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A Study of the ^{13}C NMR Shifts in Two Tetradehydrocyclodecabiphenylenes and Related Aryl and Biphenylenylacetylenes.

Charles F. Wilcox, Jr.* and Karl A. Weber

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

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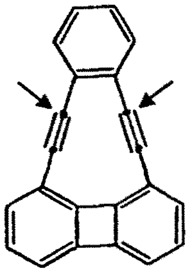
Abstract: The ^{13}C spectra of 5,6,9,10-tetradehydrocyclodeca[1,2,3,4-def]-benzo[7,8]biphenylene, **1**, and 5,6,9,10-tetradehydrocyclodeca[1,2,3,4-def]-naphtho[2,3-7,8]biphenylene, **2**, are reported as are those of a number of simpler acetylenic hydrocarbons used as spectral references. Most of the shifts can be assigned unambiguously. The acetylenic shift assignments were verified by ortho-proton, sp-carbon ($^{1}H(1)$-$^{13}C_{sp}(3)$) decoupling experiments. A simple additive shift correlation is found for the hydrocarbons containing unstrained acetylenic groups. However, significant discrepencies are found for the ^{13}C shifts for the strained hydrocarbons **1**, **2**, 1,2-bis(phenylethynyl)-benzene, **12**, and 2,3-bis(phenylethynyl)-naphthalene, **13**. The discrepencies are particularily large for carbons near the triple bonds and are attributed to a combination of strain, rehybridization, and other proximity effects related to the interaction between the ortho-substituted acetylenic carbons.

Introduction

The synthesis of hydrocarbons 1 and 2 has recently been reported.[1] These compounds are of particular interest because of their structural relationsip to the known hydrocarbons 3[2] and 4,[3] which are members of a general class of schizoid hydrocarbons possessing unusual magnetic and electronic properties.[4] The pairs of hydrocarbons 1,3 and 2,4 have nearly identical π-electronic networks that differ in connectivity only as a result of the differing separations of the carbons marked by arrows in Chart I. These carbons are separated in the acetylenes by only about 2.8 Å,[5] which is well within the sum of their Van der Waals radii. The particular question addressed in this paper is whether the ^{13}C spectra of 1 and 2 provide evidence for a strong interaction between these carbons.[6]

The general approach was to examine the ^{13}C spectra of a number of simpler hydrocarbons which contain the separate structural elements found in 1 and 2. These observed shifts were reduced to an additive structural scheme that could be used to determine if the spectra of 1 and 2 deviated in any unusual way.

Chart I



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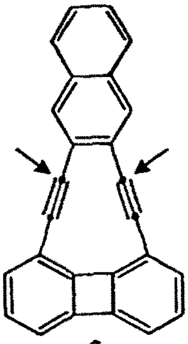

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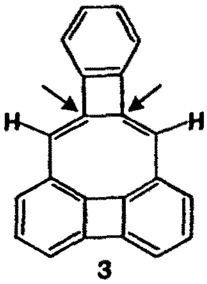

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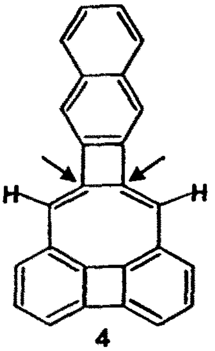

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Results and Discussion

The ^{13}C NMR spectra of aryl-acetylenes **1**, **2**, and **5** through **13** were recorded in $CDCl_3$, and their spectra assigned as discussed in detail in the next section. The ^{13}C shifts for hydrocarbons **1**, **2**, and **5** through **13**, relative intensities, and their assignments, as well as the previously assigned literature values for benzene, naphthalene, and biphenylene, are recorded in Table I and Chart II.

Spectral assignments. The ^{13}C shifts for the aryl and biphenylenyl carbons of compounds **1**, **2**, and **5** through **11** were partially assigned on the basis of the gross features of their proton-decoupled spectra. Such features include their region of occurrence in the spectrum, the number of recorded lines, and their signal intensities (i.e., relative NOE's, relaxation effects, and superimposed lines). The assignments were completed on the basis of the additivity of substituent effects that are derived from the previously assigned shifts (Chart II and Table I) for naphthalene,[7] biphenylene,[8] and also assignments for acetylenes **5** and **8**.[9,10] The reasoning behind these assignments is described in the following paragraphs.

Chart II

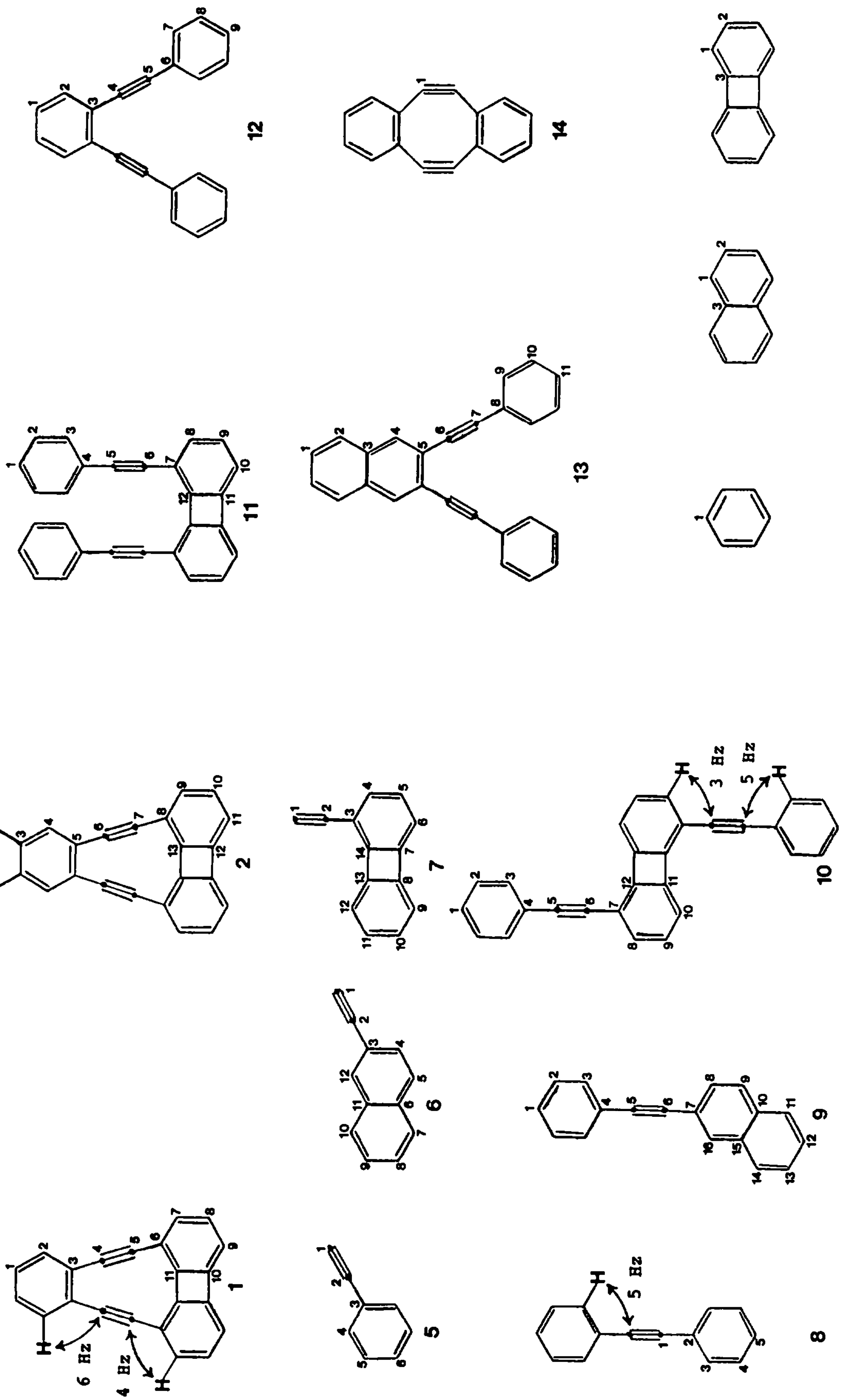

Table I. The Observed Shifts, Assignments, and Relative Intensities for the Hydrocarbons (in ppm).

Compound	C(n)	δ_n	% Int.	Compound	C(n)	δ_n	% Int.	Compound	C(n)	δ_n	% Int.	Compound	C(n)	δ_n	% Int.
1	1	127.4	100.0	**2**	1	127.2	94.8	**9**	1	128.2	37.5	**10**	1	128.5	62.2
	2	129.0	92.8		2	128.0	100.0		2,8	128.3	100.0		2	128.3	98.2
	3	127.0	23.6		3	131.9	22.1		3	131.6	50.2		3	131.7	100.0
	4	96.0	12.0		4	129.1	77.9		4	123.3	11.4		4	123.0	17.4
	5	95.2	12.7		5	123.3	16.9		5,6	89.8	11.0		5	92.4	7.1
	6	112.5	21.3		6	95.4	8.2		7	120.6	6.9		6	85.6	7.4
	7	128.9	89.8		7	94.1	5.8		9	128.0	38.1		7	113.2	16.1
	8	127.7	92.6		8	112.8	13.3		10	132.8	19.6		8	131.1	54.4
	9	116.7	78.8		9	128.8	90.7		11,14	127.8	49.6		9	128.7	51.5
	10	150.8	32.9		10	127.6	97.2		12,13	126.5	44.4		10	117.3	51.9
	11	155.0	8.5		11	117.1	92.9		12,13	126.6	30.4		11	150.2	16.0
					12	150.8	22.0		15	133.0	17.2		12	152.3	5.8
					13	155.4	6.0		16	131.4	33.4				
5[a]	1	77.1	52.0	**6**	1	77.5	47.4	**11**	1	128.0	54.1	**12**	1,8	128.3	100.0
	2	83.6	12.9		2	84.0	12.0		2	127.9	100.0		2	131.8	46.0
	3	122.1	10.7		3	119.3	17.7		3	131.6	81.5		3	125.8	12.5
	4	132.1	100.0		4	128.4	52.9		4	122.7	14.2		4	93.6	10.5
	5	128.2	91.2		5	127.9	40.5		5	92.6	6.1		5	88.3	11.7
	6	128.7	67.1		6	132.9	18.9		6	86.2	7.9		6	123.3	6.8
					7,10	127.7	100.0		7	113.8	6.7		7	131.6	91.4
					8,9	126.5	54.9		8	131.9	35.1		9	128.0	51.2
					8,9	126.8	47.0		9	128.6	35.3				
					11	132.7	17.3		10	116.5	35.5				
					12	132.2	39.0		11	150.2	15.4				
									12	151.5	4.9				
7	1	79.7	87.6	**8**[a]	1	89.3	8.7								
	2	80.1	23.9		2	123.3	9.9	**13**	1	127.1	34.4	benzene	-	128.3	---
	3	111.5	22.8		3	131.6	95.0		2,10	128.2	100.0				
	4	130.8	72.5		4	128.3	98.6		3	132.2	16.4	naphthalene[b]	1	128.0	---
	5	128.2	100.0		5	128.2	100.0		4,9	131.6	94.1		2	125.9	---
	6	118.1	85.1						5	122.2	13.9		3	133.6	---
	7	150.1	24.1						6	93.0	6.3				
	8,13	150.5	30.5						7	88.6	7.3	biphenylene[c]	1	117.8	---
	9,12	117.1	77.1						8	123.3	9.3		2	128.4	---
	10,11	128.6	71.8						11	127.5	43.1		3	151.7	---
	10,11	129.0	83.0												
	9,12	117.7	80.8												
	14	151.1	28.7												

[a] Assignments, ref. 9. [b] Ref. 7. [c] Ref. 8.

Acetylenic carbon shifts. The acetylenic carbon (C_{sp}) shifts of the mono-aryl-acetylenes 5, 6, and 7 may be confidently assigned from their relative intensities, since the NOE of the terminal carbon is much greater. With these acetylenic carbons assigned, the C_{sp} shifts in the diaryl-acetylenes 8 through 11 could be assigned by analogy. If one considers the shifts for 6 and 7 relative to the analogous shifts in phenylacetylene, 5, and likewise those of 9 through 11, relative to diphenylacetylene, 8, parallel trends in the aryl substituent shifts may be noted. The naphthyl group shifts both C_{sp} signals slightly downfield, whereas the biphenylenyl shifts the nearer C_{sp} signal upfield and the further downfield, relative to phenylacetylene (see Table I). The consistency of these assignments is demonstrated by the fact that the $^{13}C_{sp}$ shifts for aryl-acetylenes 5 through 11 fit equation 1[11] rather well with an average deviation of 0.3 ppm (12 shifts, 15.5 ppm range):

$$\delta^i = 71.9 + S_\alpha + S_{\alpha'}, \qquad (1)$$

for the general aryl acetylenes:

$$Ar_\alpha\text{-}^iC{\equiv}C\text{-}Ar_{\alpha'}.$$

("Ar" represents either a hydrogen or an aryl substituent.) The substituent parameters are recorded in Table II. The C_{sp} shifts for 12 and 13 were assigned by comparison with those of 8 and 9, and the assumption that the shifts of the C_{sp}'s nearer the terminal phenyl rings should be similar in all four compounds.

Table II. Aryl-Substituent C_{sp} Shift Parameters.

Substituent	S_α	$S_{\alpha'}$
hydrogen	0.0	0.0
phenyl	11.9	5.4
2-naphthyl	12.3	5.8
1-biphenylenyl	8.4	8.0

The acetylenic carbon shift assignments for hydrocarbons 1 and 2 pose a special challenge, since their acetylenic shifts are separated by only ca. 1 ppm. This small separation implies that several factors are involved in determining these shifts and that it is quite possible that the signals may have crossed over. Based on the assignments for aryl-acetylenes 5 through 13, the upfield C_{sp} shifts were tentatively assigned to the C_{sp}'s nearer the biphenylene rings, and those downfield to the C_{sp}'s nearer the benzo or naphtho substituent. The shift assignments for 1, 2, (and 10)[12] were verified by $^1H(1)$-$^{13}C_{sp}(3)$ heteronuclear decoupling experiments. In these experiments it was first noted that each C_{sp} signal in the proton-coupled ^{13}C NMR spectrum is split into either a doublet or a triplet, depending on whether the aryl substituent has one or two ortho protons. The observed $^1H(1)$-$^{13}C_{sp}(3)$ coupling constants ($^3J_{CH}$) constants are in the range of 3 to 6 Hz.[13] The spectrum is again recorded, this time while the signal of the splitting proton(s) in the ^1H NMR spectrum is irradiated. In the ortho-proton decoupled spectrum, the previously-coupled C_{sp} signal collapses into a singlet. For example, when one irradiates the phenyl multiplet for diphenylacetylene, **8**, the triplet in the undecoupled spectrum collapses into a singlet. If the phenyl protons in **10** are irradiated the downfield C_{sp} triplet collapses to a singlet while the upfield C_{sp} doublet remains unscathed. When the A and A' protons of the AA'BB' splitting pattern for the benzo substituent in **1** are irradiated the downfield C_{sp} doublet collapses to a singlet. Similarly, when the furthest downfield singlet in the proton spectrum of **2** is irradiated the downfield C_{sp} signal collapses to a singlet while that upfield remains a doublet.[14] The coupling constant ($^3J_{CH}$) data for compounds **1**, **8**, and **10** are summarized in Chart II. When one applies equation 1 to the acetylenic carbon shifts in **1**, **2**, **12**, **13** and to the shift in Sondheimer's sym-dibenzo-1,5-cyclooctadien-3,7-diyne, **14**,[15,16] significant deviations are found (see Table III). A large portion of these deviations presumably arise from angle bending in these strained acetylenes.

Table III. Deviant $^{13}C_{sp}$ Shifts and Angle Corrections.

Compound	C(n)[a]	δ_{obs}	δ_{pred}	$\Delta\delta$	$\Delta\theta$	$\Delta\delta_\theta$
1	4	96.0	91.8	+4.2	12.1	+10.3
	5	95.2	85.7	+9.5	11.4	+ 9.7
2	6	95.4	92.2	+3.2	11.9	+10.2
	7	94.1	86.1	+8.0	11.3	+ 9.6
12	4	93.6	89.2	+4.4	---	---
	5	88.6	89.2	-0.6	---	---
13	6	93.0	89.6	+3.4	---	---
	7	88.6	89.6	-1.0	---	---
14[b]	1	109.3	89.2	+20.1	26.4 (24.2, X-ray)[c]	+22.5 (+20.7)

[a]For assignments see Chart II. [b]Ref. 15. [c]Ref. 22.

Meier, et. al.[15] have reported a linear correlation between $^{13}C_{sp}$ shifts (δ_{Csp}, relative to TMS in $CDCl_3$) and C_{sp} bend angles away from 180°. Unfortunately, their data set included a number of questionable shifts. We have reevaluated their angular dependence using a restricted data set, consisting of their simplest cyclic acetylenes,[17] and introduced corrections of -13.0 ppm (C_{sp}-α) and +2.9 ppm (C_{sp}-β) for the effect of a conjugated vinyl group in 1-cyclooocten-3-yne.[18] The vinyl corrections were derived from the differences between the shifts for the essentially strainless acetylenes: cyclododecyne and

1-cyclododecen-3-yne.[19] This restricted data set, including the corrections, gave the following line (eq 2):

$$\delta_{Csp} = 0.8534\ \Delta\theta_{Csp} + 79.49,\ s_{\delta} = 2.12 \text{ ppm (11 shifts).} \qquad (2)$$

The sample standard deviation of 2.12 ppm is significantly better (F-test at 97.4% confidence level) than the original Meier fit.[20]

The slope of the empirical angular-dependence line was used to correct the C_{sp} shifts in **1**, **2**, and **14** for the strain-rehybridization effects at those centers. The C_{sp} angles in hydrocarbons **1**, **2**, and **14** were estimated using a modified 2-dimensional Boyd force field (i.e., all atoms are restricted to the same plane).[21] The estimated deviations from linearity ($\Delta\theta$) and shift corrections ($\Delta\delta_{\theta}$) are recorded in Table III. The shift corrections agree reasonably well with the shift deviations ($\Delta\delta$) for acetylenic carbon 1 in compound **14**, carbon 5 in **1**, and carbon 7 in **2** (these last two carbons lie near the biphenylene rings). However, they overcorrect the shifts for the carbons near the biphenylenyl rings in **1** and **2**, but they overcorrect the C_{sp}'s near the benzo and naphtho rings in **1** and **2** by ca. 6.5 ppm. It is peculiar that the corrected shift of **14** is close to the observed C_{sp} shift of **14** - especially when the correction is based on the X-ray[22] angle value. The poor agreement of the C_{sp}'s near the benzo and naphtho rings could be attributed to a failure of the force field to correctly predict the angles but the evidence presented in the next section suggests that a more fundamental problem is responsible.

Aryl and biphenylenyl shifts. The shift discrepencies in hydrocarbons **1** and **2** are not restricted to the sp-carbons. If one compares the shifts for the carbons adjacent to the triple bonds in the benzo and biphenylenyl groups of **1** with those of **11**, almost as large deviations occur. The same holds for the adjacent rings in **2**. In examining the biphenylenic carbons it is reasonable to use hydrocarbon **11** as a model. However, with the benzo and naphtho ring carbons one must take into account their double substitution. Thus, for example, an ipso carbon of the benzo ring in **12** is in both an ipso- and ortho-relationship to the acetylenic carbons. If the substituent effects are assumed to be additive, the expected shift would be given by equation 3:

$$\delta^{pred}_{ipso-12} = \delta_{ipso-8} + \delta_{ortho-8} - \delta_{benzene} \qquad (3)$$

with similar expressions for the other two positions in **12**. The expected shifts for hydrocarbons **1**, **2**, and **13** can be calculated analogously using **9** and **11** as reference. On the basis of these additively-predicted shifts, subtle deviations were found for the benzo and naphtho[23] shifts of **12** and **13**, whereas more pronounced deviations remained for the aryl shifts for **1** and **2**. These deviations are most pronounced near the acetylenes and fall off with distance. The predicted shifts (δ_{pred}) and deviations ($\Delta\delta$) in the aryl and biphenylenyl rings of **1**, **2**, **12**, and **13** are recorded in Table IV.

The contrast between the shift deviations in **1** and **2**, on the one hand, and **12** and **13**, on the other, is striking. If one were to adopt the view that **12** and **13** were suitable models for **1** and **2** then there are 2 ppm downfield discrepencies for the ipso positions and 2 ppm upfield discrepencies for the ortho positions. This clearly indicates that there are special interactions in **1** and **2** that go

Table IV. Aryl and Biphenylenyl ^{13}C Shift Deviations.

Compound	C(n)[a]	δ_{pred}	$\Delta\delta$	Compound	C(n)	δ_{pred}	$\Delta\delta$
				2	1	127.1	+0.1
					2	127.6	+0.4
1	1	127.6	-0.2		3	131.6	+0.3
	2	131.0	-2.0		4	131.0	-1.9
	3	126.0	+1.0		5	122.4	+0.9
	6	113.8	-1.3		8	113.8	-1.0
	7	131.9	-3.0		9	131.9	-3.1
	8	128.6	-0.9		10	128.6	-1.1
	9	116.5	+0.2		11	116.5	+0.6
	10	150.2	+0.6		12	150.2	+0.6
	11	151.5	+3.5		13	151.5	+3.9
				13	1	127.1	0.0
					2	127.6	+0.6
12	1	128.2	+0.1		3	132.2	0.0
	2	131.6	+0.2		4	131.4	+0.2
	3	126.6	-0.8		5	123.0	-0.8
	6	123.3	0.0		8	123.3	0.0
	7	131.6	0.0		9	131.6	0.0
	8	128.3	0.0		10	128.3	-0.1
	9	128.2	-0.2		11	128.2	-0.7

[a] For assignments see Chart II.

beyond simply having two acetylenes close together as in **12** and **13**.[24] One can speculate that the additional strains present in **1** and **2** alter the local anisotropies of the acetylene groups and possibly their electronegativities as well. It is possible that such effects could account for the extra downfield shift of the acetylenic carbons nearest the benzo and naphtho groups and the alternating discrepencies of the nearest benzo and naphtho carbons. Either a good theory or different examples would be required to sort out these effects. We hope to be able to obtain X-ray structures of the more strained acetylenes.

Conclusions

Unstrained arylacetylenes have ^{13}C shifts that fit a simple additive scheme. When strain is introduced either by proximity or by geometric constraints large deviations from the simple scheme are introduced. Much of the shift deviations can be accounted for in terms of a linear angle bending relationship, but there are residual local and remote effects left unexplained. Since these residual shifts are associated with the non-bonded acetylenic carbons in closest proximity, it is speculated that the orbital interactions alter the local anisotropies and electronegativities that give rise to the effects.

Experimental

General. The ^{13}C NMR spectra were recorded on a JOEL FX-90Q 90 MHz (^{13}C, 22.49 MHz) FT-NMR spectrometer in $CDCl_3$ and referenced to the $^{13}CDCl_3$ triplet at 77.0 PPM (relative to TMS). The decoupler oscillator power was set at "LO 8" and the spectral width at 1000 Hz during the decoupling experiments. The ^{1}H NMR spectra for all of the final products were recorded on a Bruker WM-300 300 MHz spectrometer, the others were recorded on a Varian CFT-20 80 MHz instrument.

All UV-vis 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. Melting points were determined with a Thomas Hoover melting point apparatus and are uncorrected. Dimethylsulphoxide (DMSO) and CCl_4 were dried over 4 Å molecular sieves and tetrahydrofuran (THF) was distilled freshly from Na/benzophenone ketyl under argon. Potassium t-butoxide (KOtBu) was purchased from Aldrich and stored over P_2O_5. Organic extraction phases, where unspecified, were dried over $MgSO_4$ and filtered prior to evaporation.

The reference acetylenes **9** (mp 115-116 °C),[25] **10**, **11**, **12** (mp 51-52 °C),[26] and **13** were prepared by the Wittig reaction[27] between appropriate aryl-aldehydes and aryl-methyl triphenylphosphonium salts and the alkenes converted into acetylenes by bromination followed by dehydrobromination. Phenylacetylene, **5**, was purchased from Aldrich and diphenylacetylene, **8**, was a gift from Prof. M. Goldstein. 2-Ethynylnaphthalene, **6**, (tan oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.032 (s, 1H), δ 7.80-7.77 (m, 3H), δ 7.54-7.48 (m, 3H), δ 2.343 (s, 1H))[28] was prepared from 2-ethenylnaphthalene (Aldrich) by bromination followed by dehydrobromination. The preparation of 1-ethynylbiphenylene, **7**, involved α-lithiation[29] of biphenylene[30] followed by reaction with excess acetaldehyde to afford 1-(1-biphenylenyl)-ethanol, **15**. The alcohol **15**, was dehydrated with $POCl_3$/pyridine[31] to 1-ethenylbiphenylene, **16**, and then brominated and dehydrobrominated to acetylene **7**. The Wittig-reaction products were obtained as unresolved mixtures of cis and trans geometrical isomers. The bromination adducts were carried on, uncharacterized, unless otherwise specified.

Preparation of 7. 1-(1-Biphenylenyl)-ethanol, **15**. In a dry 100-mL flask, flushed with argon, were placed a magnetic stir bar, biphenylene (2.6488 g, 17.40 mmol), THF (50 mL), N,N,N',N'-tetramethylethylenediamine (3.29 mL, 21.8 mmol), and (2.0 M) n-butyllithium/pentane (11 mL, 22 mmol). The solution was stirred for ca. 30 min at room temperature during which time it turned dark green. Next it was cooled to -77 °C in a Dry Ice®/2-propanol bath. Excess acetaldehyde was distilled through a $CaSO_4$ (Drierite®) column into the cooled mixture, which turned yellow. After the addition, the reaction mixture was warmed to room temperature, and then partitioned between hexanes and dilute K_2CO_3. The aqueous phase was washed with fresh hexanes, the hexanes phases were combined, and then back-extracted with a sat'd $NaHCO_3$ wash, two water washes, and a sat'd NaCl wash. The dried hexanes solution was evaporated to a yellow residue, which was chromatographed on a 25 X 250 mm silica (ca. 40 micron) column with CS_2 and then 6:1 (v/v) CS_2/diethyl ether (anhyd.). The second yellow band was collected and evaporated to obtain **15** (1.64 g, 48%), as a yellow oil: ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.84-6.46 (complex mult., 7H), δ 4.70 (q, J = 6.5 Hz, 1H), δ 2.21 (s, 1H), δ 1.45 (d, J = 6.5, 3H); mass spectrum m/e 196.0897, calc. 196.0888 for $C_{14}H_{12}O$.

1-Ethenylbiphenylene, **16**. In a 50-mL flask were placed **15** (1.64 g, 8.34 mmol), pyridine (25 mL), $POCl_3$ (0.90 mL, 9.66 mmol), and a magnetic stir bar. The mixture was stirred at room temperature (ca. 12 hr) and then partitioned between hexanes and $NiCl_2{\cdot}6(H_2O)$ (ca. 25 g) dissolved in H_2O. After the hexanes phase was washed with sat'd $NaHCO_3$, H_2O, sat'd NaCl, and dried over K_2CO_3, it was evaporated to a yellow oil. The oil was chromatographed on a 15 X 300 mm silica (ca. 40 micron) column with hexanes. The first yellow band was collected and evaporated to obtain **16** (0.060 g, 4%) as a yellow oil: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.37-7.11 (complex mult., 3H), δ 6.84-6.35 (complex mult., 4H; incl. δ 6.52 (dd, J_{cis} = 10.3 Hz and J_{trans} = 17.4 Hz)), δ 5.63 (dd, J_{trans} = 17.4 Hz and J_{gem} = 1.4 Hz), δ 5.35 (dd, J_{cis} = 10.3 Hz and J_{gem} = 1.4 Hz); mass spectrum m/e 178.0806, calc. 178.0782 for $C_{14}H_{10}$.

1,2-Dibromo-1-(1-biphenylenyl)-ethane, **17**. In a 25-mL flask were placed 16 (0.0600 g, 0.337 mmol), CCl_4 (12 mL), and a magnetic stir bar. The stirred mixture was cooled to 0 °C (ice bath), for ca. 15 min, and then 0.708 M Br_2/CCl_4 solution (0.50 mL, 0.354 mmol) was added. The reaction mixture was stirred in the dark[32] at room temperature (ca. 12 hr). The mixture was evaporated to a yellow residue, which was passed through a 6 X 50 mm silica (ca. 40 micron) pipette column with CS_2 and evaporated to obtain **17** (0.0926 g, 81%), as a yellow oil: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.45-7.19 (complex mult., 3H), δ 6.83-6.52 (complex mult., 4H), δ 4.93 (dd, J= 6.3 Hz and 9.5 Hz), δ 3.96 (dd, J = 3.3 Hz and 9.6 Hz); mass spectrum m/e 337.9138, calc. 337.9131 for $C_{14}H_{10}{}^{79}Br^{81}Br$.

1-Ethynylbiphenylene, **7**. In a 25-mL flask, flushed with argon, were placed **17** (0.0926 g, 0.274 mmol), THF (15 mL), potassium t-butoxide (0.10 g, 0.89

mmol), and a magnetic stir bar. The solution was stirred at room temperature (ca. 12 hr), and then partitioned between hexanes and H_2O. The aqueous phase was washed with fresh hexanes and the two hexanes phases combined. The hexanes were back-extracted with four H_2O washes, a sat'd NaCl wash, and then dried over K_2CO_3. The hexanes were evaporated to a yellow residue, which was chromatographed on an 11 X 300 mm silica (ca. 40 micron) column with 40:60% (v/v) CS_2/hexanes. The first yellow band was collected and evaporated to obtain **7** (0.0255 g, 82%), as a yellow oil. The oil was crystallized from CH_3OH to obtain yellow needles (mp 115-116 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.27 (cent. δ 7.280, mult., 1H), δ 6.77-6.55 (complex mult., 6H), δ 3.117 (s, 1H); mass spectrum m/e 176.0632, calc. 176.0626 for $C_{14}H_8$.

Preparation of **10** and **11.** 1,5-Bis(2-phenylethenyl)-biphenylene, **18.** In a 500-mL flask, flushed with argon, were placed triphenylphosphonium-methylbenzene chloride (1.73 g, 4.45 mmol; Aldrich), DMSO (250 mL), KOtBu (1.0 g, 8.9 mmol), and a magnetic stir bar. The mixture turned red as it was stirred at room temperature (ca. 1 hr). A 0.04 M solution of 1,5-biphenylenedicarboxaldehyde[33]/DMSO (50 mL, 2.02 mmol) was added, and the reaction mixture stirred at room temperature (ca. 12 hr). The mixture was partitioned between benzene and 60% sat'd NaCl solution, and the aqueous phase was extracted twice with benzene. The benzene washes were combined, and then back-extracted with four H_2O washes, a sat'd NaCl wash, and dried. The solution was evaporated to a yellow residue which was chromatographed on a 15 X 250 mm silica (ca. 40 micron) column with CS_2. The first yellow band was collected and evaporated to **18** (0.4273 g, 60%), as a yellow amorphous solid: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.63-7.09 (complex mult., 10H), δ 7.09-6.39 (complex mult., 10H); mass spectrum m/e (relative intensity) 358 (4.1), 357 (27.9), 356 (84.5, M^+), 328 (8.4), 327 (26.0), 326 (100.0), 278 (11.6), 277 (15.8), 276 (19.9), 263 (10.1), 252 (11.7), 169 (9.5), 138 (9.4), 43 (11.8).

1,5-Bis(phenylethynyl)-biphenylene, **10.** In a 250-mL flask were placed **18** (0.4273 g, 1.199 mmol), CCl_4 (150 mL), and a magnetic stir bar. After cooling to 0 °C (ice bath), a 0.708 M solution of Br_2/CCl_4 (3.1 mL, 2.18 mmol) was added. The mixture was stirred at room temperature (ca. 12 hr) while protected from light.[32] A yellow ppt formed which was collected by suction filtration and then boiled in benzene. Next, the mixture was frozen, thawed, and then the ppt collected by suction filtration.

In a 100-mL flask, flushed with argon, were placed the ppt (0.4425 g, crude 1,5-bis(1,2-dibromo-2-phenylethyl)-biphenylene) dry THF (50 mL), KOtBu (0.5 g, 4.46 mmol). The mixture was stirred at room temperature (ca. 8 hr) and then partitioned between hexanes and 50% sat'd NaCl solution. The aqueous phase was washed with hexanes, the hexanes phases combined, and then back-extracted with five H_2O washes, a sat'd NaCl wash, and dried. The solution was evaporated to a yellow residue which was chromatographed on a 15 X 250 mm silica (32-60 micron) column with CS_2 and the first yellow band was collected. The eluent was evaporated to **10** (0.202 g, 48%), as a yellow solid: mp 168 - 170 °C; UV λmax (log ϵ_0) 256 (4.48), 313 (4.82), 307 (4.80), 300 (4.74), 318 (4.87), 382 (3.75), 402 (3.75); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.49 (cent. δ 7.504, mult., 4H), δ 7.35-7.31 (cent. δ 7.332, mult. 6H), δ 6.833, 6.772, 6.725 (ABC, J_{AB} = 8.49 Hz, J_{BC} = 6.84 Hz, J_{AC} = 0.53 Hz, 6H);[1] mass spectrum m/e 352.1249, calc. 352.1252 for $C_{28}H_{16}$.

1,8-Bis(2-phenylethenyl)-biphenylene, **19.** Hydrocarbon **19** was prepared from triphenylphosphonium-methylbenzene chloride (1.42 g, 3.65 mmol), 1,8-biphenylenedicarboxaldehyde[33]/DMSO (50 mL, 1.66 mmol),and KOtBu (0.821 g, 7.32 mmol) in DMSO (300 mL) in a manner analogous to the preparation of **18.** **19** was isolated as a yellow amorphous solid (0.262 g, 44%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.47-6.52 (complex mult. 20H); mass spectrum m/e (relative intensity) 358 (4.5), 357 (30.4), 356 (100.0, M^+), 339 (7.0), 326 (4.42), 279 (4.42), 278 (4.52), 277 (9.9), 276 (11.9), 252 (7.1), 250 (4.2), 177 (4.2), 176 (6.7), 169 (9.6), 163 (4.2), 138 (4.4), 44 (6.0).

1,8-Bis(phenylethynyl)-biphenylene, **11.** Hydrocarbon **11** was prepared by tetrabromination of **19** with 0.708 M Br_2/CCl_4 solution (1.89 mL, 1.34 mmol) followed by dehydrobromination with KOtBu (0.35 g, 3.1 mmol), in a manner analogous to that used for **10.** Hydrocarbon **11** was isolated as a yellow solid (0.1325 g, 51% yield based on **19**): mp 96-98 °C; UV λ_{max} (log ϵ_0) 269 (4.65), 280 (4.66), 324 (4.19), 360 (3.63), 381 (3.78), 400 (3.76); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.15 (cent. δ 7.173, mult., 4H), δ 7.05-7.00 (cent. δ 7.025, mult., 6H), δ 6.859, 6.755, 6.584 (ABC, J_{AB} = 8.03 Hz, J_{BC} = 7.26 Hz, J_{AC} = -0.16 Hz, 6 H);[1] mass spectrum m/e 352.1231, calc. 352.1252 for $C_{28}H_{16}$.

Preparation of **13.** 2,3-Bis(2-phenylethenyl)-naphthalene, **20.** Hydrocarbon **20** was prepared from 2,3-bis(triphenylphosphonium-methyl)-naphthalene dibromide (1.16g, 1.38 mmol),[34] benzaldehyde (excess; Fisher, freshly distilled), and KOtBu (0.7 g, 6.2 mmol) in DMSO (100 mL) in a manner analogous to that used with **18.** Hydrocarbon **20**[35] was isolated as an off white solid (0.4264 g, 93%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 8.15-8.05 (crude doublet), δ 7.85-7.03 (complex mult.), δ

6.86-6.71 (crude doublet); mass spectrum m/e (relative intensity) 334 (2.0), 333 (12.9), 332 (46.7, M^+), 255 (15.7), 254 (10.3), 253 (9.8), 252 (8.4), 242 (21.5), 241 (100.0), 240 (4.9), 239 (12.7), 167 (10.5), 127 (10.4).

2,3-Bis(phenylethynyl)-naphthalene, **13**. Aryl-acetylene **13** was prepared by tetrabromination of **20** with 0.708 M Br_2/CCl_4 solution (4.00 mL, 2.83 mmol) in CCl_4 and then dehydrobromination with KOtBu (0.70 g, 6.2 mmol) in THF in a manner analogous to that used with **10**.[36] Hydrocarbon **13** was isolated as an off-white solid (0.1323, 31% yield based on **20**), which was recrystallized twice from CH_3OH: mp 136-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.072 (s, 2H), δ 7.61-7.54 (cent. δ 7.576, mult., 4H), δ 7.50-7.47 (cent. δ 7.488, mult., 2H), δ 7.34-7.29 (cent. δ 7.314, mult., 8H); UV λ_{max} (log ϵ_o) 229 (4.23), 245 (3.93), 278 (4.94), 289 (4.90), 310 (4.33), 323 (4.42);[37] mass spectrum m/e 328.1256, calc. 328.1252 for $C_{26}H_{16}$.

References

(1) (a) Synthesis of 1 and 2 in Wilcox, C.F., Jr.; Weber, K.A., manuscript submitted to J. Org. Chem. (b) For the electrochemical reduction of 1, 2 and related cyclooctabiphenylenes see also Wilcox, C.F., Jr.; Weber, K.A., manuscript submitted to J. Electroanal. Chem.

(2) (a) Wilcox, C.F., Jr.; Grantham, G.D.; Tetrahedron 1975, 31, 2889-2895.

(3) Bekiarian, P.G.; Ph.D. Dissertation, Cornell University, Ithaca, NY, 1981.

(4) (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.

(5) This distance is based on modified 2-dimensional Boyd empirical force field calculations (see ref. 21).

(6) Misumi, S.; Kaneda, T.; "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; John Wiley and Sons, Inc.: New York, 1978; Part 2, Chapter 16, p 722.

(7) Levy, G.C.; Lichter, R.L.; Nelson, G.L.; "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; John Wiley and Sons, Inc.: New York, 1980; 2nd Ed., Chapter 4, pp 109-116.

(8) (a) Jones, A.J.; Garratt, P.J.; Vollhardt, K.P.C.; Angew. Chem. 1973, 85, 260-261. (b) Jones, A.J.; Garratt, P.J.; Vollhardt, K.P.C.; Angew. Chem. Internat. Edit. 1973, 12, 241-243.

(9) White, D.M.; Levy, G.C.; Macromolecules 1972, 5, 526-531.

(10) (a) Levy, G.C.; White, D.M.; Anet, F.A.L.; J. Mag. Res. 1972, 6, 453-455. (b) The enhanced intensity of the signal for the para carbons, in diphenylacetylene, with respect to other phenyl para-carbon signals, is from the enhanced relaxation of this carbon due to motional anisotropy from rotation about its principal symmetry axis.

(11) Hobold, V.W.; Radeglia, R.; Klose, D.; J. Prakt. Chem. 1976, 318, 519-522.

(12) The shifts of the protons in the 90 MHz spectra of **11**, **12**, and **13** were too close for selective irradiation at the required power.

(13) (a) The coupling constant between the cis methylene proton on $C_{sp}2$-1 in 1-buten-3-yne and C_{sp}-3 is 9.5 Hz. (b) Levy, G.C.; Lichter, R.L.; Nelson, G.L.; "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; John Wiley and Sons, Inc.: New York, 1980; 2nd Ed., Chapter 3, p 94.

(14) The coupling constants for either signal could not be determined, because of baseline noise associated with the poor solubility of 2 in $CDCl_3$.

(15) (a) Meier, H.; Hermann, P.; Kolshorn, H.; Chem. Ber. 1980, 113, 2398-2409.

(16) Synthesis of **14**: Wong, H.N.C.; Garratt, P.J.; Sondheimer, F.; J. Am. Chem. Soc. 1974, 96, 5604-5605.

(17) Compounds **8**, **11**, **12**, **1**, **5**, **6**, **7**, **17**, and **19** in "Tab. 2" of ref. 15.

(18) Compound 5 in "Tab. 2" of ref. 15.

(19) Compounds 8 and 10 in "Tab. 2" of ref. 15.

(20) A linear regression fit for their raw data yielded a standard deviation of 4.14 ppm (ref. 15).

(21) (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 at their nuclei. (f) See also ref. 1a.

(22) Destro, R.; Tullio, P.; Massimo, S.; Acta. Cryst. 1977, B33, 447-456.

(23) Only the shift effects on the acetylene-substituted naphthyl ring, due to replacing the phenyl of 9 with a biphenylenyl, are taken into account.

(24) (a) In an earlier study of the chemistry of 12, Whitlock and Sandvick suggested the presence of proximal interactions 10. It was reported that bromination of 12 in $CHCl_3$ induces cyclization of the phenylacetylene substituents to form, as its dibromo-adduct, a benzofulvene. (b) Whitlock, H.W.; Sandvick, P.E.; J. Am. Chem. Soc. 1966, 88, 4525-4526.

(25) Ruggli, P.; Reinert, M.; Helv. Chim. Acta 1926, 9, 67-79.

(26) (a) Muller, E.; Heib, J.; Sauerbier, M.; Ege, G.; Justus Liebigs 1969, 723, 61-75. (b) Muller, E.; Munk, K.; Fritz, H-G.; Sauerbier, M.; Justus Liebigs 1969, 723, 76-82.

(27) March, J.; "Advanced Organic Chemistry"; McGraw-Hill, Inc.: New York, 1977; 2nd Ed., Chapter 6-47, p 864-872.

(28) Okamoto, Y.; Chellappa, K.L.; Kundu, S.K.; J. Org. Chem. 1972, 37, 3185-3187.

(29) (a) Boulton, A.J.; Chadwick, J.B.; Harrison, C.R.; McOmie, J.F.W.; J. Chem. Soc. (C) 1968, 328-330. (b) Seager Magde, M. A.; Ph.D. Dissertation, Cornell University, Ithaca, NY, 1971.

(30) Friedman, L.; Seitz, A.H.; Logullo, F.M.; Org. Syn. 1968, 48, 12-17.

(31) (a) Norman, R.O.C.; Thomas, C.B.; J. Chem. Soc. (C) 1967, 1115-1120. (b) Dauben, W.G.; Boswell, G.A.; J. Am. Chem. Soc. 1961, 83, 5003-5005.

(32) Barton, J.W.; Henn, D.E.; McLaughlan, K.A.; McOmie, J.F.; J. Chem. Soc. 1964, 1622-1625.

(33) (a) Grantham, G.D.; Ph.D. Dissertation, Cornell University, Ithaca, NY, 1975. (b) Sheffy, F.K.; Ph.D. Dissertation, Cornell University, Ithaca, NY, 1982.

(34) Cava, M.P.; Hsu, A.-F.C.; J. Am. Chem. Soc. 1972, 94, 6441-6444.

(35) Siegrist, A.E.; Liechti, P.; Meyer, H. R.; Weber, K.; Helv. Chim. Acta 1969, 52, 2521-2554.

(36) The bromination procedure differed in that the Br_2/CCl_4 solution was added at ambient temperature and light was not excluded.

(37) Bazyl, O.K.; Maier, G.V.; Kopylova, T.N.; Danilova, V.I.; Chaikovskii, V.K.; (USSR). Zh. Prikl. Spektrosk. 1981, 35, 261-267.