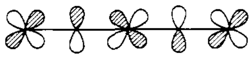
Table I. Parameters for C and Co Atoms

atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
C	2s	−21.4	1.62			
	2p	−11.4	1.62			
Co	4s	−7.8	2.00			
	4p	−3.8	2.00			
	3d	−9.7	5.55	2.10	0.5680	0.6060

[a] Coefficients used in the double-ζ expansion of the 3d orbitals.

energy window is now a little larger than in Figure 1, so as to include the C 2s band. This decomposition confirms the characterization of the bands of Figure 1 as mainly carbon or cobalt. The Co δ level of course is all metal; the σ z^2 band also has very little carbon mixing (see above). The only significant carbon mixing in the metal d band is π-type, with xz, yz.

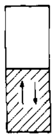
There is substantial π bonding in these chains. The right-hand side of Figure 2 shows the crystal orbital overlap population (COOP) curve[10] for the system. Note the large peak near −12 eV. That is the contribution of the in-phase Co–C π bonding combinations, exemplified by the representative orbital **8** at X. The corresponding antibonding combinations (near −8 to −9 eV) are only half-filled. The net result is strong π bonding. Of the 0.777 Co–C total overlap population, 0.560 is σ and 0.217 is π.



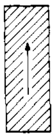
8

One interesting consequence of this picture is that the CoC^{3-} electron count does not correspond to maximal π bonding. Greater π bonding could be achieved, and with it a still shorter metal–carbon distance, if the polymer could be oxidized, or made with Fe or Mn instead of Co.

In the CoC^{3-} chain we have a half-filled (xz,yz) band. Little is as yet known about the conducting or magnetic properties of this material.[1] Two extreme possibilities are that the material is non-magnetic and the lower half of the xz,yz band is doubly filled, **9**. Or the electrons could unpair, **10**, resulting in a ferromagnetic or high-spin system.



9

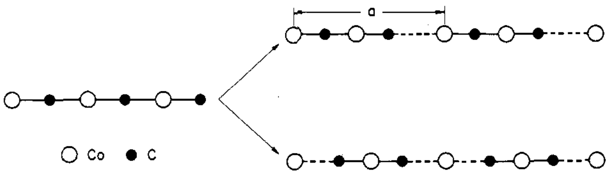


10

Whangbo has discussed the physical factors guiding this choice;[7] extended Hückel calculations are not capable of deciding which (**9** or **10**) will be the ground state of the system.

But if the polymer is low spin, **9**, then the half-filled band raises the possibility of a Peierls distortion.[6,7] This is the solid-state analogue of a Jahn–Teller effect, the stabilization of a polymer by deformation along a lattice vibration which opens up a band gap just at the Fermi level.

We have examined two such possible distortions, shown in **11**. Both open up substantial gaps of ~1 eV at the Fermi level and stabilize the system significantly. There are still other distortions that will accomplish the same thing. Since the observed crystal structure of YCoC shows no unit cell doubling distortion,[1] we think the material is likely to be magnetic, of type **10**.



11

Further studies of the properties of this fascinating organometallic material and the synthesis of related polymers should be encouraged.

Acknowledgment. We are grateful to the National Science Foundation for its support of this research through Grant DMR 821722702 to the Materials Science Center at Cornell University. We thank Jane Jorgensen and Elisabeth Fields for the drawings.

Appendix

Calculations are performed with the extended Hückel tight-binding method. Atomic parameters for Co and C are listed in Table I. A 50 k-point set is chosen in calculating the average properties of the CoC^{3-} chain system. The geometry is taken from the experimental data.

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[10] See, for example: Wijeyesekera, S. D.; Hoffmann, R. *Organometallics* **1984**, *3*, 949. Kertesz, M.;Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 3453. Saillard, J.-Y.; Hoffmann, R. *Ibid.* **1984**, *106*, 2006.

Nature of Carbon–Lithium Bonding in Dilithiated Polynuclear Aromatics: An MNDO Study

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Received January 23, 1987

Abstract: An MNDO study shows that the nonsymmetric crystal structures of dilithionaphthalene and dilithioanthracene are not the result of crystal-packing forces, but rather reflect the internal minimum energy arrangement of the molecules considered. On the other hand, the optimal structures of the complexes of the respective dianions with two positive charges are symmetrical. This difference suggests that partial covalency of the carbon–lithium bonding may be responsible for the nonsymmetric arrangement becoming the most stable in the crystal state.

The metal–ammonia reduction of polynuclear aromatics provides an intriguing array of intermediates during the course of reaction.[1] The most interesting and least explored of these intermediates are the dianions. These species, albeit antiaromatic, are nonetheless quite stable.[2] The nature of metal bonding in these anions, especially with lithium, is perplexing. The dianions

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† Permanent address: Department of Chemistry, Jagiellonian University, 30-060 Krakow, Poland.

[1] (a) Harvery, R. G. *Synthesis* **1970**, *4*, 161. (b) See also: Rabideau, P. W. In *Chemistry of Polynuclear Aromatics*; Ebert, L. B., Ed.; ACS Symposium Series 217; American Chemical Society: Washington, DC, 1987.

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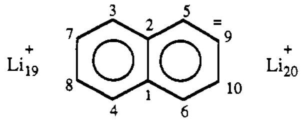
Table I. Net Atomic Charges and HO–LU Gaps for Li_2–Naph's **1–5**



atom no.	molecule 1	2	3	4	5
1	0.11	0.04	0.12	0.09	0.10
2	0.11	0.04	0.13	−0.07	−0.06
3	−0.31	−0.41	−0.29	−0.33	−0.28
4	−0.31	−0.41	−0.29	−0.38	−0.36
5	−0.31	−0.14	−0.29	−0.08	−0.13
6	−0.31	−0.14	−0.29	−0.13	−0.12
7	−0.07	−0.07	−0.06	−0.14	−0.16
8	−0.07	−0.07	−0.06	0.00	0.01
9	−0.07	−0.07	−0.06	−0.14	−0.12
10	−0.07	−0.07	−0.06	−0.03	−0.04
19	0.41	0.42	0.33	0.41	0.46
20	0.41	0.42	0.33	0.41	0.33
HOMO	−5.6406	−5.4345	−5.757	−5.8625	−5.9883
LUMO	0.6897	0.6937	0.4258	0.6853	0.3139
DE	6.3303	6.1281	6.1915	6.5478	6.3022

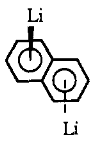
should be delocalized: They are not expected to have regions of high negative charge density. They should not have lone-pair lobes with much s-character directed toward the metal and, as such, could form several different ion triplets[3] in solution or the solid.

Simple Coulombic bonding between lithium cations and the organic dianion is not sufficient to explain the X-ray determined structures of dilithionaphthalene bis(tetramethylethylenediamine)[4] and dilithioanthracene bis(tetramethylethylenediamine),[5] although most recent investigations have concluded that the C–Li bond is mostly ionic.[6] To avoid this inconsistency, it has been proposed that the "nonsymmetric" crystal structures of Li_2–Naph and Li_2–Anth are dictated by crystal-packing or Madelung forces. We agree in part with this assessment; crystal lattices certainly should induce molecular distortions in these and related systems, but we find that the "lattice" is often used as a convenient dumping grounds for inconsistencies. In this paper we report on the structural features, charge distributions, and bonding in several antiaromatic dilithio dianions. We find that the origin of the observed structures lies within the nature of the carbon–lithium bonding, not necessarily crystal-packing forces.

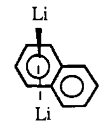
Results

We consider the structural features of naphthalene, anthracene, and phenanthrene dilithio dianions by exploring their multidimensional potential energy surfaces. We limit ourselves to a semiempirical molecular orbital approach to the problem because the size of the molecules preclude a rigorous ab initio treatment. We rely extensively on Dewar's MNDO[7] method with Thiel's lithium parameters.[8] All internal degrees of freedom are relaxed during the geometry optimizations unless otherwise noted. All molecules are considered to exist as ground-state singlets. MNDO is an especially useful method for successfully predicting the structures of mono and dilithiated hydrocarbons.[9]

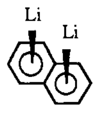
1. Dilithium Naphthalenide. Six Li_2–Naph structures, **1–6**, were investigated. The computed heats of formation ($\Delta H_f°$, kcal/mol) are listed directly below each structure, and Table I contains the electronic charge distribution for selected atoms. In general the bis-η^6 arrangement (**1–3**) is more favorable than the η^3-η^6 alternatives (**4** and **5**). Furthermore, the di-η^3 structure **6** appears not to be a local minimum on the potential energy surface because it relaxes to structure **4**.



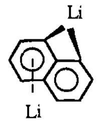
1 (-1.0)



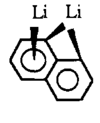
2 (2.5)



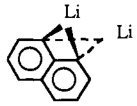
3 (5.3)



4 (7.8)

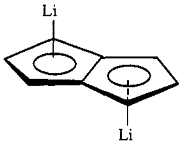


5 (11.7)

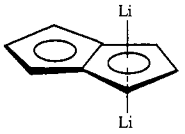


6

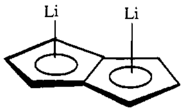
These results should be compared with those for dilithium pentalenide, an aromatic 10π-electron dianion that has previously been studied experimentally and theoretically.[10] The MNDO structures and heats of formation are, in decreasing stability, depicted as structures **7–11**. The similarities between these sets of calculations are evident, and we note that the bonding motif in these systems demonstrates the same pattern whether the dianion is formally aromatic or antiaromatic.



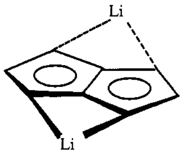
7 (9.4)



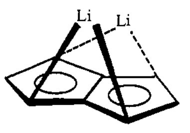
8 (14.4)



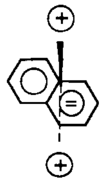
9 (30.7)



10 (39.5)



11 (43.5)



12

The lowest energy arrangement for Li_2–Naph has both lithium atoms bridging different rings on opposite faces. Hence the MNDO-predicted structure closely reproduces the crystal structure of dilithionaphthalene bis(tetramethylethylenediamine) as determined by Stucky et al.[4] On the other hand, inspection of electrostatic potential maps (EPM) shows two minima with the cations on opposite sides of the naphthalene rings approximately over and under the C_{1a}–C_{4a} bond. However, EPM analysis does not take into account the core–core repulsions between the cations and the carbon atoms of the organic moiety. We repeated the MNDO calculations for the naphthalene dianion associated with two positive "sparkles" (unpolarizable cations with an atomic radius of 0.7 Å, no orbitals, and no ionization potentials). In this case we were able to locate only one minimum (**12**) on the potential energy surface, regardless of starting geometry. This seems consistent with the structure predicted by EPM analysis, slightly

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(2) Streitwieser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2187.

(3) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

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

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

(6) Bachrach, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 6406 and references therein.

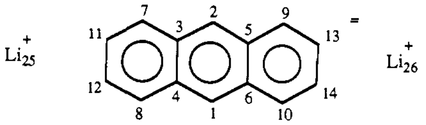
(7) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(8) Thiel, W. *QCPE Catalog* **1983**, *15*, 438.

(9) For leading references see: Schleyer, P. v. R.; Kauffman, E.; Spitznagel, G. W. *Organometallics* **1986**, *5*, 79.

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

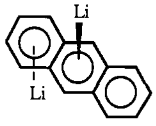
Table II. Net Atomic Charges and HO-LU Energies for Li_2-Anth's **13–18**



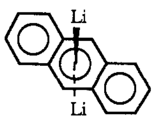
atom no.	molecule **13**	**14**	**15**	**16**	**17**	**18**
1	−0.33	−0.40	−0.30	−0.15	−0.30	−0.32
2	−0.33	−0.40	−0.30	−0.15	−0.30	−0.32
3	−0.01	0.02	0.08	−0.02	0.08	0.00
4	−0.01	0.02	0.08	−0.02	0.08	0.00
5	0.10	0.02	0.08	0.04	0.08	0.11
6	0.10	0.02	0.08	0.04	0.08	0.11
7	−0.07	−0.11	−0.22	−0.05	−0.22	−0.06
8	−0.07	−0.11	−0.22	−0.05	−0.22	−0.06
9	−0.26	−0.11	−0.22	−0.38	−0.22	−0.23
10	−0.26	−0.11	−0.22	−0.38	−0.22	−0.23
11	−0.08	−0.08	−0.08	−0.07	−0.08	−0.08
12	−0.08	−0.08	−0.08	−0.07	−0.08	−0.08
13	−0.08	−0.08	−0.08	−0.08	−0.08	−0.08
14	−0.08	−0.08	−0.08	−0.08	−0.08	−0.07
25	0.41	0.45	0.42	0.43	0.41	0.31
26	0.43	0.45	0.42	0.43	0.41	0.39
HOMO	−5.9159	−5.7818	−5.3218	−5.6541	−5.3465	−6.0574
LUMO	0.2324	0.2641	−0.1325	0.4174	−0.1726	0.1844
DE	6.1483	6.0459	5.1893	6.0715	5.1739	6.2428

modified by core–core repulsion—the sparkles are not located over and under the C_{1a}–C_{4a} bond but are shifted by 0.28 Å toward the center of one of the rings. However, structure **12** is quite different from either **1** or **2** and does not resemble the structure determined for the crystal state.

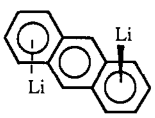
2. Dilithioanthracenide. Six structures (**13–18**) were taken into consideration; the edge-lithiated alternatives were not examined because of the results obtained for Li_2-Naph. Electronic charge information is found in Table II.



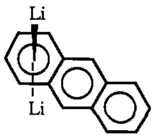
13 (12.3)



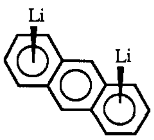
14 (16.2)



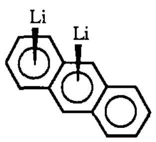
15 (19.5)



16 (15.9)

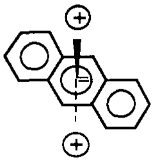


17 (21.5)



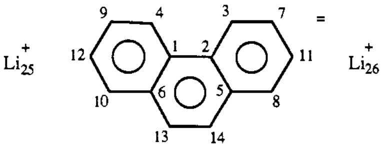
18 (18.7)

Again, the most stable structure (**13**) with two lithium atoms facing the anthracene plane on opposite sides—one over the central ring and another under the end ring—reproduces closely the crystal structure of dilithioanthracene bis(tetramethylethylenediamine) as determined by X-ray analysis.[5] This arrangement is quite different from that expected by considering only Coulombic interactions between two lithium cations and the anthracene dianion. MNDO calculations carried out for the anthracene dianion with two positive point charges actually led to the minumum energy structure **19**, which is in accord with both Streitweiser's predictions and analysis of electrostatic potential maps.



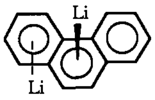
19

Table III. Net Atomic Charges and HO-LU Gaps for Li_2-Phen's **20–25**

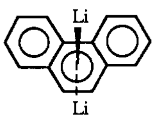


atom no.	molecule **20**	**21**	**22**	**23**	**24**	**25**
1	−0.14	−0.22	−0.11	−0.16	−0.20	−0.11
2	−0.15	−0.22	−0.11	0.13	−0.09	−0.12
3	0.05	0.05	0.02	−0.32	0.03	0.03
4	−0.00	0.05	0.02	0.00	0.03	0.02
5	−0.14	0.09	−0.01	−0.17	−0.09	−0.00
6	0.11	0.09	−0.01	0.05	0.12	−0.00
7	−0.36	−0.22	−0.33	−0.26	−0.33	−0.32
8	−0.22	−0.20	−0.24	−0.38	−0.27	−0.23
9	−0.15	−0.22	−0.33	−0.12	−0.17	−0.33
10	−0.14	−0.20	−0.24	−0.08	−0.13	−0.24
11	0.07	0.04	0.07	0.05	0.10	0.07
12	−0.01	0.04	0.07	−0.03	0.00	0.07
13	−0.37	−0.30	−0.12	−0.21	−0.34	−0.11
14	0.02	−0.30	−0.12	0.03	0.00	−0.11
25	0.44	0.48	0.44	0.46	0.37	0.41
26	0.45	0.48	0.44	0.46	0.40	0.41
HOMO	−5.6086	−5.5028	−5.5227	−5.3862	−5.7674	−5.5579
LUMO	0.2624	0.1986	0.2833	0.1781	0.2457	0.2574
DE	5.8710	5.7014	5.8060	5.5643	6.0131	5.8153

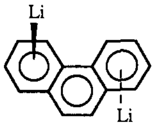
3. Dilithium Phenanthrenide. The results of our MNDO calculations for Li_2–Phen are analogous to those for Li_2–Anth. Again, the "unsymmetrical" arrangement, **20**, appears to be the most favorable of the six η^6–η^6 alternatives considered. Although the crystal structure of Li_2–Phen has not been determined, we predict that it would be close to **20** taking the above results into consideration. Consistent with Li_2–Naph and Li_2–Anth, the calculated structure of phenanthrene dianion with positive point charges (**26**) is different from the optimal structure of Li_2–Phen (**20**). Structure **26** is symmetrical with the sparkles located over and under the central ring.



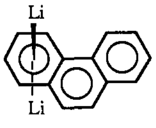
20 (20.3)



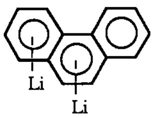
21 (24.7)



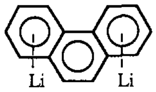
22 (21.6)



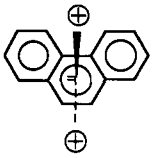
23 (25.2)



24 (27.1)



25 (24.0)



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Discussion

To fully address the lithium binding motifs in these planar dianions, one must consider both the ionic and covalent nature of the C–Li bond as well as the facial selectivity and regioselectivity. Facial selectivity refers to which side of the molecule the metals prefer to bind. Regioselectivity refers to which ring the metals are associated. Of all the structures examined, we find the most stable orientation to have anti-facial selectivity. That is to say, the metals prefer to bind to opposite sides of the dianion regardless of whether the ion is formally aromatic or antiaromatic. Such facial selectivity was noted by Schleyer in the pentalenides.[10] In these systems the destabilization of **9** was attributed to the fact that the lithium-based dipoles are aligned in a destabilizing orientation when both metals are on the same face of the anion. If this type of Coulombic rationalization were true, we would expect to see *syn*-dilithio species **17** more stable than **18** because the two dipoles are farther apart. This is not found and implicates an overriding covalent interaction between metal and ligand. Interstingly though, the *syn*-dilithio dianion **25** is more stable than its isomeric structure **24**. In any event, all global minima demonstrate a clear preference for anti-facial selectivity.

The regioselectivity of metal binding is complex. However, all minimum energy structures, in addition to demonstrating anti-facial selectivity, display a preference for lithium binding to adjacent rings. This is in direct conflict with purely ionic bonding interpretations based on EPM analyses and sparkle calculations. Both EPM and sparkle calculations predict the metals will lie over the same ring. This is not observed experimentally, and crystal forces were subsequently invoked to rationalize this discrepency.

The second most stable binding motif is in fact the one anticipated if we consider the carbon–lithium bond as purely ionic. In all cases but one, the second most stable structure involves lithium binding on opposite sides of the same ring (consistent with the sparkle results). The sole exception is the phenanthrenide where **22** actually is more stable than **21**. Again these observations attest to the fact that a purely ionic treatment of lithium coordination is incorrect and misleading. We must admit that in these molecules there is a substantial overriding covalent contribution that offsets the ionic bonding.

The key message we impart here is that, at the level of MNDO approximation and parameterization (which has accurately predicted many organolithium structures), the unsymmetrical X-ray structures of Li_2–Naph and Li_2–Anth are not necessarily forced by crystal-state interactions, but rather reflect the minimum energy arrangements of the molecules themselves. One need not invoke lattice effects to explain these structures.

Lattice-induced distortions may, nonetheless, take place in these and related systems. Changes in regioselectivity may be expected in Li_2–Phen where the second most stable regioisomer **22** is only 1.3 kcal mol^{-1} above the global minimum **20**. These isomerizations would require low-energy transits over the surface of the delocalized dianions.

In contrast, isomerization from anti to syn forms is less likely. The energy difference between the most stable anti metal alignment and the most stable syn alignment is 6.3 kcal mol^{-1} for Li_2–Naph, 6.4 kcal mol^{-1} for Li_2–Anth, 3.7 kcal mol^{-1} for Li_2–Phen, and 20.3 kcal mol^{-1} for the dilithium pentalenide. Boltzman-weighted populations clearly indicate only the anti species will exist in solution. In the crystal, only the Li_2–Phen could be expected to exist in the syn form. This is highly unlikely though because the isomerization pathway for syn–anti interconversion involves edge-lithiated structures, which are generally high-energy species. Overall, therefore, we anticipate lattice effects may alter the regioselectivity of lithium binding but not the facial selectivity.

Conclusions

The structural features of several dilithiated dianions have been investigated. The propensity for anti-facial selectivity with regioselectivity such that lithiums are on adjacent rings is clearly established regardless of whether the dianion is aromatic or antiaromatic.

Our calculations show that, at the level of MNDO approximation and parameterization, the unsymmetrical X-ray structures of Li_2–Naph and Li_2–Anth are not forced by crystal-state interactions but rather reflect the internal minimum energy arrangements of the molecules considered. Moreover, comparison of the results of calculation for lithiated (**1**, **13**, and **20**) and sparkle-coordinated (**12**, **19**, and **26**) molecules shows significant differences. We therefore conclude that partial covalency of the C–Li bonding is responsible for the nonsymmetric arrangement being most stable in the crystal state.

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