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The properties and Chemistry of the Aromatic 3H-Cyclonona[def]biphenylenyl Anion

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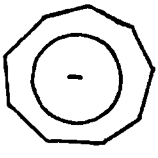
Abstract. 3H-Cyclonona[def]biphenylene, 6, was deprotonated with n-butyllithium to form the mono-trans anion 7. This anion was fully delocalized and aromatic, with the interior proton having a ^1H NMR absorption at -2.79 ppm. This downfield shift was attributed to the proton being in the middle of a ring with a large diamagnetic ring current, calculated to be +0.96 (relative to +1.00 for benzene). Molecular mechanics calculations predicted that 7 was not planar, the interior carbon and the attached proton come out of the plane to relieve severe Van der Waals interactions. Anion 7 was quenched with a variety of electrophiles to give products with the electrophile in the exo position. Attempted generation of the anion of 3-methyl-3H-cyclonona[def]-biphenylene, 10, predicted to be less stable than anion 7 for both steric and electronic reasons, was unsuccessful. Instead, the n-butyllithium added to the π-system to give the stabilized benzylic anion, 13, which was quenched with methanol-d to give compound 14.

Introduction. The preparation of the 10-π-electron aromatic all-cis cyclononatetraenyl anion, 1, was reported in the early 1960's.[1] Since then, several annelated derivatives have been synthesized. Of these, 3 and 5, described below, have a trans double bond, which forces a proton into the center of the aromatic ring, with a consequent upfield shift of its ^1H NMR resonance.



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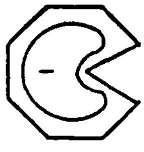

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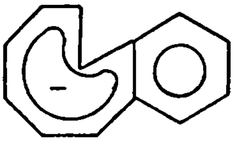

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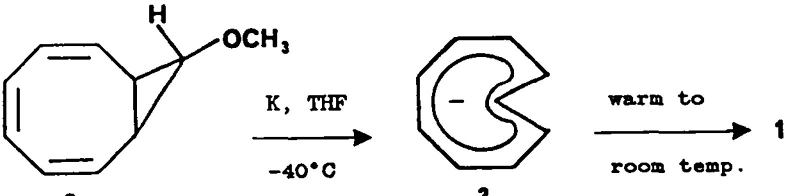
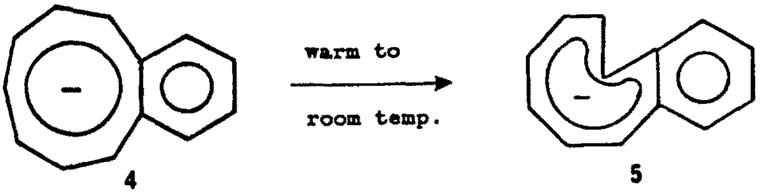
When trans-9-methoxy-cis-bicyclo[6.1.0]nona-2,4,6-triene, 2, is treated with potassium in THF at -40°C, the mono-trans cyclononatetraenyl anion, 3, is formed by a symmetry-allowed ring opening.[2] The interior proton of 3 absorbs at -3.52 ppm. Upon warming to room temperature, 3 isomerizes to the all-cis 1.



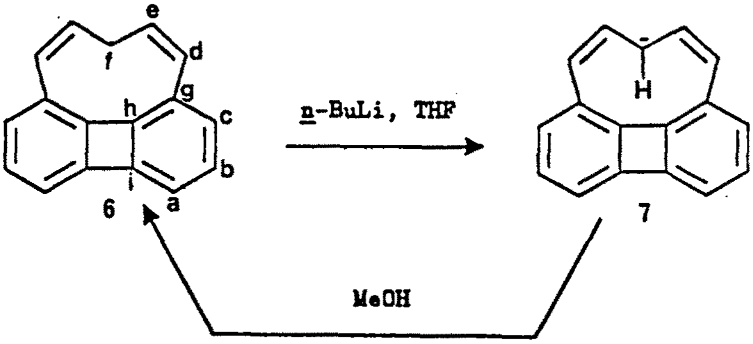
2 3

The benzocyclononatetraenyl anion, on the other hand, isomerizes from the all-cis anion, 4, to the mono-trans anion, 5, ($\delta_{H(int)}$ = -2.35 ppm) upon warming to room temperature.[3] This contrasting behavior was attributed to relief of strain caused by peri H-H interactions in 4.



Two isomers of the all-*cis* dibenzocyclononatetraenyl anion have also been synthesized.[4] An attempt was made to deprotonate a naphthalene-annelated cyclononatetraene, but due to severe *crowding only rearrangement products were observed.*[5]

Recently, the neutral homoantiaromatic 3*H*-cyclonona[*def*]biphenylene, 6, has been synthesized.[6] With the above results in mind, the anion derived from 6 was generated and studied.



Preparation and Structure of the Anion from 6. Treatment of 6 with *n*-butyllithium in dry THF immediately produced a deep reddish-brown solution of anion 7. Reprotonation with methanol gave back 6, indicating that no skeletal rearrangements had taken place. The ^{1}H NMR spectrum of 7 in THF-d_8 was consistent with a delocalized mono-*trans* anion with a proton pointing into the center of the nine-membered ring. The absorption of this proton, which appears at 4.88 ppm in 6, is shifted upfield in 7 to -2.79 ppm (see Table I). The large coupling constant of 14.6 Hz between protons e and f is also indicative of a transoid arrangement. These numbers are consistent with the chemical shifts and coupling constants reported for the interior protons of 3 (-3.52 ppm, 15 Hz)[2] and 5 (-2.35 ppm, 16 Hz).[3]

The energies of various conformations of 7 were calculated using Allinger's molecular mechanics force field.[7] In the lowest energy conformation (see Figure 1), the central proton is

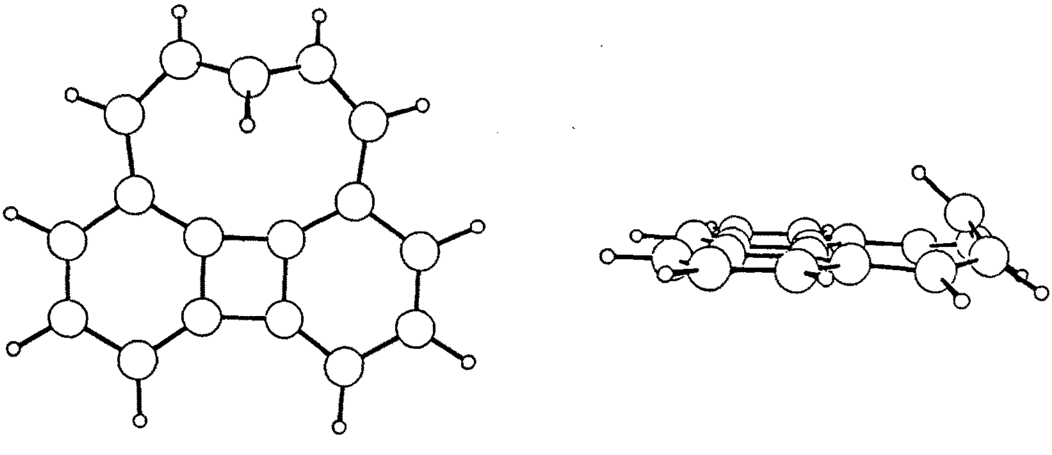


Figure 1. The molecular mechanics generated structure of anion 7.

Table I. ^{1}H NMR Chemical Shifts for Compounds 6 and 7, δ

Proton	6^{a}	7
a	6.43	6.11
b	6.64	6.38
c	6.38	7.07
d	5.86	6.39
e	5.80	7.39
f	4.88,2.63	-2.79

^{a}Reference 6.

canted in towards the biphenylene, lying 58° out of the plane of the biphenylene.[8] If the atoms are constrained to lie in a plane, the calculated heat of formation increases by 21.7 kcal/mol. The energy of the planar structure in which the central proton lies on the outside of the system away from the biphenylene, was also calculated and found to be 20.5 kcal/mol above the bent minimum-energy conformation. In both planar structures the central C_e-C_f-$C_{e'}$ bond angle is spread to about 145°. This relaxes to 118° in the non-planar structure. The interior proton of the planar-in structure has 15.8 kcal/mol of Van der Waals strain due to the four closest biphenylene carbons. This is almost totally eliminated when the proton moves out of the plane. In the planar-out structure the energy is raised by increased angle strain throughout the pentadienyl bridge.

^{1}H NMR Analysis of Anion 7. The most striking feature of the ^{1}H NMR chemical shifts of anion 7 is the 7.7 ppm upfield shift of the inner proton relative to the equivalent proton in 6 (see Table I). An upfield shift would be expected both from the development of negative charge at C_f and from the conversion of an homoantiaromatic, paramagnetic eight-membered ring in 6 into an aromatic, diatropic nine-membered ring in 7. An attempt to determine the balance between these two effects was made by calculating the ring currents for 6 and 7 by the Hückel-McWeeny method[9] combined with an estimation of the shift due to charge for 7.

The locations of the atoms were determined by X-ray crystallography for 6[6] and assigned by molecular mechanics[7] for 7. There is a pseudo eight-membered ring in 6 and a pseudo three-membered ring in 7 formed by homoconjugation between carbons e and e'. The areas of the six and four-membered rings were assigned their usual values; the areas of the nine-membered ring and the three-membered ring were approximated by the areas of the polygons formed by projecting the carbon atoms onto the plane defined by the biphenylene.

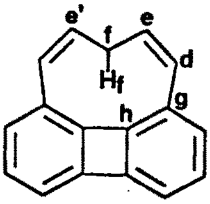
In the Hückel calculations, the twists away from planarity in the carbon skeletons were accounted for by reducing the appropriate β's by the relationship $\beta = \beta_0 \cos\theta$, where θ is the angle between the axes of the adjacent p-orbitals.[10] Because of the slight tetrahedral character of carbon f (and to a much lesser degree carbons e and e') there is an ambiguity as to the proper axes for the p-orbitals at these carbons. Two sets of values for the ring currents in 7 are given in Table II correspond to the assumption that either (Model I) the p-orbital is perpendicular to the plane defined by the plane C_e-C_f-$C_{e'}$ or (Model II) the p-orbital is perpendicular to the plane defined by C_e-C_f-H_f. In Model I the axis of the p-orbital at C_f lies at an angle of 51.5° relative to the axes of the p-orbitals at C_e and $C_{e'}$; in Model II this angle is reduced to 23.7°(see Table III). In the latter case, since the axes of the p-orbitals are twisted less away from each other, there is greater overlap resulting in a larger ring current in the nine-membered ring. There are also slight secondary effects in the other rings.[11] The two situations described are the extremes; the actual orientation of the p-orbital at C_f is probably somewhere between. In either extreme, the slightly paratropic ring current calculated for the nine-membered ring of 6, caused by homoantiaromatic conjugation,[6] becomes larger and diamagnetic upon formation of the anion. The chemical shifts due to these ring currents are reported in Table V.

Table II. Calculated Ring Currents for Compounds 6 and 7[a]

Ring Size	6	7 I[b]	7 II[c]
9	-0.26	+0.67	+0.96
6	+0.51	+0.66	+0.70
4	-0.78	-0.82	-0.84
3		-0.15	-0.10

[a] Relative to benzene unit ring current = +1.00. [b] Calculated using defe' MMPM calculated torsional angle (see Table III). [c] Calculated using defH$_f$ MMPM calculated torsional angle.

Table III. Selected Torsional Angles for 6, 7, 12 and 10



	6[a]		7	12	10
Angle	X-ray[a,b]	MMPM[c]	MMPM[c]	MMPM[c]	MMPM[c]
hgde	32.0	38.7	13.8	10.9	40.4
gdef	1.5	3.5	20.2	25.4	4.3
defH$_f$	21.8	20.2	23.7	47.0	18.6
defe'	256.3	255.4	231.5	231.5	256.1

[a] Reference 6. [b] From X-ray structure. [c] From MMPM calculated structures.

Table IV. ^{13}C NMR Chemical Shifts for Compounds 6 and 7, δ

Carbon	6[a]	7	Δδ	Charge Density
a	116.33	102.48[b]	-13.85	-0.087[b]
b	129.60	119.43[b]	-10.17	-0.064[b]
c	131.18	131.76[b]	+0.58	+0.004[b]
d	127.40	109.98[b]	-17.42	-0.109[b]
e	133.30	125.50	-7.80	-0.049
f	31.17	c		-0.208[e]
g	128.73	125.67[d]	-3.06	-0.019[d]
h	151.39	150.52[d]	-0.87	-0.005[d]
i	150.24	139.61[d]	-10.63	-0.066[d]

[a] Reference 6. [b] These assignments may be backwards.
[c] Unassignable. [d] These assignments may be backwards.
[e] By difference.

Table V. Calculated ^{1}H NMR Chemical Shifts for Anion 7

Proton	Charge Shift[a,b] ppm	Ring Current[b,c] Shift, ppm		Total Calc. Shift[d], δ		Expt. Shift, δ
		I[e]	II[f]	I[e]	II[f]	
a	-0.87	-0.43	-0.28	5.97	6.12	6.11
b	-0.64	-0.34	-0.20	6.29	6.43	6.38
c	+0.04	-0.15	+0.11	7.16	7.42	7.07
d	-1.09	-0.31	+0.25	5.88	6.43	6.39
e	-0.49	-0.75	-0.33	6.03	6.46	7.39
f	(-2.09)[g]	-4.29	-6.17	0.89	-0.99	-2.79

[a]Calculated from the ^{13}C Shifts. [b]A negative shift is upfield, a positive is downfield. [c]Relative to ring current shift of benzene = +0.02. [d]Charge Shift + Ring Current Shift + 7.27. [e]Calculated using defe' MMPM calculated torsional angle (see Table III). [f]Calculated using defH$_f$ MMPM calculated torsional angle. [g]By difference.

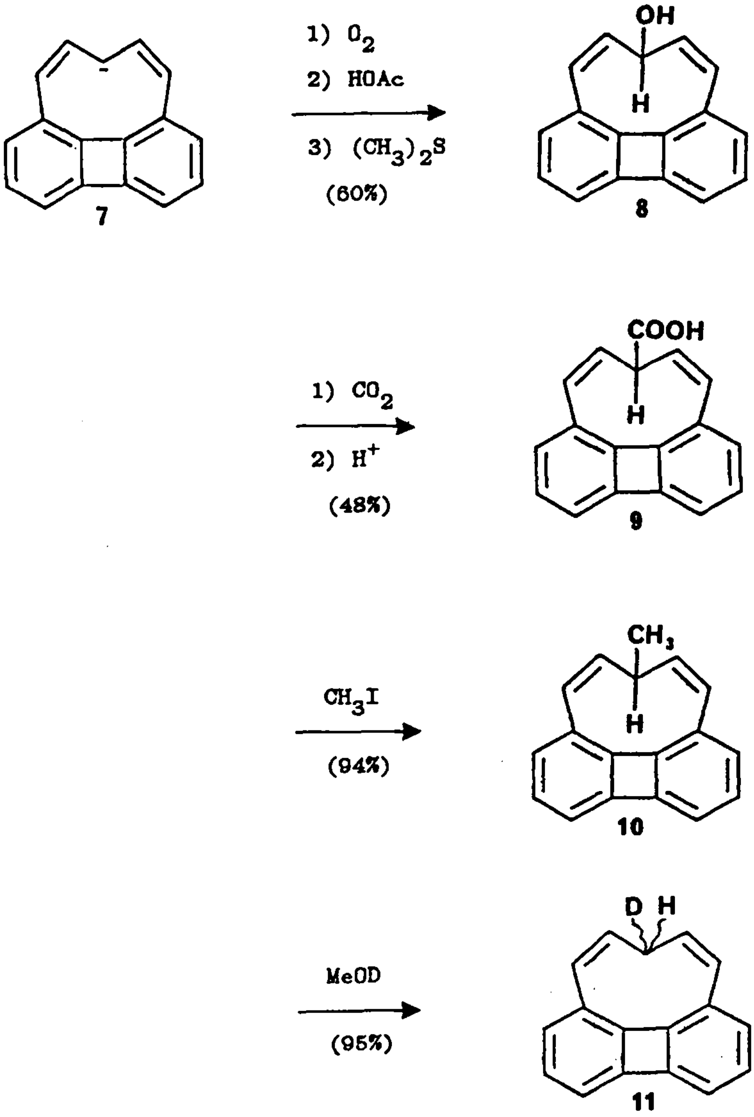
Although the Hückel calculations yield charge densities, the lack of explicit electron-electron repulsions in the model make it desirable to use an alternate method to estimate the charge densities used to calculate chemical shifts in 7. The charge density at each carbon of 7 was assigned by using the increments in ^{13}C chemical shifts in going from 6 to 7 (see Table IV), and the assumption that a full negative charge causes a 160 ppm upfield shift.[12]

The ^{13}C chemical shifts for the anion were assigned using 2D heteronuclear correlation NMR spectroscopy.[13] The shifts of carbons g, h, and i, not bearing protons, could not be directly assigned by this method. By analogy to the ^{13}C shifts of other related biphenylene-based compounds,[14] the two furthest downfield peaks were assigned to carbons h and i. Carbons b and d could not be differentiated by this method due to the similarity of the ^{1}H chemical shifts of their attached protons. Carbon d was assigned the further upfield shift of the two using the assumption that it would bear more negative charge as predicted by both iterated Hückel and PPP calculations.[7] The C$_f$ peak did not appear in the recorded 2D spectrum, possibly because of relaxation effects of the lithium counter-ion.[15] This was unfortunate because there were several field peaks due to solvent that confused the assignment of the ^{13}C peak for C$_f$. However, because all of the other shifts were known, the charge at C$_f$ could be estimated as the "missing" charge after assigning charges to the remaining carbons (see Table IV). In this way the charge at C$_f$ was estimated to be -0.21. The sum of the charges on the biphenylene carbons is -0.47, indicating that almost half the charge has been delocalized onto the biphenylene.

The ^{1}H chemical shifts of protons attached to carbons with a net negative charge are shifted upfield by 10 ppm per charge unit.[16] Thus by using the charge densities in Table IV, proton shifts due to charge densities for 7 can be calculated (see Table V). When these charge shifts are combined with the ring current shifts calculated by using Hückel-McWeeny[9] ring currents and an in-plane segmented (Biot-Savart[17]) geometric model,[18] the shifts reported in Table V are obtained. In calculating the ring current contributions to these shifts, both sets of ring currents from Model I and Model II (see Table II and discussion in text) were employed. In general, the shifts calculated using the smaller twist angle (Model II) give better results. In both cases the shifts for the biphenylenic protons are within the expected error of the calculations (0.3 ppm).[18] The results are not as good for the protons on the nine-membered ring, especially for the interior proton (H$_f$). The shift of this proton is very sensitive to its position over the ring. The calculated shifts of protons d, e, and f would all be closer to the experimental shifts if the diamagnetic ring current in the nine-membered ring were larger. This discrepancy could result from errors in the molecular mechanics generated coordinates or from the way the area of the ring was assigned. Finally, the discrepancies could result from the misassignment of charges, particulary at C_f. Considering the above problems, the quality of the fit of the calculated shifts to the experimental shifts is satisfying. The question posed at the begining of this section cannot be answered precisely, but it would appear that the 7.7 ppm upfield shift of proton H_f in passing from 6 to 7 arises roughly 70% from a ring current shift and 30% from a charge shift.

Chemistry. Anion 7 was quenched by a variety of electrophiles (see Scheme 1). The stereochemistry of products 8, 9, and 10 was assigned by the ^{1}H NMR shift of the remaining apical proton. These protons resonate at 7.28, 6.19, and 5.40 ppm for compounds 8, 9, and 10, respectively. In hydrocarbon 6, H-*endo* absorbs at 4.88 ppm and H-*exo* at 2.63 ppm, with the shift difference being due to a combination of ring current and local anisotropy effects[6]. The chemical shifts of the apical protons in the substituted compounds are consistent with relacement of H-*exo* and an additional downfield shift of 0.52 to 2.40 ppm from the added substitutent.[19] The observation of exclusive *exo* product would be expected for attack from the less hindered face of the anion.

Scheme 1

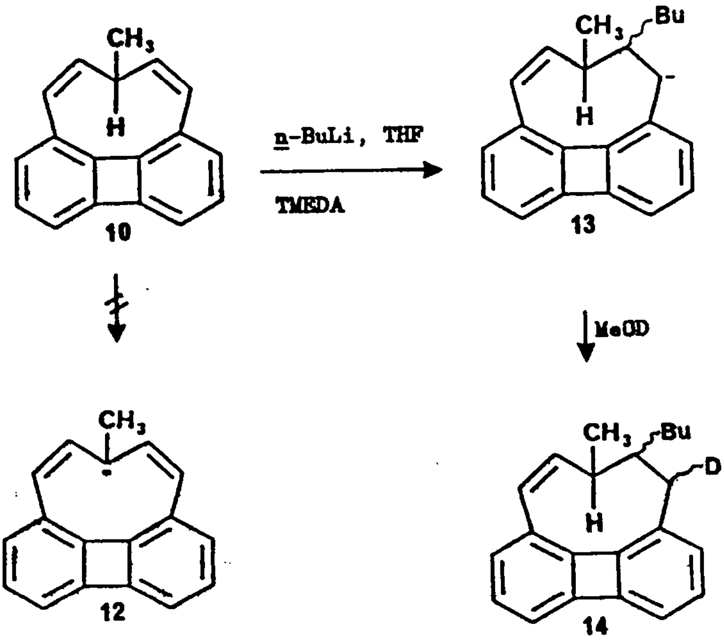


Integration of the ^{1}H NMR spectrum of 11 showed about 95% deuterium incorporation. Approximately 45% of the deuterium was in the exo position with the remainder endo. This small difference could be due to a steric isotope effect with the deuterium favoring the more sterically congested endo site.[20] Attempts to get quantitative data for the equilibration of 11 by NMR techniques were unsuccessful, although the results were qualitatively consistent with exo deuterium addition followed by equilibration to the observed 45:55 mixture. The barrier to this equilibration for the non-deuterated compound 6 has been found to be 21 kcal/mol both by experiment and by molecular mechanics calculations.[6] This corresponds to a half life of 11.1 minutes at room temperature.

The comparison of 12, the anion derived from 10, with anion 7 was of particular interest due to the extra steric requirements posed by the additional methyl group. The remaining apical hydrogen of 10 is in the more hindered endo position and thus may be more difficult for a base to remove. If the planar-in anion formed, the planar geometry needed for maximum delocalization would be unattainable because of the severe Van der Waals repulsions. If the planar-out structure were to be formed instead, it would suffer from the large angle distortions described above for 7. Clearly the methyl group will be forced out of the plane to lessen these effects, but whether the in or out geometry is preferred is unclear.

Molecular mechanics calculations favor the in-geometry and predict the out-of-plane bend of the methyl group to be 83.3°,[8] greater than the 57.7° predicted for the hydrogen in 7. The calculations also predict that 10 will have 1.4 kcal/mol more steric energy than 6. This difference in steric energy increases to 5.5 kcal/mol when comparing the two anions. These differences can be partially explained by looking at the calculated torsional angles for compounds 6, 7, 10, and 12 (see Table III). In the neutral compounds the planarity of the ethylenic groups is preserved, but the double bond planes are twisted relative to the plane of the biphenylene.

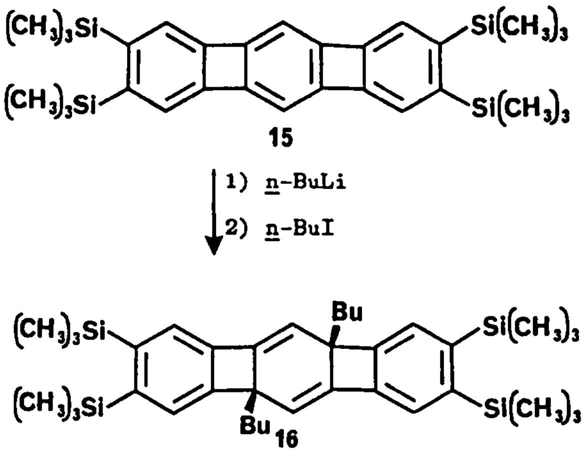
In forming the anion, the conjugation in the double bonds decreases, but the p-orbitals on the carbons α to biphenylene move closer to being perpindicular to the biphenylene plane, resulting in better overlap and charge dispersal. The calculated π-delocalization energy is slightly greater in 7 than in 12 (21.22 β vs. 21.09 β), as would be expected for the slightly more planar 7. It follows from these considerations that not only should 12 be harder to form than 7, but once generated it should be less stable than 7.



Treatment of 10 with n-butyllithium and TMEDA at 0°C in THF resulted in the gradual formation of a deep blue solution. This color quickly dispersed upon addition of methanol-d. After an extractive work-up, TLC with hexane elution showed the presence of two hydrocarbons which were separated by HPLC. The slower moving compound was starting material. The ^1H NMR spectrum of the faster moving compound was rather complex. The typical ABC pattern for biphenylenic protons was present, but broadened, indicative of an unsymmetrically substituted biphenylene. There were two one-proton resonances (a doublet and a triplet) in the vinyl region and a large number of aliphatic proton peaks. Mass spectroscopy revealed that both a butyl group and a deuterium had been added.

Apparently, for the reasons discussed above, anion 12 does not form. Instead the n-butyl anion undergoes a nucleophilic addition to one of the ethylenic groups to give 13, presumably the blue species observed. This anion is then quenched by the methanol-d to give 14. It is also possible that the n-butyl anion first donates an electron to the π-system followed by a radical coupling to make 13. The absence of any other products, however, makes the radical route unlikely.

Recently, Vollhardt[21] reported the alkylation of the biphenylenic compound, 15. In that case the alkyl group adds to one of the carbons of a four-membered ring. Upon quenching with n-butyl iodide, compound 16, the stereochemistry of which was determined by X-ray crystallography, was isolated. While Vollhardt concludes that the LUMO coefficient controls at least the initial alkylation of 15, in 10 it seems likely that the regiochemistry of attack is determined by the stability of the anion formed.



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Experimental Section

General Methods. ^1H NMR spectra were recorded on a Brucker WM-300 (300 MHz) spectrometer in $CDCl_3$. Shifts are relative to the residual $CHCl_3$ peak (δ 7.240). ^{13}C NMR spectra were recorded on a JEOL FX-90 (22.49 MHz) spectrometer in $CDCl_3$ with shifts relative to the central peak of the solvent triplet (δ 77.00). The 2D NMR spectrum was recorded on a Varian XL-400 (400 MHz) spectrometer in THF-d_8 with shifts relative to the central peak of the solvent (δ 64.7). Mass spectra were obtained on an AEI MS902 mass spectrometer. Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Benzene and THF were freshly distilled form sodium/benzophenone. The silica gel used for column chromatography was ICN 32-63 mesh. Anion-forming reactions were done in oven-dried glassware under N_2.

Preparation of anion 7 for NMR. The following procedure was carried out in duplicate. To an NMR tube fused to a glass tube with two male ground-glass joints was added 7.5 mg (0.035 mmol) 6 in 1 mL benzene. One of the joints was connected to a vacuum line, the NMR tube was cooled to 0°C, and the benzene was removed by vacuum transfer. Under positive N_2 pressure, the solid was dissolved in 0.5 mL THF and 0.4 mL (0.25 mmol) n-butyllithium in hexanes was added.

The solution immediately turned dark red. The THF and hexanes were removed by vacuum transfer and 0.4 mL THF-d_8 was transferred in from a reservoir where it had been stored over K/Na/Cs alloy (use of THF-d_8 stored over K quenched the anion). After submerging the bottom of the NMR tube into liquid N_2, the system was evacuated to 2.5x10^{-6} torr and the tube was sealed with a torch. ^{1}H NMR δ 7.07, 6.38, 6.11 (ABC, J=8.82, 5.84, 6H), 7.39, 6.39, -2.79 (ABX, J_{AB} = 6.32, J_{BX} = 14.58, 5H); ^{13}C NMR δ 150.52, 139.61, 131.76, 125.67, 125.50, 119.43, 109.98, 102.48. One tube was opened and quenched with several drops of MeOH. After an extractive work-up only starting material was recovered.

(*Z*,*Z*)-3*H*-Cyclonona[*def*]-biphenylen-3-ol (8). To a stirred solution of 6 (20 mg, 0.093 mmol) in THF (10 mL) at 0°C was added *n*-butyllithium in hexanes (0.12 mL, 0.19 mmol). The resulting red solution was stirred for 5 min and then O_2 (passed through a silica-filled drying tube) was bubbled through the reaction mixture, causing it to turn yellow within 5 sec. Acetic acid and dimethyl sulfide (ca. 1 mL of each) were added and the yellow suspension was stirred for an additional 2 hr at 0°C. The reaction mixture was added to Et_2O and the mixture was washed with water, 2 portions of sat $NaHCO_3$ (aq), and again with water. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. Purification by flash chromatography on a silica gel column with CH_2Cl_2 elution yielded 8 as yellow needles (13 mg, 60%): mp 212-215°C; ^{1}H NMR δ 7.28 (t, J=8.8, 1H, CHOH), 6.62, 6.43, 6.35 (ABC, J=6.81, 6.30, 6H, ArH), 5.83 (d, J=11.2, 2H, ArCH), 5.66 (dd, J=11.2, 8.8, 2H, ArCHCH), 1.65 (s, 1H, OH); ^{13}C NMR δ 150.57, 149.81, 134.91, 130.25, 128.84, 127.38, 126.52, 116.49, 65.89; mass spectrum m/e (relative intensity) 233 (28.18), 232 (M^{+} 84.96), 231 (10.66), 216 (15.36), 215 (28.36), 214 (9.05), 213 (20.35), 205 (12.24), 204 (44.04), 203 (100.00), 202 (26.31), 201 (15.43), 200 (15.97), 190 (7.47), 189 (28.71), 187 (9.58); mass spectrum m/e 232.0890, calc. 232.0888 for $C_{17}H_{12}O$.

(*Z*,*Z*)-3-Methyl-3*H*-cyclonona[*def*]biphenylene (10). To a stirred solution of 6 (9.8 mg, 0.045 mmol) in THF (4 mL) at 0°C was added *n*-butyllithium in hexanes (0.2 mL, 0.32 mmol). The resulting red solution was stirred for five min and was then quenched with methyl iodide (0.25 mL, 4.0 mmol). The reaction mixture was added to Et_2O and the mixture was washed with several portions of water, dried ($MgSO_4$), and filtered. Removal of solvent in vacuo gave an orange oil which was sublimed at 85-110°C (0.1 torr). The oily sublimate was flash chromatographed on silica gel with CS_2 elution to remove a baseline impurity and two faster moving products. The product came off as an orange band. Removal of solvent in vacuo yielded 10 as an oily solid (9.8 mg, 94%): mp 89-94°C (pentane); ^{1}H NMR δ 6.62, 6.41, 6.34 (ABC, J=8.3, 6.8, 6H, ArH), 5.71 (d, J=10.6, 2H, ArCH), 5.49 (t, J=10.3, 2H, ArCHCH), 5.4 (m, 1H, CHMe), 1.08 (d, J=5.88, 3H, CH_3); ^{13}C NMR δ 150.53, 149.55, 139.41, 130.34, 128.63, 128.19, 124.59, 115.81, 34.14, 20.93; mass spectrum m/e (relative intensity) 231 (25.16), 230 (M^{+} 100.00), 229 (23.33), 228 (8.99), 216 (13.21), 215 (41.35), 214 (8.01), 213 (14.82), 203 (12.31), 202 (12.70), 189 (24.98); mass spectrum m/e 230.1083, calc. 230.1095 for $C_{18}H_{14}$.

(*Z*,*Z*)-3*H*-Cyclonona[*def*]biphenylene-3-carboxylic acid (9). To a stirred solution of 6 (5.2 mg, 0.024 mmol) in THF (2 mL) at 0°C was added *n*-butyllithium in hexanes (0.04 mL, 0.064 mmol). The resulting red solution was stirred for ten min and then CO_2 (passed through a silica-filled drying tube) was bubbled through it. The reaction mixture was added to Et_2O and the mixture was extracted with dilute NaOH (aq). The yellow basic layer was acidified with HCl and extracted with Et_2O. The Et_2O extracts were combined and washed with water, dried ($MgSO_4$), filtered, and the solvent was removed in vacuo to give 9 (3 mg, 48%) as a yellow solid: mp 243-250°C (dec); ^{1}H NMR δ 6.65, 6.45, 6.38 (ABC, J=8.36, 6.78, 6H, ArH), 6.19 (t, J=10.2, 1H, CHCOOH), 5.95 (d, J=10.9, 2H, ArCH), 5.79 (t, J=10.6, 2H, ArCHCH); ^{13}C NMR δ 150.53, 149.11, 130.39, 129.56, 129.12, 128.19, 127.02, 116.44, 34.34 (COOH not seen); mass spectrum m/e (relative intensity) 261 (19.6), 260 (M^{+} 100.0), 216 (15.8), 215 (70.7), 214 (36.6), 213 (67.5), 211 (10.1), 189 (40.0), 188 (11.2), 187 (17.0); mass spectrum m/e 260.0834, calc. 260.0837 for $C_{18}H_{12}O_2$.

(*Z*)-2-Butyl-1-deuterio-2,3-dihydro-1*H*-cyclonona[*def*]biphenylene (13). To a stirred solution of 10 (3 mg, 0.013 mmol) in THF (2 mL) at 0°C was added N,N,N',N'-tetramethylethylenediamine (0.05 mL, 0.33 mmol) and *n*-butyllithium in hexanes (0.1 mL, 0.16 mmol). The solution was stirred for 25 min during which time it gradually turned deep blue. After MeOD (0.5 mL) was added, the reaction mixture was poured into Et_2O and the mixture washed with water, dilute HCl, water, and brine. After drying ($MgSO_4$) and filtering, removal of solvent in vacuo gave an oily yellow solid which gave two spots upon hexane TLC (R_f's 0.19 and 0.25). The two components were separated by HPLC with hexane elution. The second compound off the column was recovered starting material (2 mg). The less polar compound was a colorless oil (< 1 mg): ^1H NMR δ 6.64, 6.49 (m, 6H, Ar$\underline{H}$), 6.13 (d, J=11.3, 1H, ArC$\underline{H}$), 5.34 (t, J=11.3, 1H, ArCHC$\underline{H}$), 3.22 (broad m, 1H, C$\underline{H}$Me), 2.38 (m, 1H, ArCHD), 1.68 (broad m, 2H, ARCHDC$\underline{H}_2$), 1.5-1.2 (broad m, C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$), 0.98 (d, J=6.57, 3H, CHC$\underline{H}_3$) 0.9 (t, J=7, 3H, $CH_2C\underline{H}_3$); mass spectrum m/e (relative intensity) 290 (23.34), 289 (M^+ 100.00), 288 (8.04), 232 (12.23), 231 (13.39), 230 (15.88), 218 (14.26), 217 (16.21), 216 (22.01), 215 (16.50), 204 (15.75), 203 (23.76), 202 (16.38), 190 (10.49), 189 (10.57); mass spectrum m/e 289.1940, calc. 289.1941 for $C_{22}H_{23}D$.

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