^{1}H NMR Study of Two Tetradehydrocyclodecabiphenylenes

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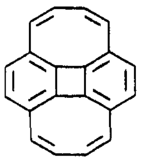
5,6,9,10-Tetradehydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**2**) and 5,6,9,10-tetradehydronaphtho[2,3:7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**3**) were prepared by a "bis-Wittig" reaction between 1,8-bis((triphenylphosphoranylidene)methyl)biphenylene (**5**) and *o*-phthalaldehyde (**8**), or 2,3-naphthalenedicarboxaldehyde (**9**), respectively. Bromination of the resultant alkenes and subsequent dehydrobromination gave the presumably planar alkynes, **2** and **3**. The experimental proton shifts of **2**, **3**, and three other arylalkynes were derived with the aid of the LAOCN3 program and compared with the shifts predicted by using ring currents calculated by an iterated HMO–McWeeny model and in-plane segmented current loops. It was found that the calculated shifts were typically upfield from those observed but that the differences could be accounted for by the inclusion of corrections for the both the electronegativity and local anisotropy of the triple bonds.

Introduction

Previous work from this laboratory has been concerned with the synthesis of various cyclooctabiphenylenes and a study of their frequently bizarre electronic and magnetic properties.[1] To cite a particularly striking example, dicyclooctabiphenylene (**1**) is an unstable blue-black hydrocarbon that was predicted to have virtually zero ring currents in the benzene rings.[1a,2] An empirical model was developed to relate chemical shifts with calculated ring currents that gave a precision of about 0.1 ppm.[3] When this model was applied to **1**, it successfully predicted the unprecedented ^{1}H NMR δ values of 4.5 and 3.6 for the benzene and cyclooctatetraene protons.[1]



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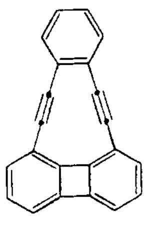

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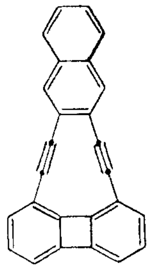

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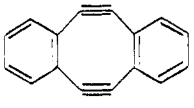
We wished to explore the extension of this empirical model to biphenylene-fused [10]annulenes. As a result of our previous work, we focused on hydrocarbons **2** and **3**. Although the inclusion of triple bonds introduces special challenges for any chemical- shift model, the overriding concern was to preserve planarity. This paper describes the synthesis of these hydrocarbons and the corrections that had to be introduced into the ring-current-chemical-shift model to take into account the special local anisotropy and electronegativity effects of the C_{sp} centers.

Synthesis

Construction of the [10]annulene was accomplished by means of a "bis-Wittig" reaction.[4] The cyclization and steps that follow are related to those employed by Sondheimer et al.[5,6] in the synthesis of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**4**). The biphenylene unit was introduced as 1,8-bis((triphenylphosphoranylidene)methyl)biphenylene (**5**), generated in situ from a mixture (ca. 1:1) of 1,8- and 1,5-bis((triphenylphosphonium)methyl)biphenylene dibromides (**6** and **7**) and excess (ca. 4 equiv) potassium *tert*-butoxide (KO-*t*-Bu) in Me$_2$SO. The bis(phosphonium) salts, **6** and **7**, were synthesized as described by Bekiarian.[7]



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Either *o*-phthalaldehyde (**8**) or 2,3-naphthalenedicarboxaldehyde (**9**) (2 equiv), was added over a 20-h period to the bis(ylide) to afford benzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**10**) or naphtho[2,3,7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**11**) in 20 or 14% yield, respectively (based on **6**). The hydrocarbons were purified by an extractive workup and then by column chromatography. Both products were mixtures of cis,cis, cis,trans, and trans,trans geometric isomers (Scheme I).

While protected from light,[8] the alkenyl-bridged compounds, **10** and **11**, were brominated (2 equiv) at 0 °C and then stirred (ca. 12 h) at room temperature. After the recovered dibromo adducts of **10** and **11** were recycled, separation by column chromatography afforded 5,6,9,10-tetrabromo-5,6,9,10-tetrahydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**12**) and 5,6,9,10-tetrabromo-5,6,9,10-tetrahydronaphtho[2',3':7,8]cyclodeca[1,2,3,4-*def*]biphenylene (**13**) in 56 and 48% yields, respectively. The tetrabromides were isolated as an inseparable mixture of diasteromers.

The difficulty in tetrabromination of **10** and **11** is similar to that encountered by other workers[9] in the bromination of dibenzo[*a*,*e*]cyclooctene, which was carried out under irradiation at an elevated temperature (60 °C) to obtain addition of the second equivalent of Br$_2$, even though the first equivalent added at 0 °C. Our conditions were restricted to low temperature and exclusion of light in order to avoid bromination of the biphenylene four-membered ring.[8]

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(1) (a) Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195–7200, and references therein. (b) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351–356.

(2) For an interesting nonalternant example see: Nazuhiro, N., et al. *J. Am. Chem. Soc.* **1983**, *105*, 5136–5137.

(3) Wilcox, C. F., Jr.; Rigos, A. A., manuscript in preparation.

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

(5) Wong, H. N. C.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1974**, *96*, 5604–5605.

(6) Huang, N. Z.; Sondheimer, F. *Acc. Chem. Res.* **1982**, *15*, 96–102.

(7) (a) Bekiarian, P. G. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1981. (b) In the ethylene glycol codistillation the spinning-band column was omitted.

(8) Barton, J. W.; Henn, D. E.; McLaughlan, K. A.; McOmie, J. F. W. *J. Chem. Soc.* **1964**, 1622.

(9) (a) Cava, M. P.; Pohlke, R.; Erickson, B. W.; Rose, J. C.; Fraenkel, G. *Tetrahedron* **1962**, *18*, 1005–1011. (b) Avram, M.; Dinulescu, I. G.; Dinu, D.; Mateescu, G. *Tetrahedron* **1963**, *19*, 309–317.

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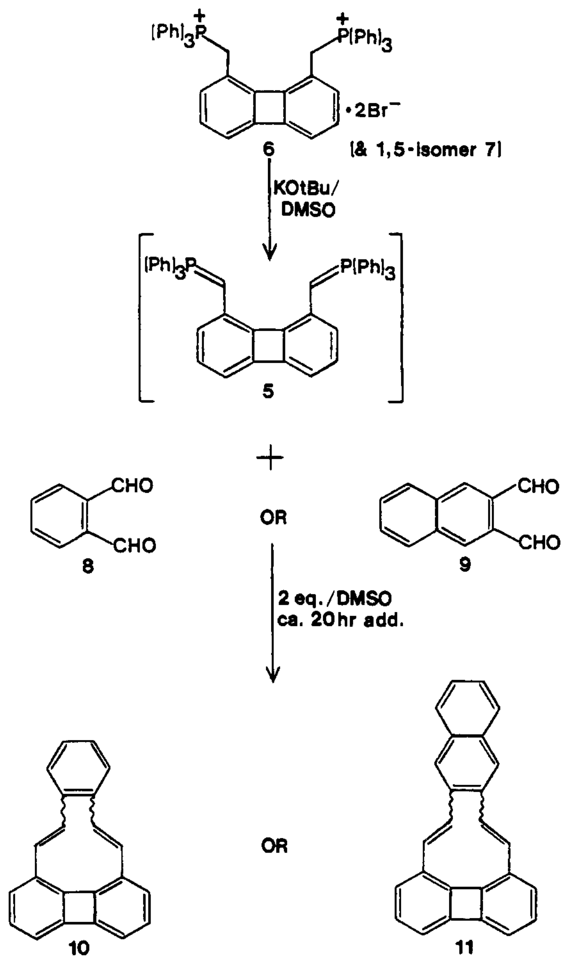
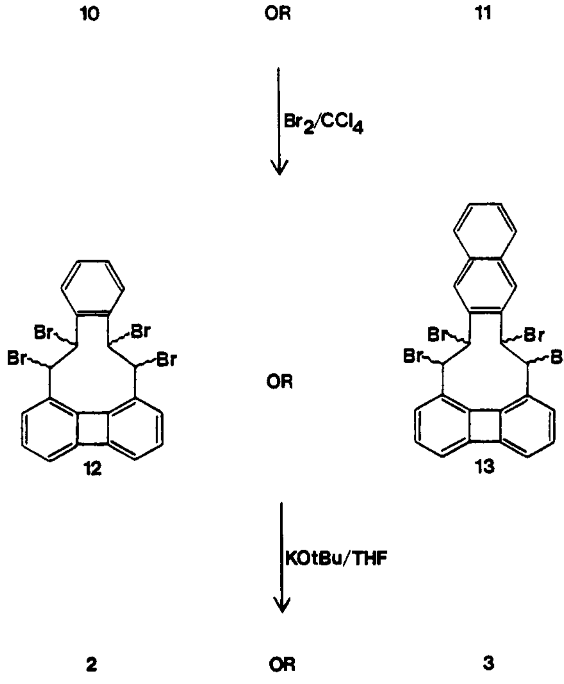
Scheme I



Scheme II



Tetradehydrobromination of the tetrabromides was accomplished with 6 equiv of KO-*t*-Bu in dry tetrahydrofuran (THF),[5] which after 1 h afforded **2** and **3** in 88 and 84% yields, respectively (Scheme II).

Dialdehyde **9** is a known compound but we chose to prepare it by a different route. Reduction of 2,3-naphthalenedicarboxylic acid (**14**) with 2 equiv of borane–THF complex (BH_3·THF) in THF[10] afforded 2,3-bis(hydroxymethyl)naphthalene (**15**) in 82% yield. Diol **15** was in turn brominated with 2 equiv of phosphorus tribromide (PBr_3) in dichloromethane (CH_2Cl_2) to afford 2,3-bis(bromomethyl)naphthalene (**16**) in 85% yield. Finally, **16** was converted, via a solvolytic oxidation in Me_2SO and 5 equiv of 2,4,6-collidine,[11] to **9** in 42% yield (Scheme III).

Scheme III

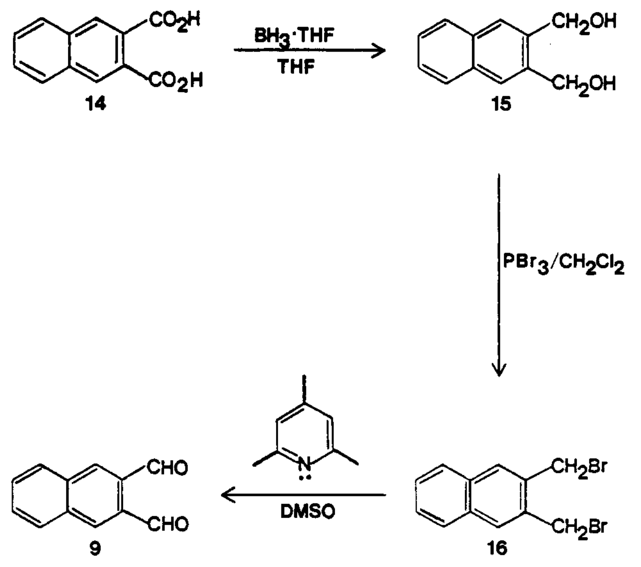


Table I. Derived[a] ^{1}H NMR Spectral Constants for Hydrocarbons 2 and 3 and Related Arylalkynes

compd	type (no. of H's)	shift, δ	range, δ	coupling constants, Hz
2	AA'BB' (4H)	7.892 (A,A')	7.91–7.55	0.58 (AA')
		7.564 (B,B')		6.83 (BB')
				7.83
				1.34 (AB')
	ABC (6 H)	7.121 (A)	7.14–6.80	8.53 (AB)
		6.989 (B)		6.80 (BC)
		6.815 (C)		−0.12 (AC)
3	singlet (2 H)	8.332		
	AA'BB' (4 H)	7.955 (A,A')	7.97–7.58	0.58 (AA')
		7.592 (B,B')		5.94 (BB')
				8.13 (AB)
				1.37 (AB')
	ABC (6 H)	7.041 (A)	7.06–6.75	8.50 (AB)
		6.935 (B)		6.85 (BC)
		6.765 (C)		−0.16 (AC)
17	ABC (6 H)	6.859 (A)	6.88–6.57	8.03 (AB)
		6.755 (B)		7.26 (BC)
		6.584 (C)		−0.16 (AC)
18	multiplet (4 H, phenyl ortho)	7.504	7.52–7.49	
	ABC (6 H)	6.833 (A)	6.85–6.71	8.49 (AB)
		6.772 (B)		6.84 (BC)
		6.725 (C)		0.53 (AC)
19	multiplet (4 H, ortho)	7.525	7.55–7.50	

[a] The spectral constants were derived using the LAOCN3 program (see ref 12).

^{1}H NMR Results

^{1}H NMR spectra of hydrocarbons **2** and **3** and also of arylalkynes **17**, **18**,[12] and **19** were recorded in $CDCl_3$[1] rel-

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(10) Brown, H. C.; Krishnamurthy, S.; Stocky, T. P. *J. Org. Chem.* **1973**, *38*, 2786–2792.

(11) Grantham, G. D. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1975.

Table II. Observed and Calculated ^{1}H NMR Chemical Shifts (ppm)

compd	H(n)	δ_{exptl}	δ_{RC}[a]	$\delta_{\text{RC+LA}}$[b]	$\delta_{\text{RC+LA+CHG}}$[c]
2	1	7.564	7.330	7.227	7.457
	2	7.892	7.390	7.221	7.624
	3	7.121	6.875	6.752	7.048
	4	6.989	6.810	6.756	6.770
	5	6.815	6.693	6.650	6.826
3	1	7.592	7.463	7.428	7.512
	2	7.955	7.737	7.678	7.735
	3	8.332	7.817	7.644	8.198
	4	7.041	6.868	6.746	7.040
	5	6.935	6.802	6.748	6.760
	6	6.765	6.683	6.639	6.814
17	1	6.859	6.711	6.661	6.958
	2	6.755	6.714	6.665	6.674
	3	6.584	6.605	6.549	6.724
18	1	7.504	7.289	7.227	7.622
	2	6.833	6.744	6.679	7.004
	3	6.772	6.738	6.701	6.669
	4	6.725	6.652	6.672	6.893
19	1	7.525	7.296	7.241	7.636
std dev:			0.222	0.302	0.140

[a] The ring current predicted shifts. [b] The predicted shifts corrected for the triple bond local anisotropy. [c] The predicted shifts corrected for both local anisotropy and charge effects.

ative to Me_4Si as an internal standard. The chemical shifts and coupling constants of compounds **2**, **3**, and **17**–**19** were derived from their observed spectra by line matching with the aid of the NMR spectral analysis program LAOCN3.[13] This analysis yielded 19 distinguishable shifts, including 11 for hydrocarbons **2** and **3**, which together span a range of over 1.7 ppm. The derived constants are recorded in Table I.

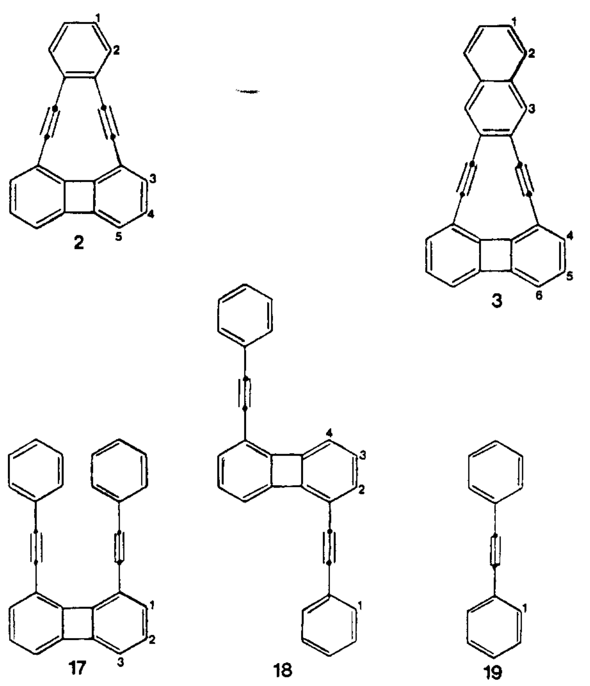
Discussion

The ^{1}H NMR shifts were predicted for compounds **2**, **3**, and **17**–**19**[14] with the semiclassical ring current (RC) model employed previously.[1,3] This model, originally proposed by Mallion,[15] calculates the induced magnetic field at each proton as a sum of the fields resulting from induced in-plane current segments (Biot–Savart law) between each pair of π-bonded atoms. The model requires as input the geometries of the carbon skeleton and the attached protons[16] as well as the ring currents for each ring. Predicted chemical shifts are obtained from the calculated induced fields by using the empirical relationship[3]

$$\delta_{\text{RC}} = 2.147\left[\frac{\text{H}'}{\text{H}'_{\text{benzene}}}\right] + 5.893 \qquad (1)$$

where the constants were obtained by fitting a set of 97 benzenoid and biphenylenoid proton shifts.[3] The standard deviation[3] (s_{ref}) for the entire set of 97 protons was 0.096 ppm, and 0.150 ppm for the subset of 13 biphenylenoid shifts. The ring currents were calculated by using the McWeeny perturbational method[17] on self-consistent Hückel molecular orbitals (SCHMO).[18] The molecular geometries of the arylalkynes were optimized with a modified two-dimensional (i.e., the atoms are constrained to a plane) Boyd force field[16]—a refinement that has only a subtle effect[19] on the predicted values. The proton assignments and predicted shifts for the arylalkynes are presented in Chart I and Table II (in the column headed δ_{RC}).

Chart I



The shifts predicted for the arylalkynes, by the RC model are, on the average, 0.176 ppm upfield from the experimental values (s_{RC} = 0.222 ppm). The deviations are particularly large for protons in the vicinity of the triple bonds. That the upfield bias is significant can be inferred from an F-test comparison with the reference model,[3,20] which shows that the upfield bias is significant at a confidence level of almost 100.0% ($s^2_{\text{RC}}/s^2_{\text{ref}}$ = 5.348). If a similar comparison is made with the model precision for the subset of biphenylenoid protons,[3] the bias is still significant at a confidence level of 90.8% ($s^2_{\text{RC}}/s^2_{\text{biphenylenoid}}$ = 2.190). The small, but statistically significant, upfield bias of hydrocarbons **2**, **3**, and **17**–**19** has been noted before for other hydrocarbons containing triple bonds and attributed to a combination of local triple bond anisotropy and induced charges.[21] A correction for the local an-

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(12) (a) Preparation of **17** and **18** in Wilcox, C. F., Jr.; Weber, K. A. *Tetrahedron*, in press. (b) For the electrochemical reduction of **2**, **3**, and related cyclooctabiphenylenes, see also: Wilcox, C. F., Jr.; Weber, K. A. *J. Electroanal. Chem.*, in press.

(13) (a) Bothner-By, A. A.; Castellano, S. In "Computer Programs for Chemistry"; Detar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. I. (b) Bothner-By, A. A.; Castellano, S. *QCPE* **1967**, *10*, 111, LAOCN3.

(14) The out-of-plane phenyl conformations in the arylalkynes **18** and **19** were modeled by averaging the shifts predicted for the in-plane phenylarylalkyne and the appropriate monoarylacetylene. The phenyl rings in arylalkyne **17** were assumed to be out of plane.

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

(16) (a) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574–2583. (b) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168–2176. (c) Obendorf, S. K.; Wilcox, C. F., Jr.; Grantham, G. D.; Hughes, R. E. *Tetrahedron* **1976**, *32*, 1327–1330. (d) Allinger, N. L.; Meyer, A. Y. *Tetrahedron* **1975**, *31*, 1807–1811. (e) All of the C–H bond lengths were fixed at 1.09 Å, and the centers of electron density for the hydrogens were taken to be their nuclei. (f) The geometries of the phenylarylalkynes **17**, **18**, and **19** were constructed by "grafting" optimized monoarylacetylene fragments. (g) See ref 18.

(17) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311–321.

(18) The SCHMO-calculated triple-bond lengths were incremented by −0.130 Å to compensate for the orthogonal π-bonding, which is not formally included in the Hückel approximation.

(19) The shifts predicted for biphenylene using either an idealized (benzene lengths and angles) geometry or an optimized geometry differed by only 0.03 ppm (rms).

(20) The F-test used here compares the ratio of variances found for fitting a single set of data using two different models with the variance ratios expected if the deviations followed the same distribution (i.e., the models give the same quality of fit). A larger than expected ratio indicates, with a probability determined by the observed ratio and the sample size, that the second model gives a statistically significant improved fit of the data.

(21) (a) Castellano, S.; Lorenc, J. *J. Phys. Chem.* **1965**, *69*, 3552–3564. (b) Vogler, H. *J. Am. Chem. Soc.* **1978**, *100*, 7464–7471.

isotropy (LA) of the triple bonds was included using the modification of the McConnell approximation,[22] proposed by Pople (eq 2).[23] In this model, the anisotropy arises from

$$\Delta\delta_{\mathrm{LA},i} = \left(\frac{-\Delta\chi_{\mathrm{C_{sp}}}}{N_{\mathrm{A}}}\right)_j \frac{1-3\cos^2\theta_{ij}}{3R_{ij}^3} \qquad (2)$$

the readily induced diamagnetic currents in the cylindrical π-orbitals of the triple bond. The induced moment is approximated by placing a magnetic point dipole at the center of each acetylenic carbon and calculating the resultant field at each proton.

In eq 2, R_{ij} denotes distance vector between the center of acetylenic carbon j and proton i; θ_{ij} denotes the angle between vector R_{ij} and the triple-bond axis.

One difficulty in applying eq 2 is the choice of a suitable value for the anisotropy of an acetylenic carbon, $\Delta\chi_{\mathrm{C_{sp}}}$, from among the many widely varying literature values.[24] A recent measurement on methylacetylene[25] gave -7.90×10^{-6} cm^3/mol for the triple bond, and a value of -8.39×10^{-6} cm^3/mol has been calculated theoretically for acetylene.[26] We chose to employ a value of -8.0×10^{-6} cm^3/mol, which corresponds to an average anisotropy per sp-carbon, $\Delta\chi_{\mathrm{C_{sp}}}$, of -4.0×10^{-6} cm^3/mol.

The geometric factors were calculated on the basis of the optimized geometries,[16] employed in the RC-model predictions. Most of the protons, in arylalkynes **2**, **3**, and **17**–**19**, lie in the shielding regions of the triple bonds.[27] Thus inclusion of the LA corrections only leads to larger upfield deviations (average, 0.246 ppm). The calculated shifts are recorded in Table II in the column headed $\delta_{\mathrm{RC+LA}}$. It is important to note that the individual deviations are again greatest for the protons "ortho" to the triple bonds. It would be tempting to conclude that one needs a positive (diamagnetic) correction but that is "unphysical" and, as discussed in the next few paragraphs, the need vanishes when one takes into account the π-charges induced by the acetylenic groups.

A correction should be made for the electronegativity difference between the sp-hybridized acetylenic carbons and the sp^2-hybridized atoms of the remaining carbon skeleton. As a result of its enhanced electronegativity, the acetylenic carbon functions as a mild electron-withdrawing substituent in the σ framework. The resulting displacement of σ-electrons towards the acetylenic carbons reduces the electronegativity of the π-orbitals on the same carbons. This phenomenon works in reverse for the sp^2 carbon attached to the acetylenic carbon. The reduced π-electronegativity of each acetylenic carbon produces an alternating pattern of π-electron polarization toward the sp^2 carbon to which it is bonded.

In the SCHMO method, the resonance-integral parameters (β_{ij}) are varied, in accordance with eq 3 and 4,[1,3] until

$$\beta_{ij} = \beta_{ij}^{\,0} \exp[3.80(1.393 - r_{ij})] \qquad (3)$$

$$r_{ij} = 1.504 - 0.167P_{ij} \qquad (4)$$

the π-bond orders (P_{ij}) and calculated bond lengths (r_{ij}) are self-consistent. The coulomb-integral parameters (α_i) are varied through eq 5.

$$\alpha_i = \alpha_i^{\,0} - 0.10|\beta^0|(1.0 - q_i) \qquad (5)$$

In order to mimic the consequences of the dipole moment of the C_{sp}–$C_{sp}2$ bonds, α_i's of the sp and attached sp^2 carbons were changed to reflect the changes in the π-electronegativity induced by the underlying σ-electron displacements. This alteration has the net effect of shifting the π-electron density toward the carbons to which the triple bonds are attached. For example, when an aryl ring is bonded to the triple bond, as in the case of diphenylacetylene, density is shifted toward the ipso carbon and primarily away from the ortho and para positions. Because the SCHMO method is highly empirical, there is no independent way to estimate the required perturbations in the α parameters. Instead, the adjustment was treated as a new parameter and selected so as to minimize the deviations between the observed and predicted chemical shifts. The effect of a unit π-charge was assumed to displace the chemical shift of the attached proton by 10.0 ppm.[28] The parameters derived for the sp and attached sp^2 carbons were +0.327 and −0.327, respectively, in absolute β units. The charge-corrected shifts are recorded in Table II in the column headed $\delta_{\mathrm{RC+LA+CHG}}$.

After the introduction of both the LA and charge corrections, the fit of the predicted shifts was significantly improved, and the upfield bias removed. The improvement of the fit can be inferred from an F-test comparison[20] of the new standard deviation ($s_{\mathrm{RC+LA+CHG}} = 0.140$ ppm) with that of the original set of RC shifts ($s^2_{\mathrm{RC}}/s^2_{\mathrm{RC+LA+CHG}} = 2.514$), which shows that the added parameters are significant at the 97.4% confidence level. The standard deviation is now reasonably close to that of the original[3] RC model and is statistically indistinguishable from the subset of biphenylenoid shifts for compounds without triple bonds.

The charge corrections had the greatest effect on the ortho-proton shifts and a lesser effect on the para shifts of the arylalkynes. There were slight effects on the meta shifts, and they were, in general, predicted to be upfield of the experimental shifts. An electron-withdrawing substituent on a benzene ring tends to deactivate the ortho and para positions, and to a lesser extent, deactivate the meta positions. This deactivation at the ortho and para positions is attributable to "resonance" or π-delocalization effects whereas the slight deactivation at the meta positions is attributed to "inductive" or primarily σ effects. The larger than predicted downfield shifts at the meta positions are presumably an artifact of the omitted σ framework.[29]

As a test of its range of applicability, the fully corrected (RC+LA+CHG) model was applied to the reported proton shifts of eight presumably planar noncumulenic dehydroannulenes, **4** and **20**–**26**, from the literature[5,6,30-36] (Chart

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[22] McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226–229.

[23] (a) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811–4815. (b) Pople, J. A. Discuss. Faraday Soc. **1962**, *34*, 7–14. (c) Bothner-By, A. A.; Pople, J. A. *Ann. Rev. Phys. Chem.* **1965**, *16*, 43–66.

[24] Mallory, F. B.; Baker, M. B. *J. Org. Chem.* **1984**, *49*, 1323–1326.

[25] Geschka, H.; Pferrer, S.; Haussler, H.; Huttner, W. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 790–795. (b) See also: Shoemaker, R. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 5417–5421.

[26] Kato, Y.; Fujimoto, Y.; Saika, A. *Chem. Phys. Lett.* **1972**, *13*, 453–456.

[27] Charrier, C.; Dorman, D. E.; Roberts, J. D. *J. Org. Chem.* **1973**, *38*, 2644–2650.

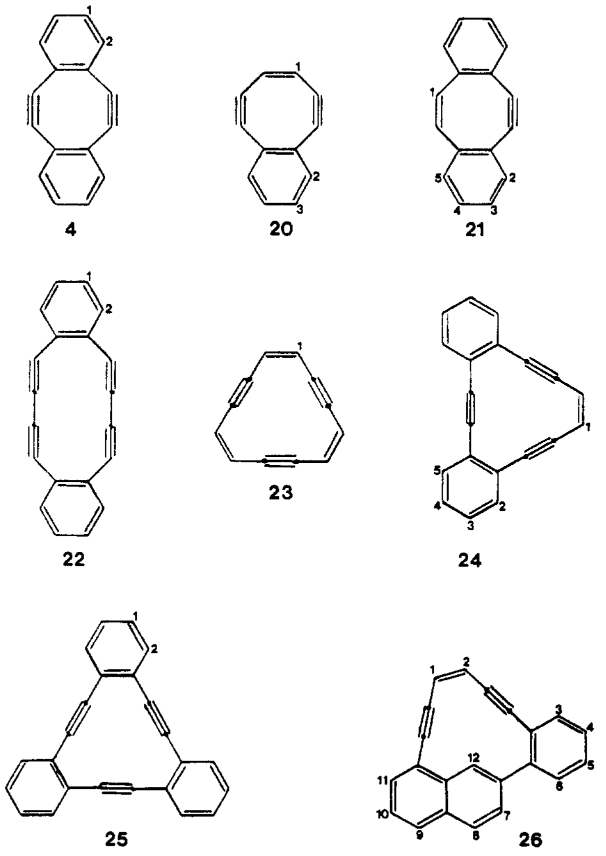
[28] Garratt, P.; Sargent, M. V. In "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York and London, 1971; Vol. 2, Chapter 4, pp 207–277.

[29] Wu, T. K.; Dailey, B. P. *J. Chem. Phys.* **1964**, *41*, 2796–2804.

[30] (a) Due to their size and the unexceptional nature of their reported NMR spectra, calculations were not carried out on the two dehydro[18]annulenes reported by Endo et al. (b) Endo, K.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1970**, 2557–2560. (c) Endo, K.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2465–2468. (d) Bicyclo[9.3.0]tetradeca-1,5,7,11,13-pentaene-3,9-diyne was omitted since the Hückel model does not properly treat the charge densities in nonalternant hydrocarbons. (e) Mayer, J.; Sondheimer, F. *J. Am. Chem. Soc.* **1966**, *88*, 602–603.

[31] Wong, H. N. C.; Sondheimer, F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 117–118.

Chart II



II). In each case that involved a complex splitting pattern only the center and, in most cases, the range of the shifts were reported. To facilitate comparison, both the predicted shifts (δ_{pred}) and their averages ($\langle\delta_{\text{pred}}\rangle$) are recorded in Table III.

The predictions are, in general, reasonably good ($s_{\langle\delta\rangle}$ = 0.203, for 65 shifts)[37] with the exception of the two vinyl protons in compound **24** and also the vinyl and intraannular protons in **26**. The predicted aryl-proton shifts for the benzannelated compounds are quite good ($s_{\langle\delta_{\text{aryl}}\rangle}$ = 0.116, for 53 shifts),[35] whereas the nonaryl shifts are reasonable ($s_{\langle\delta_{\text{non aryl}}\rangle}$ = 0.346, 12 shifts).[37]

The LA model is quite sensitive to the chosen molecular geometry, particularly for protons at small angles with respect to the triple-bond axis, which may account for the discrepencies in the vinyl shifts of compound **26**. In contrast, the predicted shift of trisdehydro[12]annulene **23** is strikingly good, since the reported value is over 2.0 ppm upfield from the shifts of arylalkynes **2**, **3**, and **17–19**. It is most peculiar that the observed vinyl proton shifts in compounds **23** and **24** differ by over 1.0 ppm—especially in comparison with the relative degree of localization introduced by dibenzannelation of annulene **23**. The large downfield shift of the intraannular proton in **26** is primarily attributable to LA effects and is grossly underestimated by our corrections. This underestimate is probably due to both the inherent deficiency of the dipole approximation at close distances[21,23,38] and the inadequacies arising from using a planar geometry for **26**.

Table III. Observed and Calculated ^{1}H NMR Chemical Shifts of Literature Compounds[a]

compd	type (no. of H's)	δ_{exptl} (center)	H(n)	δ_{pred}	$\langle\delta_{\text{pred}}\rangle$
4	AA′BB′ (8 H)	6.8[b]	1	7.22	7.22
		(range: 7.24–6.36)	2	7.21	
20	singlet (2 H)	4.93[c]	1	4.63	4.63
	(AA′BB′ not avail.)		2	7.08	7.11
			3	7.13	
21	singlet (2 H)	5.50[d]	1	5.68	5.68
	ABCD (8 H)	6.75	2	7.00	6.91
		(range: 7.0–6.5)	3	6.80	
			4	7.12	
			5	6.73	
22	multiplet (8 H) (CH_2Cl_2)	7.05[e] (40 MHz)	1	7.34	7.38
			2	7.42	
23	singlet (6 H)	4.48[f] (4.56 at −60 °C)	1	4.73	4.48
24	singlet (2 H)	5.60[g]	1	4.96	4.96
	ABCD (8 H)	7.10	2	7.45	7.39
		(range: 7.3–6.9)	3	7.30	
			4	7.31	
			5	7.48	
25	AA′BB (12 H)	7.28[h]	1	7.35	7.45
		(range: 7.47–7.09	2	7.54	
26	AB (2 H) (unassigned)	5.77,5.74[i]	1	4.00	4.47
	multiplet (9 H)		2	4.94	
		7.38	3	7.53	7.45
		(range: 7.70–7.05)	4	7.04	
			5	7.37	
			6	7.38	
			7	7.55	
			8	7.62	
			9	7.76	
			10	7.15	
			11	7.61	
	singlet (1 H)	13.13	12	9.40	9.40

[a] All shifts in τ units are converted to δ (ppm) and were recorded in $CDCl_3$ unless otherwise specified. [b] References 4,5. [c] References 5, 29. [d] Reference 4. [e] Reference 30; shift reported as $\sigma = -1.75$ relative to cyclohexane, and was converted using $\delta = 5.3 - \sigma$ ($\delta_{H_2O} = 5.3$). [f] Reference 31. [g] Reference 32. [h] Reference 33. [i] Reference 34.

In spite of the reasonable fits that are obtained with the fully corrected (LA+RC+CHG) model for a wide range of ^{1}H NMR data, it should be applied cautiously. The Huckel model, even with variable α's, cannot handle a wide range of π-charges properly because of the absence of explicit electron repulsion terms. That the present model copes with the π-charges induced by the acetylenic carbons, probably reflects the smallness of the effect and possibly a certain similarity of the structures.

Summary and Conclusions

Two biphenylene-fused planar tetradehydro[10]annulenes, a previously unknown class of compounds, have been synthesized and characterized. Their ^{1}H NMR spectra, along with those of three other acetylenic hydrocarbons, were recorded and the derived chemical shifts were assigned. The shifts were then predicted with a simple ring current model and found to be upfield from those determined experimentally. Corrections were introduced to account for the electronegativity and local

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anisotropy effects due to the presence of the triple bonds. It was found that these corrections reduced the prediction errors to within acceptable limits. Finally, the extended model was applied to eight previously known dehydroannulenes, and the calculated shifts were found to compare well with observed values.

Experimental Section

General. The ^{1}H NMR spectra of hydrocarbons **2**, **3**, and **17–19** were recorded on a Bruker WM-300 spectrometer in $CDCl_3$, and referenced to tetramethylsilane (Me_4Si) as an internal standard. Other ^{1}H NMR spectra were recorded on either a Varian CFT-20 or EM-390 spectrometer. ^{13}C NMR spectra were recorded on a Jeol FX-90 Q spectrometer in $CDCl_3$ and referenced to the $^{13}CDCl_3$ triplet at δ 77.0 ($\delta_{Me_4Si} = 0.0$).

UV–vis electronic spectra in cyclohexane (Fisher Spectranalyzed) were recorded on a Hewlett-Packard 8450A double-beam spectrophotometer. Both low- and high-resolution electron-impact mass spectra were recorded on an AEI-MS902 instrument except those for compounds **2** and **12**, which were recorded on a Finnigan 3300 instrument. Melting points were determined with a Thomas Hoover melting point apparatus and are uncorrected. Me_2SO, DMF, and CH_2Cl_2 were dried over 4-Å molecular sieves, and THF was distilled freshly from Na/benzophenone ketyl under argon. Potassium *tert*-butoxide was purchased from Aldrich and stored over P_2O_5. All organic extraction phases were dried over anhydrous $MgSO_4$ and filtered prior to concentration.

Preparation of 9. 2,3-Bis(hydroxymethyl)naphthalene (15). In a 250-mL flask, flushed with argon, were placed 99% (Aldrich) 2,3-naphthalenedicarboxylic acid (**14**) (5.4 g, 25.0 mmol), THF (20 mL), and a magnetic stir bar. Next 1 M $BH_3 \cdot THF$/THF (66 mL, 66 mmol) was added dropwise (ca. 1 h) to the stirred mixture, kept at 0 °C (ice bath). During the addition a gelatinous white cake formed. It was left at 0 °C for ca. 1 h and then allowed to warm to room temperature (ca. 12 h). To the mixture was added 50% (v/v) aqueous THF (25 mL). The solution was saturated with anhydrous K_2CO_3 and the phases were partitioned. The aqueous phase was washed twice with THF, and then the organic layers were combined, dried, and evaporated. The residue was recrystallized from acetone/hexane to yield as an off-white powder (crude) diol **15** (3.87 g, 82%): mp 155–160 °C (lit.[39] 160 °C); ^{1}H NMR (80 MHz, acetone-d_6) δ 7.89 (s, 2 H), δ 7.93–7.40 (centered δ 7.67, AA′BB′, 4 H), δ 4.87 (d, J = 5.6 Hz, 4 H), δ 4.44 (t, J = 5.6 Hz, 2 H).

2,3-Bis(bromomethyl)naphthalene (16). In a 500-mL flask, flushed with nitrogen, were placed **15** (4.15 g, 22.0 mmol), 99% PBr_3 (5.27 mL, 56 mmol), CH_2Cl_2 (300 mL), and a magnetic stir bar. The white suspension dissolved upon stirring for ca. 5 min. The solution was stirred for ca. 12 h, and then partitioned between CH_2Cl_2 and H_2O. The organic phase was washed with saturated $NaHCO_3$, H_2O, and saturated NaCl and then dried and evaporated. The residue was dissolved in CS_2 and passed through a 25 × 38 mm pad of silica (ca. 40 μm) and evaporated to obtain the dibromide **16** as an off-white solid (5.89 g, 85%): mp 145–150 °C (lit.[40] 144.3–145.5 °C); ^{1}H NMR (80 MHz, acetone-d_6) δ 8.05 (s, 2 H), δ 7.98–7.49 (centered δ 7.74, AA′BB′, 4 H), δ 5.01 (s, 4 H).

2,3-Naphthalenedicarboxaldehyde (9). In a 1-L flask were placed **16** (5.89 g, 18.8 mmol), 99% 2,4,6-collidine (15.2 mL, 115.0 mmol), Me_2SO (900 mL), and a magnetic stir bar. The solution was stirred for 5 days at room temperature and then partitioned between benzene and 60% (v/v) saturated NaCl. The aqueous phase was extracted with two benzene washes, and the benzene phases were combined. The benzene phase was back-extracted with 0.42 N H_2SO_4 (1.2 L), four H_2O washes, and saturated NaCl. The solution was dried and evaporated and the residue eluted through a 40 × 250 mm silica (60–20 mesh) column with $CHCl_3$. The chloroform was evaporated, and the residue chromatographed on a 25 × 300 mm silica (32–63 μm) column with 60:40% (v/v) benzene/$CHCl_3$. The eluent was evaporated and the residue dissolved in benzene; the solution was treated with charcoal (Norit A) and anhydrous K_2CO_3, boiled (ca. 15 min), filtered, and evaporated. The dialdehyde **9** was obtained as white needles (1.44 g, 42%): mp 127–128 °C (lit.[41] 129–132 °C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 10.65 (s, 2 H), δ 8.47 (s, 2 H), δ 8.14–7.68 (centered δ 7.94, AA′BB′, 4 H); mass spectrum, *m/e* (relative intensity) 186 (1.5), 185 (12.7), 184 (66.5, M$^+$), 156 (48.3), 155 (100.0), 128 (27.3), 127 (92.8), 126 (20.3), 77 (15.6), 75 (10.6), 51 (11.2).

Preparation of 2 and 3. Naphtho[2′,3′:7,8]cyclodeca[1,2,3,4-*def*]biphenylene (11). In a 500-mL flask, flushed with argon, were placed the mixture (ca. 50:50%) of **6** and **7**[7] (2.00 g, 2.32 mmol), Me_2SO (250 mL), KO-*t*-Bu (0.7 g, 6.2 mmol), and a magnetic stir bar. The solution, which rapidly turned deep red, was allowed to stir for ca. 1 h. A solution of **9** (0.47 g, 2.55 mmol) in Me_2SO (45 mL) was added dropwise to the ylide mixture via a syringe pump over ca. 20 h while stirring at room temperature. The yellow-brown solution was heated on a steam bath (ca. 20 min), cooled, and then partitioned between benzene and 75% (v/v) saturated NaCl. The aqueous phase was extracted with three benzene washes. The combined phases were extracted with 25% saturated NaCl, four H_2O washes, saturated NaCl, dried, and evaporated. The residue was eluted through a 40 × 300 mm silica (60–200 mesh) column with CS_2, the second band was collected and evaporated, and then the residue was chromatographed on a 15 × 300 mm silica (ca. 40 μm) column with 60:40% (v/v) hexanes/CS_2. The second yellow band was collected, evaporated, and then chromatographed on an 11 × 300 mm silica (ca. 40 μm) column with 50:50% (v/v) hexanes/CS_2. The first band was collected and evaporated to hydrocarbon **11** as a yellow solid (0.053 g, 14% yield based on the 1,8-bis(phosphonium) salt): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.64–7.25 (complex multiplet, 6 H), δ 6.68–6.18 (complex multiplet 10 H); mass spectrum, *m/e* (relative intensity) 330 (3.5), 329 (26.2), 328 (46.6, M$^+$), 327 (57.6), 326 (46.6), 324 (15.8), 163 (17.7), 162 (11.8).

5,6,9,10-Tetrabromo-5,6,9,10-tetrahydronaphtho[2′,3′:7,8]-cyclodeca[1,2,3,4-*def*]biphenylene (13). In a 25-mL flask were placed **11** (0.0530 g, 0.161 mmol), CCl_4 (15 mL), and a magnetic stir bar. The solution was cooled to 0 °C (ice bath), and 0.708 M Br_2/CCl_4 (0.50 mL, 0.35 mmol) was added while protected from light, and then the mixture was stirred at room temperature (ca. 12 h). The solution was evaporated and the residue chromatographed on an 11 × 300 mm silica (ca. 40 μm) column with CS_2. Of the first two yellow bands, the first was evaporated, again treated (as above) with the Br_2/CCl_4 (0.38 mL, 0.27 mmol), and then rechromatographed obtaining two new bands. The second bands obtained from each of the chromatographies were combined and evaporated, and then the residue was chromatographed on a third 11 × 250 mm silica (ca. 40 μm) column with CS_2. The second band was collected and evaporated to a thick yellow oil of **13** (0.0504 g, 48%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.75 (s, 2 H), δ 7.69–7.12 (complex multiplet, 4 H), δ 6.82–6.20 (complex multiplet, 7.36 H; including δ 6.52 (d, J = 8 Hz, 1.36 H)), δ 6.10 (d, J = 12 Hz, 0.64 H), δ 5.75 (d, J = 8 Hz, 1.36 H), δ 5.32 (d, J = 12 Hz, 0.64 H); ^{13}C NMR (22.49 MHz, –CHBr– signals) δ 60.2, 58.2, 54.7, 54.1;[42] mass spectrum, *m/e* (relative intensity) 652 (1.7), 651 (2.3), 650 (6.3), 649 (4.9), 648 (9.8, M$^+$), 647 (5.4), 646 (6.8), 645 (3.0), 644 (1.8), 568 (1.4, M – Br), 488 (21.2, M – 2Br), 408 (7.8, M – 3Br), 328 (56.9, M – 4Br).

5,6,9,10-Tetradehydronaphtho[2′,3′:7,8]cyclodeca[1,2,3,4-*def*]biphenylene (3). In a 25-mL flask, flushed with argon, were placed **13** (0.0504 g, 0.078 mmol), dry THF (15 mL), KO-*t*-Bu (0.055 g, 0.49 mmol), and a magnetic stir bar. The mixture was stirred at room temperature (ca. 1 h), and then partitioned between hexanes and saturated NaCl. The aqueous phase was washed again with hexanes, the hexanes phases were combined and then extracted with several H_2O washes and saturated NaCl, dried, and evaporated. The residue was chromatographed on an 11 × 300 mm silica (ca. 40 μm) column with CS_2, and then the first yellow band was collected and evaporated to yellow needles of **3** (0.0216 g, 84%): slowly dec[5] >190 °C; UV λ_{max} (log ϵ_0) 233

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[42] The two ^{1}H NMR AB patterns and four ^{13}C NMR (–CHBr–) signals are consistent with the presence of three diastereomers, a meso compound and two enantiomers, when syn addition and the cross-ring shielding effects are assumed negligible.

(4.54), 241 (4.73), 284 (4.83), 293 (4.91), 303 (5.27), 321 (4.17), 331 (4.07), 351 (3.77), 371 (3.71), 389 (3.77), 406 (3.78), 412 (3.77); ^{1}H NMR (see Table I); ^{13}C NMR δ 155.4, 150.8, 131.9, 129.1, 128.8, 128.0, 127.6, 127.2, 123.3, 117.1, 112.8, 95.4, 94.1; mass spectrum, *m/e* 324.0939, calcd 324.0939 for $C_{26}H_{12}$.

Benzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (10). Hydrocarbon **10** was prepared from *o*-phthaldehyde (0.41 g, 3.06 mmol; recrystallized from hexanes), in a manner analogous to that of **11**, and isolated as a yellow solid (0.0661 g, 21% yield based on the 1,8-bis(phosphonium) salt): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.23–6.91 (complex multiplet, 4 H), δ 6.74–6.28 (complex multiplet, 10 H); mass spectrum, *m/e* (relative intensity) 280 (2.3), 279 (21.9), 278 (100.0, M$^+$), 277 (92.6), 276 (68.3), 274 (19.6), 138 (59.6), 137 (18.0), 125 (16.2).

5,6,9,10-Tetrabromo-5,6,9,10-tetrahydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (12). The tetrabromide **12** was prepared from **10**, by the addition of 0.708 M Br_2/CCl_4 (0.58 mL, 0.41 mmol) solution, in a manner analogous to that of **13**, and isolated as a thick yellow oil (0.0742 g, 56%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.23–6.20 (complex multiplet, 11.14 H; including δ 6.48 (d, *J* = 8 Hz, 1.14 H)), δ 5.93 (d, *J* = 12 Hz, 0.86 H), o 5.53 (d, *J* = 8 Hz, 1.14 H), δ 5.00 (d, *J* = 12 Hz, 0.86 H).[42]

5,6,9,10-Tetradehydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (2). Hydrocarbon **2** was prepared by dehydrohalogenation of **12** with KO-*t*-Bu (0.1023, 0.912 mmol), in a manner analogous to that of **3**, and isolated as amber radial crystalline patches of **2** (0.0299 g, 88%): slowly dec[5] >160 °C; UV λ_{max} (log ϵ_0) 235 (4.17), 263 (4.75), 268 (4.76), 278 (4.88), 292 (4.51), 301 (4.31), 309 (4.42), 353 (3.48), 372 (3.66), 392 (3.79); ^{1}H NMR (see Table I); ^{13}C NMR δ 155.0, 150.8, 129.0, 128.9, 127.7, 127.4, 127.0, 116.7, 112.5, 96.0, 95.2; mass spectrum, *m/e* 274.0778, calcd 274.0782 for $C_{22}H_{10}$.

Registry No. **2**, 100229-92-3; **3**, 100229-93-4; **4**, 53397-65-2; **6**, 36230-18-9; **7**, 100229-97-8; **8**, 643-79-8; **9**, 7149-49-7; **10**, 100230-00-0; **11**, 100229-98-9; **12**, 100230-01-1; **13**, 100229-99-0; **14**, 2169-87-1; **15**, 31554-15-1; **16**, 38998-33-3; **17**, 100229-94-5; **18**, 100229-95-6; **19**, 501-65-5; **20**, 58150-58-6; **21**, 53397-66-3; **22**, 7203-21-6; **23**, 6555-54-0; **24**, 27559-98-4; **25**, 5385-26-2; **26**, 100229-96-7.

Diels–Alder Reactions of Protoporphyrin IX Dimethyl Ester with Electron-Deficient Alkynes

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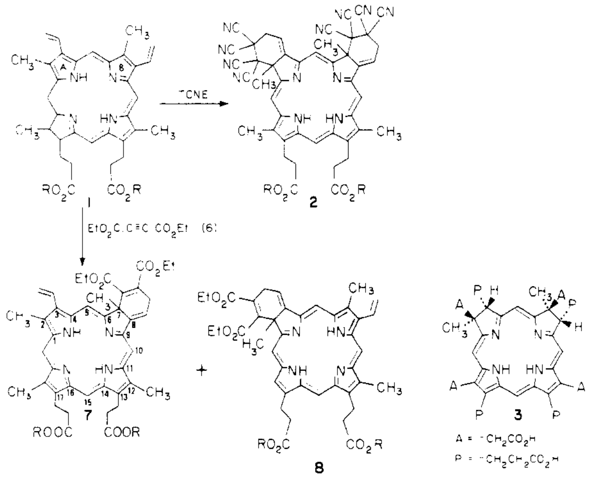
The vinyl and cross-conjugated porphyrin β,β′ double bonds of either ring A or B of protoporphyrin IX dimethyl ester react in a [4 + 2] cycloaddition with electron-deficient acetylenes. The methyl and ethyl esters of acetylenedicarboxylic acid and β-(phenylsulfonyl)propiolic acid react to give the corresponding chlorins with the ring A and B isomers being readily separable by chromatography. The initial products are rearranged by treatment with base. Reaction with triethylamine or 1,5-diazabicyclo[5.4.0]undec-5-ene gave, in every case, two diastereomers, where the former rearrangement led to the kinetically controlled and the latter the thermodynamically controlled products. The Diels–Alder reaction with the unsymmetric acetylenes is both regio- and stereospecific.

We have shown that tetracyanoethylene (TCNE) reacts with protoporphyrin IX dimethyl ester (**1**) in both [2 + 2] and [2 + 4] cycloaddition reactions.[1] One of the products from the Diels–Alder reaction at both rings A and B (**2**) had a chromophore similar to that of sirohydrochlorin[2] (**3**). The iron complex of **3**, siroheme[3] (**4**), is the prosthetic group for sulfite[4] and nitrite[5] reductases; and **3**, or a reduction product, is a biosynthetic precursor of vitamin B_{12}.[6]

Numerous isobacteriochlorin models for sirohydrochlorin have been prepared.[7-9] However, we[10] and others[11] have suggested that an internal electron transfer might account for part of the reduction processes mediated by these macrocycles. Such a process would require the specific substitution pattern found in both rings A and B of siroheme. To this end we are planning to use the Diels–Alder

Scheme I



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