J. Am. Chem. Soc. 1989, 111, 3633-3640 3633

Methylated Biphenylene Dianions: NMR Spectroscopic and Theoretical Investigation[1]

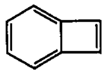
Joseph W. Bausch,[2a] Peter S. Gregory,[2b] George A. Olah,*[2a] G. K. Surya Prakash,*[2a] Paul v. R. Schleyer,*[2b] and Gerald A. Segal[2a]

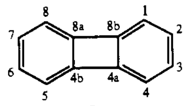
Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, and Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 8520 Erlangen, West Germany. *Received February 8, 1988. Revised Manuscript Received December 14, 1988*

Abstract: A series of methylated biphenylene dianions were generated by reduction of the respective hydrocarbons with lithium metal in THF and 2-MeTHF solutions with the aid of ultrasound and characterized by ^{1}H, ^{13}C, and ^{7}Li NMR spectroscopy. The majority of these dianions were found to be more stable than the parent biphenylene dianion toward ring opening to the corresponding dilithiobiphenyls. The enhanced stability of the dianions substituted with methyl groups at the ortho positions appears to be of steric origin, whereas the diminished stability of the meta-substituted derivatives is of electronic origin. The direction of ring opening of these dianions to substituted dilithiobiphenyls was rationalized by MO calculations. Temperature-dependent ^{13}C NMR studies as well as MNDO calculations give valuable insights concerning solvation (i.e., ion pairing) as well as the location of the lithium counterions in these delocalized dianionic networks. In the case of octamethylbiphenylene dianion an interesting aggregation phenomenon was observed, as evidenced by concentration as well as temperature-dependent NMR spectra.

The chemistry of cyclobutadiene (**1**) and related benzo derivatives is extensive and varied.[3] The parent cyclobutadiene is unstable and is not directly isolable except in an argon matrix. Benzocyclobutadiene (**2**) also has low stability and has only been spectroscopically observed in an argon matrix at low temperature.[4] Dibenzocyclobutadiene, commonly known as biphenylene (**3**), is a stable molecule first prepared by Lothrup in 1941.[5] A single-crystal X-ray study[6] of biphenylene showed the molecule to be planar with a weakly coupled benzenoid system rather than a derivative of cyclobutadiene, demonstrated by a long (1.51-Å) C_{4a}–C_{4b} bond. Molecular orbital calculations support various spectroscopic and chemical evidence that biphenylene is aromatic.


1

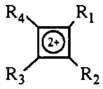

2



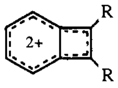
3

Two-electron oxidation of these molecules should lead to the corresponding aromatic dications ($4n + 2\pi$ electrons where n = 0, 1, 2) according to Hückel's rule. Although the parent cyclobutadiene dication **4** has not been observed, various substituted derivatives **5** have been prepared and spectroscopically characterized under long-lived superacidic conditions[7a] and, in fact, are aromatic 2π-electron Hückeloid systems.[7b] Similarly, the parent benzocyclobutadiene dication **6** is not known, but substituted derivatives like the 1,2-dimethyl derivative **7** have been prepared and observed[8] by analogous methods. These dications are 6π-electron aromatic systems. Biphenylene has also been oxidized in superacid to the corresponding dication **8a** and is stable up to 0 °C.[8] This dication and various methylated derivatives are in fact fully delocalized 10π-electron aromatic systems as characterized by ^{13}C and ^{1}H NMR spectroscopy.

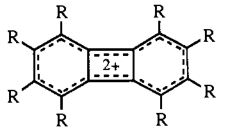

4



5



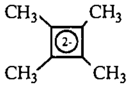
6 R=H
7 R=CH_3



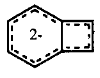
8a R=H
8b R=CH_3

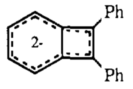
Correspondingly, two-electron reduction of these systems should, by Hückel's $4n + 2\pi$ electron rule, give dianionic aromatic systems. But if more reasonable Coulomb integrals are used in the MO calculation, the cyclobutadiene dianion **9** is unstable due to its possessing a doubly degenerate filled anti-bonding molecular orbital.[9a] Not unexpectedly, the cyclobutadiene dianion has never been observed. Attempts to generate the tetramethylcyclobutadiene dianion **10** from 3,4-dibromo-1,2,3,4-tetramethylcyclobutene and n-BuLi also failed to give the dianion even as a transient species.[9b] The benzocyclobutadiene dianion **11**, a 10π-electron system, has yet to be observed, but the 1,2-diphenyl derivative **12** has been prepared and spectroscopically characterized.[10a] MO theory predicted that the phenyl substituents would stabilize this dianion,[10b] but the phenyl groups also render this dianion not a true benzocyclobutadiene dianion, as much of the negative charge is delocalized into the phenyl substituents.


9



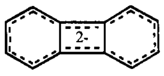
10

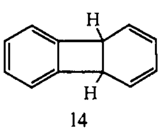

11



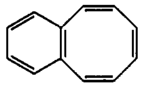
12

Early reports in the literature[11,12] on attempts to generate and observe (by UV spectroscopy) the biphenylene dianion **13**, a


13



14


15

---

[1] Considered Novel Aromatic Systems. 10. Part 9: Olah, G. A.; Grant, J. L. *J. Org. Chem.* **1977**, *42*, 2237-2240.

[2] (a) University of Southern California. (b) Universität Erlangen-Nürnberg.

[3] Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967.

[4] Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614-617.

[5] Lothrup, W. C. *J. Am. Chem. Soc.* **1941**, *63*, 1187-1191.

[6] Fawcett, J. K.; Trotter, J. *Acta. Crystallogr.* **1966**, *20*, 87-93.

[7] (a) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 6290-6304. (b) IGLO calculations by Schleyer on the cyclobutadiene dication indicate ^{13}C chemical shifts to differ by 70 ppm between the planar and puckered geometries and show conclusively that the puckered structure for the tetramethyl derivative is favored in solution. See: Bremer, M.; Schleyer, P. v. R.; Fleischer, U. *J. Am. Chem. Soc.* **1989**, *111*, 1147-1148.

[8] Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045-6049.

[9] (a) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961. (b) Adam, W.; Piedras, R. *Tetrahedron Lett.* **1963**, *21*, 1387-1392.

[10] (a) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem.* **1982**, *94*, 141. (b) Roberts, J. D.; Streitwieser, A.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579-4582.

[11] Bauld, N. L.; Banks, D. *J. Am. Chem. Soc.* **1965**, *87*, 128-129.

[12] Waack, R.; Doran, M. A.; West, P. *J. Am. Chem. Soc.* **1965**, *87*, 5508-5510.

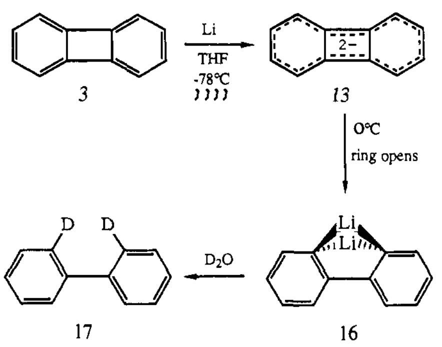
0002-7863/89/1511-3633$01.50/0

Table I. ^1H, ^{13}C, and ^7Li NMR (ppm) of Methylated Biphenylene Dianions Observed

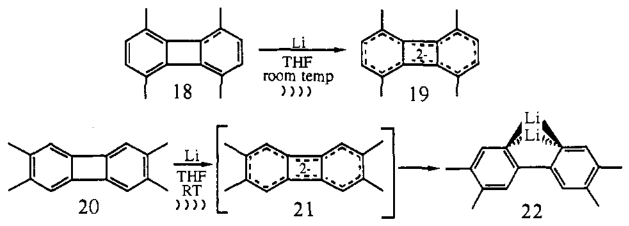
ion	$^1H^a$	$^{13}C^a$	$^7Li^c$
37^{b,d}	2.48 (s, 12 H, CH_3 at C_1, C_4, C_5, C_8) 2.18 (s, 12 H, CH_3 at C_2, C_3, C_6, C_7)	117.9 (s, C_1, C_4, C_5, C_8) 102.1 (s, C_2, C_3, C_6, C_7) 93.2 (s, C_{4a}, C_{4b}, C_{8a}, C_{8b}) 17.6 (q, CH_3 at C_1, C_4, C_5, C_8) 15.6 (q, CH_3 at C_2, C_3, C_6, C_7)	-8.7
19^b	2.56 (s, 12 H, CH_3 at C_1, C_4, C_5, C_8) 5.34 (s, 4 H, H at C_2, C_3, C_6, C_7)	121.0 (s, C_1, C_4, C_5, C_8) 100.6 (d, C_2, C_3, C_6, C_7) 98.3 (s, C_{4a}, C_{4b}, C_{8a}, C_{8b}) 21.1 (q, CH_3 at C_1, C_4, C_5, C_8)	-6.8
27^b	2.60 (s, 6 H, CH_3 at C_1, C_5) 7.03 (d, 2 H, C_4, C_8) 5.64 (t, 2 H, H at C_3, C_7) 5.33 (d, 2 H, H at C_2, C_6)	123.5 (s, C_1, C_5) 98.6 (d, C_2, C_6) 99.0 (d, C_3, C_7) 112.5 (d, C_4, C_8) 97.7 (s, C_{8a}, C_{4a}) 97.9 (s, C_{8b}, C_{4b}) 20.9 (q, CH_3 at C_1, C_5)	-4.7
24^b	2.55 (s, 6 H, CH_3 at C_1, C_8) 6.90 (d, 2 H, H at C_4, C_5) 5.62 (t, 2 H, H at C_3, C_6) 5.33 (d, 2 H, H at C_2, C_7)	122.9 (d, C_4, C_5) 112.1 (s, C_1, C_8) 100.5 (d, C_3, C_6) 99.0 (d, C_2, C_7) 98.8 (s, C_{8a}, C_{8b}) 96.5 (s, C_{4a}, C_{4b}) 21.5 (q, CH_3 at C_1, C_8)	-4.7

^{a}Referenced to external TMS. ^{b}At 22 °C. ^{c}Referenced at 1 M LiCl in D_2O (0.0 ppm). ^{d}OMBP^{2-} species predominating at 22 °C in THF.

Scheme I



Scheme II



14π-electron system were inconclusive. The first direct observation of **13** was reported by Cox in 1971[13] by reducing biphenylene with Li metal in THF and observing a δ −7.0 shift (relative to 1 M LiCl) in the ^7Li NMR spectrum. This work was part of a ^7Li NMR study of various anions, but the result was not further investigated. Another NMR study of Günther[14] failed to directly observe **13**, but its formation was implicated by the formation of dihydrobiphenylene (**14**) upon quenching with water and benzocyclooctatetraene (**15**) after rearrangement.

More recently Günther, Edlund, and co-workers[15] were able to observe the biphenylene dianion by ^1H, ^{13}C, and ^7Li NMR spectroscopy having prepared it by using Li sand with the aid of ultrasound at low temperature (see Scheme I). The dianion is aromatic by application of the Spiesecke–Schneider correlation for aromatic systems and is stable up to 0 °C. Above 0 °C ring opening to 2,2′-dilithiobiphenyl[16] (**16**) begins to occur. Quenching with D_2O yields **17**. The half-life for **13** was determined to be 1.7 h at 25 °C.

Our studies on biphenylene dianions stem from our longstanding interest in novel aromatic systems. Independent of Günther, Edlund, and co-workers' successful work[15] on the biphenylene dianion, we also found similar conditions (room temperature versus −78 °C) suitable to generate and observe the biphenylene dianions, but our studies, which we now report in full, centered mainly on the investigation of a series of methylated biphenylene dianions ranging from mono- to octamethyl systems. The methylated biphenylene dianions were characterized by ^{13}C, ^1H, and ^7Li NMR spectroscopy. Their temperature- and solvent-dependent NMR spectra indicate the complex role that solvent and lithium counterions play in the chemistry of these dianionic systems. Furthermore, the locations of the lithium cations in relation to the organic dianionic framework of these systems as well as the interesting ring opening to methylated dilithiobiphenyls were probed by experiment as well as MO theory.

Results and Discussion

From the early stages of our work we found that the biphenylene dianion could even be observed at room temperature, using Li metal and THF as solvent and vigorous sonication. Without sonication at ambient temperature the rate of ring opening (k_2) of the dianion is significantly higher than its formation rate (k_1) from the radical anion. Ultrasound irradiation can make $k_1 \gg k_2$ so that a significant concentration of the dianion is built up allowing spectroscopic observation, although rapid ring opening to 2,2′-dilithiobiphenyl (**16**) simultaneously occurs.

We extended this method of ultrasound irradiation at room temperature to a series of methylated biphenylenes. The reduction of 1,4,5,8-tetramethylbiphenylene (**18**)[17] using Li metal in THF gave the 1,4,5,8-tetramethylbiphenylene dianion (**19**), which was surprisingly stable to ring opening for several days at room temperature (see Table I for NMR data). On the other hand, the reduction of 2,3,6,7-tetramethylbiphenylene (**20**)[18] resulted only in being able to observe the ring-opened species **22**, assumed to proceed through the dianion **21**, which appears to be less stable

---

(13) Cox, R. H.; Terry, H. W.; Harrison, L. W. *Tetrahedron Lett.* **1971**, 4815-4818.

(14) Günther, M. E.; Aydin, R.; Buchmeier, W.; Engelen, B.; Günther, H. *Chem. Ber.* **1984**, *117*, 1069-1076.

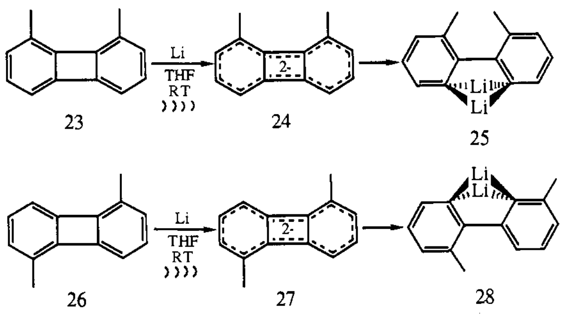
(15) Günther, H.; Puttkamer, H. V.; Finneiser, K.; Benken, R.; Edlund, U.; Eliasson, B. *Helv. Chim. Acta* **1986**, *69*, 955-961.

(16) Shown by X-ray crystallography to be a bridged system: Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184-1185. Therefore, we have represented all the dilithiobiphenyls prepared as bridging systems.

(17) Prepared from the corresponding anthranilic acid following the procedure for biphenylene from: Logullo, L. M.; Seitz, A. H.; Friedman, L. *Org. Synth.* **1968**, *48*, 12-17.

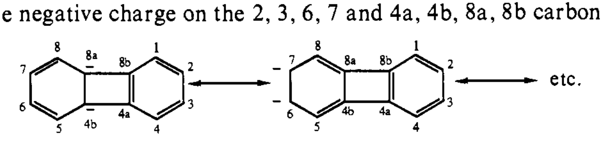
(18) Constatine, P. R.; Hall, G. E.; Harrison, C. R.; McOmie, J. F. W.; Searle, R. J. G. *J. Chem. Soc. C* **1966**, 1767-1769.

Scheme III



than the parent biphenylene dianion (see Scheme II).

Thus, it seems that methyl substitution at the 1, 4, 5, and 8 positions sterically hampers ring opening to the dilithiobiphenyls, and methyl substitution at the 2, 3, 6, and 7 positions destabilizes the dianions for electronic reasons. This is in accord with simple resonance forms of the biphenylene dianion, which place most of the negative charge on the 2, 3, 6, 7 and 4a, 4b, 8a, 8b carbons.



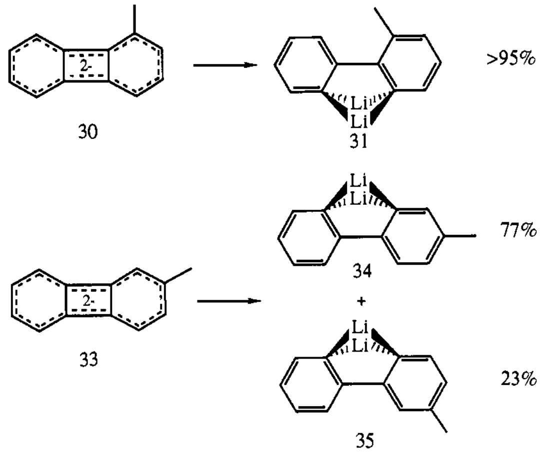
Further support for the steric inhibition of ring opening comes from the reduction of 1,8-dimethylbiphenylene (**23**),[19] which gave the dianion **24** that was stable to ring opening for several days at room temperature (for NMR data see Table I). When a mixture of 1,5- and 1,8-dimethylbiphenylenes[17] was reduced with Li metal in THF the 1,5-dimethylbiphenylene dianion (**27**) formed (see Table I for NMR data) was much less stable than the 1,8-isomer and completely ring opened to 3,6′-dimethyl-2,2′-dilithiobiphenyl (**28**) after a period of 3–4 days at room temperature. The 1,8-dimethylbiphenylene dianion eventually completely ring opened to give primarily (>95%) 6,6′-dimethyl-2,2′-dilithiobiphenyl (**25**) (see Scheme III).

Two monomethylated biphenylenes were also reduced with Li metal in THF. 1-Methylbiphenylene (**29**) when reduced gave in greater than 95% yield 6-methyl-2,2′-dilithiobiphenyl (**31**). A sample of 2-methylbiphenylene (**32**)[20] when reduced gave approximately 77% 4-methyl-2,2′-dilithiobiphenyl (**34**) and 23% 5-methyl-2,2′-dilithiobiphenyl (**35**) (see Scheme IV). Even with many attempts the 2-methylbiphenylene dianion (**33**) was not observed by NMR at room temperature, as ring opening to the dilithiobiphenyl derivatives (**34** and **35**) appears to be extremely fast.

Temperature-dependent ^{13}C NMR studies were also carried out in an attempt to identify the positions of the lithium counterions,[21] Günther, Edlund, and co-workers' data on the parent biphenylene dianion showed a shielding of C_{4a} with increasing temperature while C_1 and C_2 were being deshielded. They interpret this as the lithium ions being located above and below the four-membered ring, with increasing temperature shifting the solvent-separated ion pair/contact ion pair (ssip/cip) equilibrium toward the contact ion side causing charge polarization at the four-membered-ring carbons. This results in the observed shielding of these carbons with increasing temperature. Our studies on the 1,4,5,8-tetramethylbiphenylene dianion (**19**) gave almost the exact same behavior as in the parent biphenylene dianion (see Figure 1). Again shielding of the four-membered-ring carbons occurs with increasing temperature.

Temperature-dependent ^{13}C NMR studies were also carried out on the 1,5- and 1,8-dimethylbiphenylene dianions. The 1,5-dianion **27** gave data very similar to those of the parent biphenylene and 1,4,5,8-tetramethylbiphenylene dianions, with the four-membered-ring carbons becoming shielded with increasing temperature. However, the 1,8-dimethylbiphenylene dianion (**24**) behaved somewhat differently, with only C_{8a} and C_{8b} becoming shielded and C_{4a} and C_{4b} showing no shielding with an increase in temperature (see Figure 1).

Scheme IV

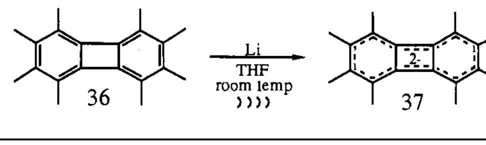


We also prepared some of the dianions in 2-methyltetrahydrofuran (2-MeTHF), a poorer cation solvator than THF. In 2-MeTHF the parent biphenylene dianion behaves very differently than in THF[15] in its temperature-dependent ^{13}C NMR spectra (see Figure 2). The C_{4a} becomes *deshielded* and the C_2 slightly *shielded* with increasing temperature, which is the exact opposite trend found in THF. These data are completely contrary to that found for the dibenzo[*b,f*]pentalene dianion on going from THF to 2-MeTHF.[21] The 1,8- and 1,5-dimethylbiphenylene dianions also showed similar trends. A possible explanation for these differing trends becomes evident from semiempirical MNDO calculations (vide infra).

To test the possibility that the temperature change induced ^{13}C chemical shift changes in the biphenylene dianion are the result of a fast aggregation equilibrium, we carried out a concentration-dependence study. In the concentration range of 0.1–0.5 M **13** in 2-MeTHF, the ^{13}C chemical shift changes were slight (<0.2 ppm) in the studied temperature range (−70 to 25 °C). Furthermore, a temperature-dependent ^{7}Li NMR study showed that the ^{7}Li resonance for the biphenylene dianion in THF becomes only slightly shielded (0.2 ppm) on going from −70 to 25 °C. Therefore, if a fast aggregation equilibrium for the biphenylene dianion is operating, larger chemical shift changes would be expected.

Further evidence for some ssip/cip equilibrium within the biphenylene dianion and the methylated derivatives thus far discussed comes from ^{7}Li NMR line widths. Normally, as temperature decreases ^{7}Li line widths increase, the result of ^{7}Li quadrupole relaxation whose rate increases with decreasing temperature.[23] However, in both THF and 2-MeTHF solution, these dianions have ^{7}Li resonances that become sharper as the temperature decreases. This could support the ssip/cip equilibrium in theory since ssip's should be preferred at lower temperatures[24] and would result in narrower line widths.

By far the most interesting and unusual methylated biphenylene dianion we observed is the octamethylbiphenylene dianion (OMBP^{2-}, **37**), prepared by reducing octamethylbiphenylene[25] (OMBP, **36**) with Li metal in THF.



---

[19] A sample was available from previous work (ref 8).

[20] Buckland, P. R.; McOmie, J. F. W. *Tetrahedron* **1977**, *33*, 1797–1801.

[21] Eliasson, B.; Edlund, U. *Org. Magn. Reson.* **1983**, *21*, 322–327.

[22] Fraenckel, G., Fraenckel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745–4747.

[23] Bauer, W.; Winchester, R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371–2379.

[24] Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829–3835.

[25] Hart, H.; Teurstein, A. *Synthesis* **1979**, 693–695.

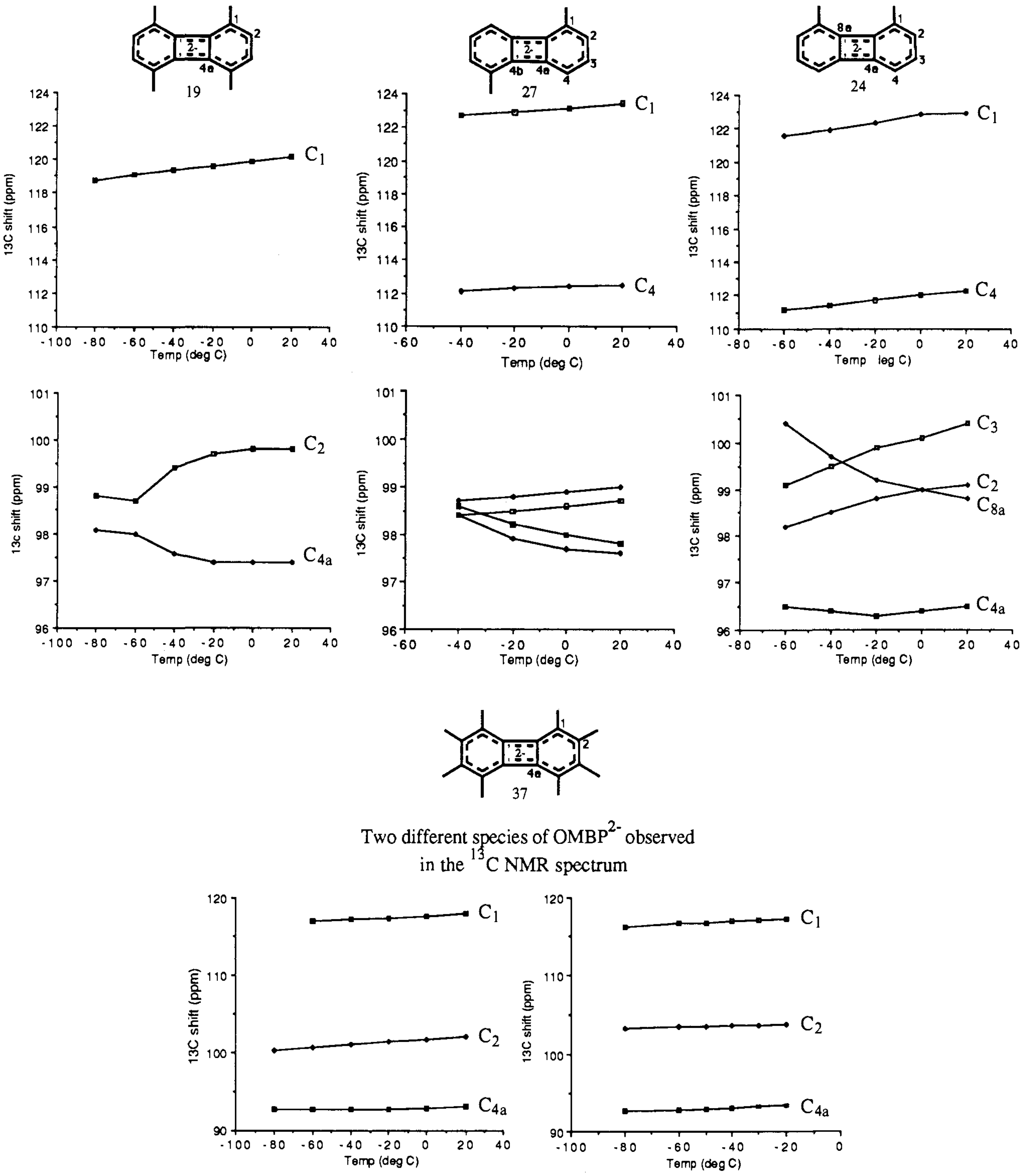


Figure 1. Temperature-dependent 50-MHz ^{13}C NMR spectroscopic data for the stable methylated dianions studied in THF.

The dianion is stable for several days at room temperature (very slow ring opening occurs). Quenching the solution with oxygen regenerated OMBP quantitatively. The ^{13}C NMR spectrum of OMBP^{2-} in THF at room temperature consists mainly of five absorptions at δ 117.9 (s), 102.1 (s), 93.2 (s), 17.6 (q), and 15.6 (q), consistent with dianion formation. The ^{1}H NMR spectrum is also in accord with formation of the dianion (see Table I for NMR data). For comparison, we also prepared the hitherto not reported octamethylbiphenylene dication (OMBP^{2+}, **8b**) by the oxidation of OMBP in SbF$_5$/SO$_2$ClF solution at −20 °C. The dication **8b** shows five absorptions in the ^{13}C NMR spectrum at δ 183.9 (s), 166.0 (s), 140.3 (s), 22.7 (q), and 16.6 (q). Both the dianion **37** and the dication **8b** fit the aromaticity criteria[26] based on Spiesecke–Schneider criterion[27] (see Table II).

The room-temperature ^{7}Li NMR spectrum of the OMBP^{2-} in THF unexpectedly consisted mainly of a sharp peak at −9.5 ppm

---

[26] A reviewer has pointed out that Hunadi's suggested probe[27a] for aromaticity relating the slope of the chemical shifts versus charge density based on the application of the Spiesecke–Schneider relationship[27b] (which itself deals only with charge density) is not fully justified. The reviewer repeated the linear least-squares calculations and found that the slopes for all three data sets are statistically indistinguishable. Although any definition of aromaticity at this time by necessity is somewhat arbitrary, the MO calculations seem to support our suggestions that these 14π-electron dianions are of aromatic nature.

[27] (a) Hunadi, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6889–6895. (b) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468–472.

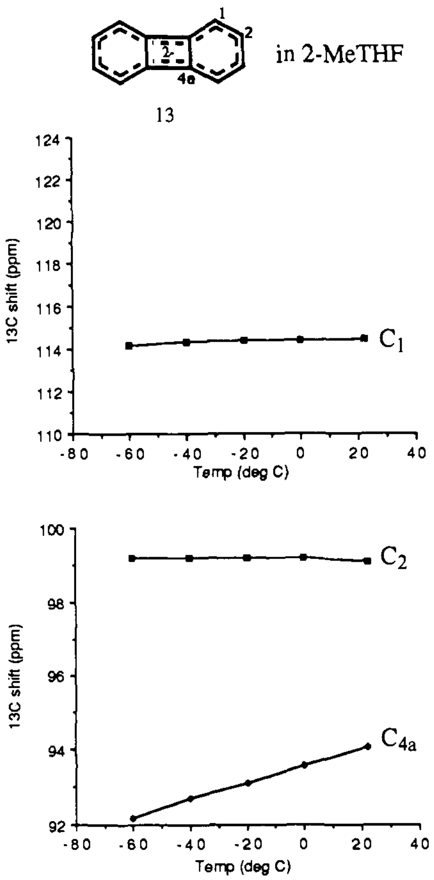


Figure 2. Temperature-dependent 50-MHz ^{13}C NMR spectroscopic data for the biphenylene dianion **13** in 2-MeTHF.

Table II. Aromaticity Criteria[27a] Based on Average ^{13}C Chemical Shifts of Biphenylene Dianions and $OMBP^{2+}$

ion	δ_{av} expectd	δ_{av} obsd[a]	ion	δ_{av} expectd	δ_{av} obsd[a]
13	105.9	103.4	**27**	105.9	104.9
37	105.9	104.4	**24**	105.9	105.0
19	105.9	106.3	**8b**	160.9	163.4

[a] Excluding methyl substitution.

and a much broader peak around −7 ppm. Both of these peaks would be reasonable for the lithium cations of $OMBP^{2-}$, but the observation of at least two signals in the ^7Li spectrum at room temperature did not seem to corroborate with the corresponding ^{13}C and ^1H NMR spectra at room temperature.

However, upon cooling of the sample the apparent discrepancy was resolved. The broad peak around −7 ppm resolved into two peaks (−7.5 and −8.2 ppm) and grew in area relative to the resonance at −9.5 ppm as the temperature was decreased to around −40 °C. At the same time another broad peak also appeared at about −5 ppm, and upon further lowering of the temperature (−70°C), this peak sharpened and grew in area relative to the other resonances. The data from the ^7Li spectra indicate an aggregation phenomenon for $OMBP^{2-}$ (e.g., monomers, dimers, trimers, etc.) analogous to the well-documented aggregation of alkyllithiums (e.g., propyllithium[22] and others[23]) and the proposed aggregation of fluorenyllithium in THF.[28] The ^{13}C and ^1H spectra at these lower temperatures usually showed only two species, as peak overlap prevents observation of other(s). The equilibrium between these different aggregates must be slow on the NMR time scale in the temperature range studied (−70 to 25 °C).

To confirm an aggregation equilibrium, the system was reexamined at varying concentrations of $OMBP^{2-}$, which demonstrated dramatic effects on the equilibrium between the species at a given temperature. Three different concentrations (0.02, 0.08, and 0.13 M) of $OMBP^{2-}$ were prepared in THF with Li metal, and their ^7Li NMR spectra were obtained at −20 °C. The most concentrated sample had the highest proportion of the species at −9.5 ppm, which is the species with the highest aggregation number. Thus, at high concentrations of $OMBP^{2-}$, the equilibrium is shifted toward higher aggregates, which supports an aggregation equilibrium. In addition, in all concentrations of $OMBP^{2-}$, the less aggregated species (those less shielded in the ^7Li spectrum) were preferred as the temperature was lowered.

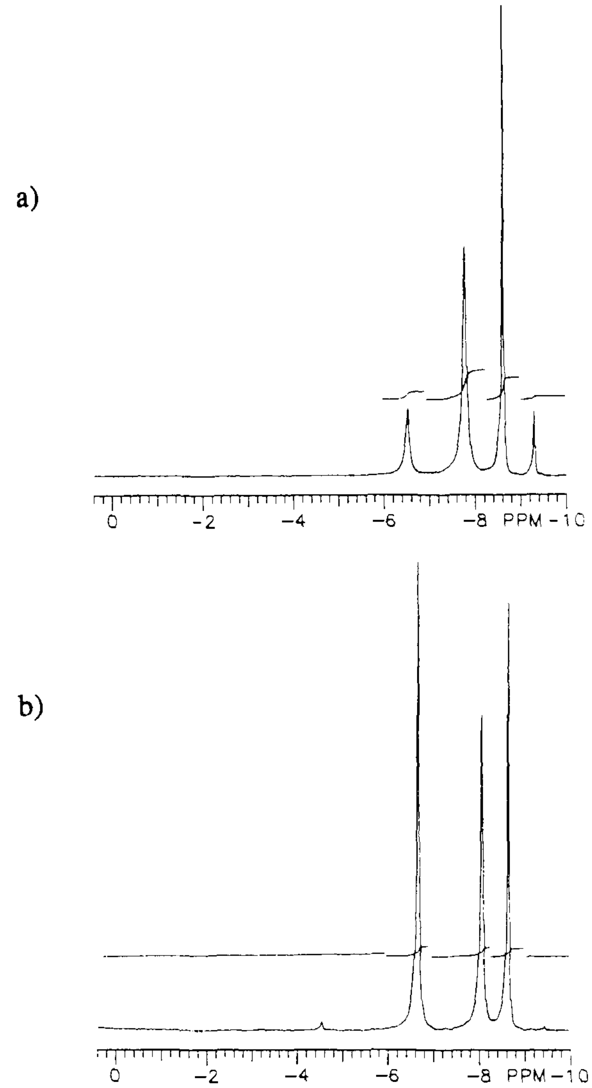


Figure 3. The 77.8-MHz ^7Li NMR spectra of 0.12 M $OMBP^{2-}$ in 2-MeTHF at (a) 22 °C and (b) -20 °C.

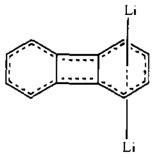
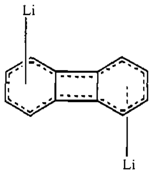
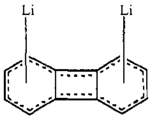
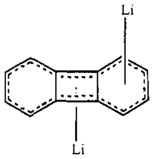
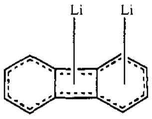
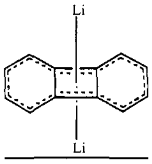
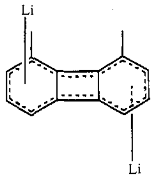
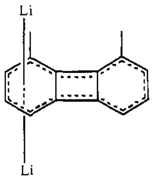
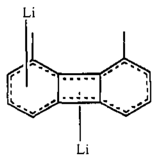
Further support for the aggregation equilibrium in $OMBP^{2-}$ came from the generation of $OMBP^{2-}$ in 2-MeTHF solution. At room temperature four sharp resonances were seen in the ^7Li NMR spectrum (see Figure 3a), indicating the presence of at least four different aggregates. A decrease in temperature again shifted the equilibrium toward the aggregates of lower coordination number (see Figure 3b) with another species (possibly the monomer?) appearing at −4.6 ppm. An increase in concentration shifted the equilibrium toward the aggregates of higher coordination number. The sharper ^7Li peaks obtained for $OMBP^{2-}$ in 2-MeTHF as compared to THF may be due to a slowing down of the intraaggregate lithium cation exchange due to diminished solvation from the more hindered solvent.

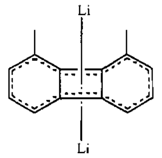
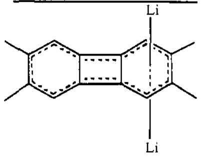
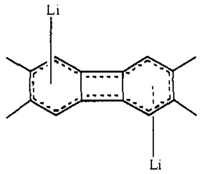
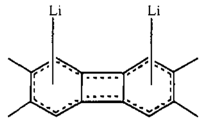
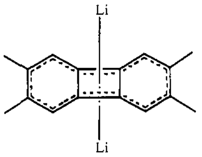
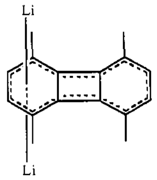
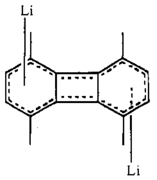
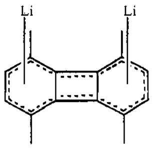
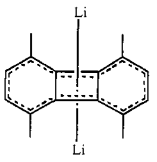
We also carried out temperature-dependent ^{13}C NMR studies of $OMBP^{2-}$ in THF. Two of the aggregates could easily be monitored (see Figure 1), and they showed behavior completely different from the other less methylated dianions studied (also see Figure 1). Both $OMBP^{2-}$ species had all their carbon resonances become slightly deshielded with increasing temperature. Similar data were found for $OMBP^{2-}$ in 2-MeTHF. These data are difficult to rationalize and show the difficulties involved in

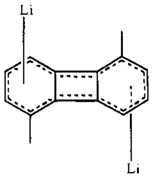
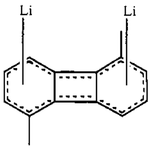
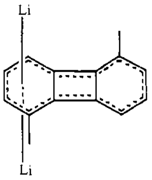
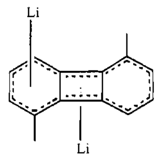
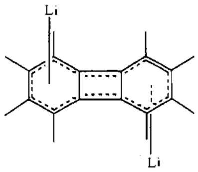
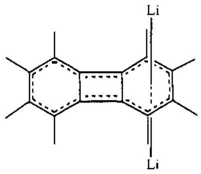
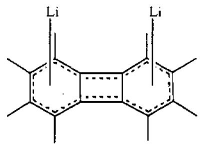
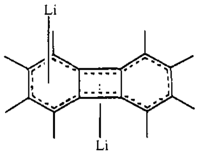
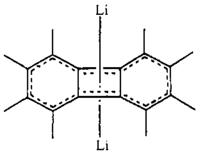
---

(28) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1967**, *89*, 2764-2765.

Table III. MNDO Heats of Formation for Various Biphenylene Systems

haptomer	heat of formtn, kcal/mol	rel energy, kcal/mol
	55.92	0.0
	56.85	0.93
	62.46	6.54
	63.79	7.87
	64.58	8.66
	70.51	14.59
	38.44	0.0, 0.0[a]
	44.85	6.41, 2.99[a]
	49.90	11.46, 8.61[a]

haptomer	heat of formtn, kcal/mol	rel energy, kcal/mol
	58.98	20.54, 18.75[a]
	34.67	0.0
	37.18	2.51
	42.18	8.14
	47.83	13.16
	34.24	0.0
	34.79	0.55
	40.62	6.38
	47.87	13.63

haptomer	heat of formtn, kcal/mol	rel energy, kcal/mol
	36.90	0.0
	38.83	1.93
	43.22	6.32
	46.64	9.74
	23.84	0.0
	28.94	5.10
	28.98	5.14
	35.40	11.56
	43.23	19.39

[a] H_2O.

determining the exact location of the lithium counterions.

Theoretical Calculations

We carried out semiempirical (MNDO)[29] calculations on biphenylene dianions with varying degrees of methyl substitution and different lithium cation locations in an attempt to rationalize the experimental results. The calculations predict the favored locations of the lithium counterions with respect to the biphenylene dianionic framework. The calculated heats of formation for various biphenylene dianion systems are shown in Table III.

Two different locations of the lithium cations compete to be the minimum for each system. The first is with the lithium cations located above and below the same six-membered ring, and the second is with the cations above and below alternate six-membered rings. The energy differences between these choices vary widely,

---

[29] Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907. Lithium parametrization was applied using Li parameters taken from MNDOC. Thiel, W. *QCPE* **1982**, *2(No. 438)*, 63.

depending on the degree of methyl substitution on the dianion. No simple relationship is apparent.

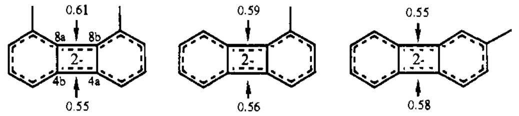
Precedents exist in the literature for MNDO studies on dilithionaphthalene,[30] dilithioanthracene,[30] dilithiophenanthrene,[30] and dilithiopentalene.[31] In all cases anti-facial selectivity was exhibited with the haptomer, with the lithium cations on opposite faces of alternate rings being the most stable and with the second most stable (by 3.5 and 5.0 kcal/mol, respectively) being the haptomer with the lithium cations located on opposite faces of the same ring. For dilithionaphthalene and dilithioanthracene the calculated minimum energy structures resemble closely the observed X-ray structures of dilithionaphthalene·bis(tetramethylethylenediamine) (TMEDA) and dilithioanthracene·(TMEDA)$_2$ reported by Stucky.[32,33] The crystal structure of dilithioacenaphthylene·(TMEDA) shows the lithium cations to be placed on opposite faces of the five-membered ring.[34]

In the present work anti-facial selectivity also is exhibited. The haptomers with the two lithium cations on the same side of the dianion are destabilized by the unfavorable orientation of the lithium-based dipoles. Syn-facial haptomers are likely to be destabilized further by steric crowding of solvation of the cations.

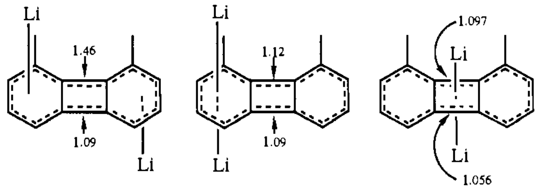
Coordination of the lithium cations to the four-membered ring is highly unfavorable, at least in the unsolvated systems. However, solvation (modeled with a water molecule), reduces the energy differences between the various haptomers. Hence, coordination to the four-membered ring should become increasingly favored on further solvation. The lithium cations would require less coordination with the anion due to the competition with the solvent. Coordination of the lithium cations by THF solvent molecules is obviously similarly important, and so the different haptomers might be more similar in energy in solution than found in calculations relating to the gas phase.

In the parent dianion and in the tetramethyl dianions, the preferred haptomers are those with the lithium ions on opposite sides of the same six-membered ring. The other main form is only 0.5–2.5 kcal/mol higher in energy. With two methyl substituents (regardless of their position) or eight methyl groups the situation is reversed, and the haptomers with the lithium ions on opposite sides of alternate six-membered rings are favored, by a margin of between 5.1 and 6.4 kcal/mol. The reason for this change in behavior is not clear, as it seems to be independent of the position of the methyl substituents.

Simple MO theory can also be used to rationalize the preference for ring opening "meta" to the methyl substituents in the 1,8-dimethylbiphenylene dianion as well as the 1-methyl- and 2-methylbiphenylene dianions. The INDO calculated bond orders are as follows: Thus, for example, the fact that 1,8-dimethylbiphenylene dianion ring opens preferentially at C_{4a}–C_{4b} rather than at C_{8a}–C_{8b} is supported by INDO calculated bond orders.



MNDO calculated bond orders for three different haptomers of the 1,8-dimethylbiphenylene dianion also gave values that support the "meta-directing" effect of the methyl substituents in the ring opening:



Our INDO and MNDO calculations also show a considerable weakening of the C_{4a}–C_{8b} and C_{4b}–C_{8a} bonds in the biphenylene dianions, which agrees with MNDO calculations of Günther.[35] Therefore, the biphenylene dianions are best represented as a continuous 14π-electron system (e.g., **13**) and not as a dibenzo derivative of the cyclobutadiene dianion. By using criteria for aromaticity[27a] based on the Spiesecke–Schneider relationship,[27b] the biphenylene dianions can be considered as 14π-electron aromatic systems (see Table II for data).

Conclusion

The current experimental and MO study of various methylated biphenylene dianions and of the parent biphenylene dianion has revealed interesting and unusual properties concerning their stability and structure. The dianions with the presence of at least two methyl substitutuents at the 1, 4, 5, and 8 positions stabilize the systems toward ring opening to dilithiobiphenyl derivatives. The reason for this is not clear,[36] and it may be of steric origin. The 2,3,6,7-tetramethyl- and 2-methylbiphenylene dianions are destabilized toward ring opening as compared to the parent dianion **13** based on electronic reasons.

Semiempirical calculations of bond orders in these biphenylene dianions support the meta-directing effect of the methyl groups for ring opening to dilithiobiphenyl moieties. The MNDO calculations also give indication of the preference for the location of the lithium counterions in relation to the organic dianionic framework. Modeling of solvation of the lithium cation with a water molecule reduces the energy differences between the various haptomers. Thus, coordination to the four-membered ring should become increasingly favored on further solvation. The ^{13}C NMR temperature-dependent data for the biphenylene dianion[15] and various methylated biphenylene dianions (except OMBP^{2-}) examined in this study appear to support this conclusion. The unusual ^{13}C NMR temperature-dependent data of the biphenylene dianion and the 1,5- and 1,8-dimethylbiphenylene dianions in 2-MeTHF may indicate that the lithium counterions prefer to be coordinated to the six-membered rings in this poorer cation-solvating medium.

The OMBP^{2-} behaves much differently from all other dianions studied. The OMBP^{2-} appears to exist as an aggregation equilibrium in both THF and 2-MeTHF solution. This observation is unprecedented for a delocalized dianion of this type and attempts for single-crystal X-ray crystallographic structure determination are underway. The reason for this aggregation equilibrium is unclear at this time, as are its degree and the structures of the different aggregated species (although "stacking" of the OMBP^{2-} units seems possible).

Experimental Section

All of the methylated biphenylenes used in our study, except 1-methylbiphenylene, were prepared by literature[17-20] methods and purified by codistillation with ethylene glycol and/or recrystallization from ethanol. The isolation of 2-methylbiphenylene from the Wolff-Kishner reduction of 2-formylbiphenylene was simplified by adding ethylene glycol to the crude reaction mixture and codistilling out the hydrocarbon. Approximately 6 h was necessary to completely form the diazonium carboxylate salt from 3-methylanthranilic acid, the benzyne precursor for the preparation of 1,5- and 1,8-dimethylbiphenylenes.

The synthesis of 1-methylbiphenylene (a yellow oil) was achieved as follows. A sample of biphenylene in diethyl ether was treated with a 10-fold excess of *n*-BuLi.[37] This solution was stirred at room temperature under argon for 4 days, after which the solution was red-brown in color. Then excess MeI was slowly added by syringe and stirring con-

---

(30) Sygula, A.; Lipkowitz, K.; Rabideau, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 6602–6605.

(31) Stezowski, J. J.; Hoier, H.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1263–1264.

(32) Brooks, J. J.; Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7346–7351.

(33) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 2079–2085.

(34) Rhine, W. E.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *134*, 139–149.

(35) Günther, H.; Benken, R. *Helv. Chim. Acta* **1988**, *71*, 694–702.

(36) Interestingly, initial MNDO calculations of the geometries of the various transition states for the ring opening (all C_2 symmetry) are almost unchanged regardless of the position of the methyl substitution, at least in the calculated monomers. Activation barriers are also similar. Therefore, no indication that steric crowding affects the ring opening is seen from these calculations. Further work is being carried out and will be reported later.

(37) Baker, W.; Boulton, A. J.; Harrison, C. R.; McOmie, J. F. W. *Proc. Chem. Soc., London* **1964**, 414.

tinued for ~2 h. A conventional workup using diethyl ether gave a yellow oil after removal of all of the volatiles. A ^{1}H NMR spectrum and analysis by GC-MS indicated that the 1-methylbiphenylene was contaminated with some starting material and a small amount of dimethylbiphenylene(s). The biphenylene was removed by dissolving the oil in a small amount of ethanol and placing the solution in a freezer. The biphenylene precipitated out of solution and was filtered. This step was repeated until all the biphenylene was removed. The dimethylbiphenylenes could not be separated from the 1-methylbiphenylene by column chromatography, so the mixture was used in the reduction. ^{1}H NMR data for 1-methylbiphenylene: δ 2.07 (s) for CH_3, and multiplets for aromatic Hs at δ 6.5 and 7.2.

Preparation of Dianions. A weighed amount of hydrocarbon was placed within a flame-dried, degassed NMR tube (5-mm tube when THF-d_8 was solvent and 8-mm tube when 2-MeTHF was solvent, with external acetone-d_6 solvent in a 10-mm NMR tube for NMR lock purposes) along with about five small strips of lithium (~30 mg) cut from a flat piece of lithium under argon. A rubber septum was used to seal the tube, and then dry solvent was added via syringe. The tube was then placed inside a commercial ultrasound bath[38] and sonicated. Within a couple of minutes the solution was deep blue, indicating radical anion formation, and further sonication, usually about 10–20 min for the stable dianions, generated a deep red-brown color indicative of dianion formation. A color change to green-yellow indicated ring opening to the dilithiobiphenyl moiety.

Preparation of the Dication. Two-electron oxidation was achieved in a solution of 1.5 g of SbF_5 and 1.5 mL of SO_2ClF with 50 mg of OMBP in a 10-mm NMR tube.

Quenching of the Ions. Quenching of the methylated dilithiobiphenyls was achieved by cooling the sample within the NMR tube to 0 °C and slowly adding water via syringe. The quenching of the biphenylene dianions was achieved by bubbling pure oxygen via a long syringe needle through the red-brown solution until the intense color disappeared. All quench products were isolated by a conventional workup using dichloromethane.

The ^{13}C, ^{1}H, and ^{7}Li NMR spectroscopic studies were carried out on a Varian VXR-200 superconducting NMR spectrometer equipped with a 5-mm variable-temperature switchable probe or a 10-mm variable-temperature broad-band probe. Analysis of the methylated biphenyls was done by NMR and by using a Finnigan INCOS-50 GC-MS apparatus by comparison with standard samples of methylated biphenyls.

Acknowledgment. We would like to thank Professors G. Fraenkel and T. E. Hogen-Esch for useful discussions. We also appreciate the critical comments of the reviewers. Support of our work at USC by the National Science Foundation is gratefully acknowledged.

---

[38] Using a 200-W Mettler ME-11 ultrasound bath from American Brand Products.

Inversion Topologies of [*n*.8.8](2,1,4)Cyclophanes: Tethering Effects on Host-Cavity Stereodynamics

Alan B. Brown[*,†] **and Howard W. Whitlock, Jr.**

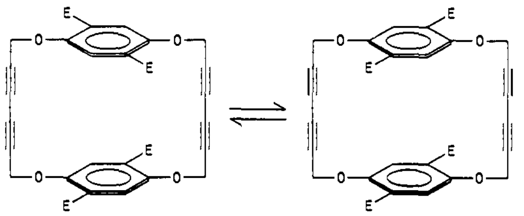
Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706.

Received August 3, 1988

Abstract: The title compounds **4** (n = 3–11; formally, the diesters of diacid **11** with various α,ω-diols) have been prepared; their ring-inversion barriers were measured by dynamic NMR. Diesters of **11** with 6,6-dimethylundecane-1,11-diol and 2-[(*tert*-butyldimethylsilyl)oxy]propane-1,3-diol were similarly made and studied. Preparation of the siloxy phane entailed development of a new glyceride synthesis. Two inversion topologies are possible: the diester bridge can pass either through the paracyclophane cavity (donut-hole pathway) or around the outside (jump-rope pathway). The donut-hole pathway is followed for $n \leq 7$, while the jump-rope pathway is followed for $n \geq 9$. Two properties are characteristic of each inversion topology: (1) relative barriers of **4.*n*** and its hexadecahydro derivative **5.*n*** and (2) an effect on inversion barrier of formal *gem*-dimethylation in the middle of the diester chain.

There is considerable current interest in host–guest chemistry, particularly in connection with the quest for "artificial enzymes".[1] Cyclophane hosts are especially attractive for stereochemical studies of cavities: intermediate in stiffness between cyclodextrins and crown hosts, cyclophanes can be made in a wide variety of shapes and substitution patterns, yet the stiff arenes make it fairly simple to design cyclophane hosts with enforced or semienforced cavities.[2,3]

What is it to fit into a cavity? More precisely, how do the interrelations of host and guest size and flexibility translate into energetics? Earlier, we studied tetraesters **1**, which can exist as syn and anti isomers (one isomer of each shown); ring inversion must involve cavity passage of an ester substituted arene side.[4] Several points are noteworthy. First, sequential methylations in the middle of ester chains raise $\Delta G^{\ddagger}_{298}$ sharply (**1c**, 17.2 kcal/mol; **1d**, 23.3; **1e**, >35); *gem*-dimethylation (cf. **1e**) suppresses inversion altogether. This is a simple fit/borderline/no-fit sequence; the difference between **1c** and **1d** is essentially all entropic.[4a] Second, hexadecahydro derivatives **2a–c**, whose macrocycles are collapsed,[4,6a,7] have higher barriers than the corresponding **1**, presumably because phanes **1** have cavities enforced in the relevant



1: E = CO_2R a: R = Me
b: R = Et
c: R = <u>n</u>-Pr
d: R = <u>i</u>-Bu
e: R = CH_2(<u>t</u>-Bu)
f: R = CH_2Ph
g: R = CH_2CH_2Ph
h: R = $(CH_2)_3Ph$
i: R = $(CH_2)_4Ph$
j: R = $(CH_2)_5Ph$

[†] Present address: Department of Chemistry, Florida Institute of Technology, Melbourne, FL 32901.

[1] Some recent reviews: (a) Stoddart, J. F. *Annu. Rep, Prog. Chem., Sect. B* **1983**, *80*, 353-378. (b) Tabushi, I. *Tetrahedron* **1984**, *40*, 269-292. (c) Breslow, R. *Adv. Enzymol.* **1986**, *58*, 1-60. (d) Sutherland, I. O. *Chem. Soc. Rev.* **1986**, *15*, 63-91. (e) Menger, F. M. *Top. Curr. Chem.* **1986**, *136*, 1-15. (f) D'Souza, V. T.; Bender, M. L. *Acc. Chem. Res.* **1987**, *20*, 146-152. (g) Rebek, J., Jr. *Science (Washington, D.C.)* **1987**, *235*, 1478-1484.

0002-7863/89/1511-3640$01.50/0 © 1989 American Chemical Society