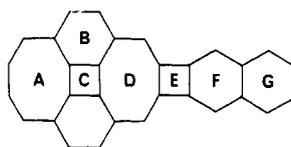
				polycycle			
ring	1	2	3	7	8	9	10
A				−1.071	−0.870	−0.927	
B	+0.369	+0.478	+0.449	−0.091	+0.138	+0.075	+0.608
C	−0.745	−0.777	−0.769	−1.164	−0.942	−1.008	−0.804
D	−0.706	−0.313	−0.408	−1.071	−0.478	−0.633	
E		+0.180	+0.110		+0.335	+0.218	
F		+0.966	+0.970		+1.030	+1.033	
G			+0.992			+1.013	

[a] Relative to benzene unit ring current = +1.000
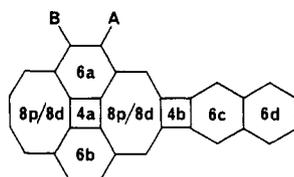
Figure 1.

proton. The J_i are expressed relative to benzene ($J_{benzene}$ = +1.00), while the K_{ri} also contain a proportionality constant reflecting the shift per unit ring current ($K_{benzene,attached} \approx$ +1.5). The usual approach to ring current/chemical shift correlations involves the calculation of both J and K by any of a variety of models, followed by linear regression to obtain δ_0 and the proportionality constant (slope) of the JK summation.[6h] This approach has worked quite well in describing the chemical shifts of systems related to 1,[25] as it has for benzenoid systems.[2,6]

The current data set presented the unusual feature of having the number of shifts $n(\delta_r)$ exceed the number of geometric factors $n(K_{ri})$ for the β protons of the biphenylene substructure. This allowed us to treat the biphenylene β proton geometric factors as unknowns, and to solve for these quantities with calculated ring currents and observed chemical shifts. The resulting "observed" geometric factor values could then be compared with theoretical values, such as those derived from the "Biot-Savart" geometric model.[7,26]

The geometric factors are designated K_{nxX}, where nx denotes the associated ring (e.g., 6c) and X designates the proton (A or B); these codes are illustrated in Figure 1. It should be noted that the four possible cyclooctene ring geometric factors are reduced to two by symmetry, then denoted K_{8p} (proximal) and K_{8d} (distal). The biphenylene ring A and B factors are also equated by symmetry, giving a total of 11 unknown geometric factors. The chemical shift data for 1–3 and 7–10 yield 12 equations, but the ring currents for this set cannot distinguish K_{6a} from K_{6b} due to ring current identity. Addition of benzene to the data set introduces the asymmetry necessary for solution, though the separation of K_{6a} from K_{6b} is fixed by the benzene data and is thus purely formal. The quantity δ_o

Table III. Theoretical and Semiempirical Geometric Factors[a,b]

factor	"observed"	theoretical[c]
K_{6a}	1.377	1.404
K_{6b}	0.146	0.067
K_{4a}	0.137	0.084
K_{8p}	0.772	0.513
K_{8d}	0.224	0.217
K_{4bA}	1.044	0.047
K_{4bB}	1.181	0.019
K_{6cA}	0.032	0.054
K_{6cB}	−0.047	0.024
K_{6dA}	0.097	0.024
K_{6dB}	0.086	0.011

[a] Units of δ per unit benzene ring current. [b] Standard deviation of fit 0.0025 ppm for 13 shifts. [c] Calculated previously for a planar segmented current model with iterative McWeeny ring currents (ref 25).

was then set to 5.913 ppm,[27] giving 13 equations and 11 parameters.

Solution of the problem by least squares[28] reproduced the chemical shift data almost exactly (as would be expected for such a gross overparameterization), with an average deviation of 0.00082 ppm and a standard deviation of 0.0025 ppm. A clearer measure of the agreement is to compare the "observed" and theoretical geometric factors (Table III). While the match is only rough, the agreement of the results is surprisingly good in light of the myriad of error sources and approximations involved.[29] Indeed, the only really disturbing discrepancy is that of the K_{4b} factors, where the "observed" values are unbelievably large for such a small and distant ring. It seems likely that the K_{4b} discrepancy arises from an inadequacy in the ring current calculations. A probable source of the discrepancy involves the bond lengths in the 4b ring. As ring current calculations for paratropic species are known to be rather sensitive to bond alternation,[24] we were led to reexamine the calculated bond lengths for hydrocarbon 2, for which an X-ray crystallographic analysis has been performed.[10d]

(25) Wilcox, C. F., Jr.; Rigos, A. A. Manuscript in preparation. These calculations follow the strategy of Haigh, Mallion, and Armour (ref 6d) with the parametric scheme $\delta_{pred}(CCl_4)$ 1.404 × (H'/H'$_{benzene}$) + 5.92. The H' values were calculated with an in-plane Biot–Savart geometric model by using ring currents obtained from the iterated Hückel scheme outlined in ref 10c.

(26) Mallion, R. B. *Mol. Phys.* **1973**, *25*, 1415–1432.

(27) This value results from a correlation of our iterative McWeeny ring currents to benzenoid (ref 6c) and biphenylenoid (1, 2, and 10) ^{1}H NMR shifts (CCl$_4$) using an in-plane Biot–Savart geometric model (ref 25).

(28) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103, 162–167.

(29) The relative calculated geometric factors depend upon the geometric model adopted, ranging from a point magnetic dipole to parallel polygonal current loops, with many variants in between; the values given here also contain a proportionality constant derived from (primarily) benzenoid chemical shift data in CCl$_4$ (ref 6c, 25). The "observed" geometric factors reflect the errors and approximations of the iterative Hückel–London–McWeeny ring current model, as well as any experimental errors in the chemical shift data of this work.

Table IV. Geometric Factors as a Function of Bond Length Correction to Higher Fused Polycycles[a]

		bond increment[b] (iterated bond length[c])				
		0.000	0.023	0.043	0.063	0.083
factor	theory[d]	(1.463)	(1.491)	(1.516)	(1.540)	(1.563)
K_{6a}	1.404	1.377	1.377	1.377	1.377	1.377
K_{6b}	0.067	0.146	0.145	0.169	0.173	0.160
K_{4a}	0.084	0.137	0.135	0.153	0.152	0.139
K_{8p}	0.513	0.772	0.775	0.764	0.767	0.775
K_{8d}	0.217	0.224	0.225	0.218	0.220	0.228
K_{4bA}	0.047	1.044	0.226	−0.053	−0.451	−0.815
K_{4bB}	0.019	1.181	0.489	0.004	−0.392	−0.762
K_{6cA}	0.054	0.032	0.125	0.089	0.123	0.166
K_{6cB}	0.024	−0.047	0.038	0.099	0.159	0.228
K_{6dA}	0.024	0.097	0.000	−0.013	−0.054	−0.094
K_{6dB}	0.011	0.086	0.014	−0.030	−0.072	−0.113
std dev[e]		0.0025	0.0107	0.0305	0.0408	0.0503
av dev[e]		0.0008	0.0031	0.0101	0.0137	0.0167

[a] In δ per unit benzene ring current. [b] Increment added before iteration (in Å); does not reflect absolute change in calculated bond length. [c] In Å; calculated for [4]/[8] fusion bond of **2**. Values for other polycycles are within ±0.002 Å. [d] Calculated previously for a planar segmented current model with iterative McWeeny ring currents (ref 25). [e] Standard and average deviations of 13 shifts used to calculate K's.

The 4b/8 fusion bond of **2** has an unusually great length of 1.546 Å, which is not completely accounted for by the iterative Hückel model[30] (predicted[10d] = 1.463 Å without inclusion of σ strain, and 1.523 Å with strain). It is assumed that a similar bond length occurs in the related polycycles **3**, **8**, and **9**.

In order to test the hypothesis that the 4b/8 bond length was in fact the source of the K_{4b} discrepancy, ring currents were recalculated for all of the higher fused polycycles, with various bond length increments added to the 4b/8 bonds. The ring currents from the incremented treatments (see Supplementary Material) showed changes (generally diatropic) for all rings, with the major change occurring in the cyclooctene ring values. Calculations for four different increments from 0.02–0.08 Å were performed, and the results from each set were used to redetermine the geometric factors. The recalculated K_{nxX} (Table IV) strongly suggest that the 4b/8 long bond is the source of the K_{4b} geometric factor discrepancy. While small changes are visible in virtually all geometric factors, the K_{4b} factors exhibit a drastic change upon inclusion of bond increments, and rapidly decline to (impossibly) negative values as the experimental bond length is passed. The bond length at which the "observed" geometric factor matches the theoretical geometric factor is about 1.507–1.515 Å (compared to the measured length of 1.546 Å for **2**, and 1.397 Å for an undistorted sp^2–sp^2 bond). Thus, the deviations in the K_{4b} geometric factors are qualitatively diagnostic for the anomalous bond length found in these systems. The geometric factors, however, do not seem to offer a reliable *quantitative* estimate of the actual bond length.

The findings of Mallion and co-workers[24] are particularly applicable to the interpretation of the present results. These authors demonstrated the importance of bond length/bond order considerations in ring current calculations for paratropic species. Specifically, bond alteration was found to considerably reduce the magnitude (or even invert the sign) of paratropic ring currents. It was shown that self-consistency of resonance integrals with respect to bond length was necessary in order to obtain even

qualitatively reasonable ring currents; it was also pointed out that experimental bond lengths could function in this capacity as well.[24b] Because of this marked sensitivity to bond length, Mallion felt that calculated ring currents for paratropic species should be viewed cautiously, impeding their use as a criterion of "aromaticity", and especially "antiaromaticity".[24c]

The present results confirm Mallion's observations. While the generally higher quality of the iterative ring currents is visible in the rough match of theoretical and observed geometric factors, the inadequacies of the self-consistency procedure must show up as deficiencies in calculated ring currents, and thus in the geometric factor analysis. That we do find such a deficiency, and a rather dramatic one at that, should serve to amplify Mallion's warning concerning the lower reliability of paratropic ring current values. Moreover, our results reinforce the importance of "realistic" resonance integrals, in that self-consistency alone is not a sufficient condition for attaining reliable calculated ring currents. Our results illustrate the potential utility of experimental bond length data for ring current calculations when it is available.

While the analysis of ring current geometric factors is obviously a technique of only limited applicability, the important point is that the calculation-sensitive paratropic hydrocarbons presented here can be treated with even partial success. This further demonstrates the general validity of the iterative Hückel–McWeeny ring current method, and suggests that a better model for predicting bond lengths in paratropic species would lead to a reliable ring current parameterization applicable to planar π systems regardless of topology.

(30) The iterative Hückel model (ref 10c) employs β's that vary with calculated π-bond order. Bond lengths, which are assumed to vary linearly with the π-bond order, indirectly reflect changes in the underlying σ framework. Strained polycycles have additional bond length increments (ref 10d, 22b).

(31) Clar, E. P.; Pickett, L. W.; Voris, D. *J. Am. Chem. Soc.* **1941**, *63*, 3231–3232.