be rate determining. Although Breslow and Wernick[10] have argued against the mixed anhydride mechanism for peptide hydrolysis, they point out that the results of their isotope-exchange studies would be accommodated by a mixed-anhydride model if not all of the water molecules in the active site are displaced by substrate binding. We have recently demonstrated[7] that the mixed-anhydride intermediate of the esterolytic reaction is a pentacoordinate metal ion species in which both the carbonyl oxygen of the substrate and a water molecule are coordinated to the metal ion. Since the stereochemical relationships for binding of specific ester and peptide substrates to the enzyme[9] and the pH profiles for their hydrolysis are similar,[5,13,20-22] all of the observations taken together are consistent with formation of a mixed-anhydride intermediate during the hydrolysis of both types of substrates.

**Registry No.** ClCPL, 61556-61-4; TEPOPL, 72250-35-2; CPA, 11075-17-5.

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## Dilithium Semibullvalenide: An Unusual Organolithium Compound Extends the Scope of Homoaromaticity[†,‡]

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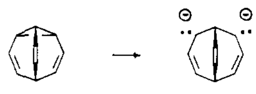
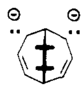
*Received August 28, 1981*

Bullvalene (**1**) is easily reduced to its dianion (**2**), whereas, under



**1** **2**



**3**

identical conditions, dihydrobullvalene is not.[1] Qualitative theory provides a simple explanation. The $C_{10}H_{10}$ dianion (**2**) is expected to be stabilized, because it is a mode (*2,0,0*) longicyclic.[2] The $C_{10}H_{12}$ dianion (**3**) is expected to be destabilized (i.e., bishomo antiaromatic), because it is an 8-π-electron pericyclic.[3]

The value of such predictions has increasingly been questioned in recent years,[4] and particularly as it applies to anions.[4a–e,h,j–l] Nevertheless, both bullvalene and dihydrobullvalene continue to behave as before, apparently oblivious to the current fashion.[5] Perhaps they do so for other reasons. The ethano bridge of dihydrobullvalene provides a rich source of alternative hypotheses. It might have prevented dianion formation by diminishing the loss of strain energy, by sterically inhibiting counter-ion stabilization, by transferring a hydrogen atom to a radical anion intermediate, etc. Whatever its role, excision of that bridge (as in semibullvalene, **4**) should then restore bullvalene-like behavior. In particular, the

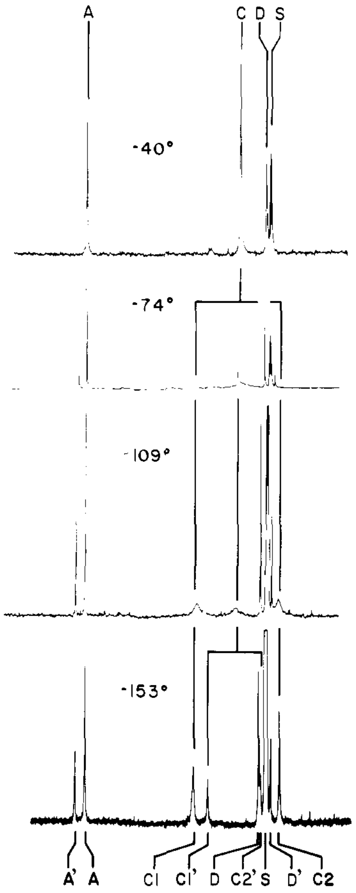
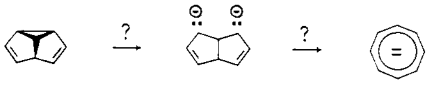


**Figure 1.** 75.47-MHz $^{13}C$ NMR spectra of dilithium semibullvalenide in dimethyl-$d_6$ ether at four temperatures. S is the solvent peak. Primed letters (e.g., **A**′) denote peaks of the minor component (cf. Table II).

Table I. NMR Spectra of Dilithium Semibullvalenide and Bicyclo[3.3.2]decatrienide at "High Temperature"[a]

| nucleus | $Li_2C_8H_8$ | | | | $Li_2C_{10}H_{10}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $\delta_H$[b] | $\delta_C$[c] | $J_{CH}$[d] | $A_H$[e] | $\delta_H$[f] | $\delta_C$[c] | $J_{CH}$[d] | $A_H$[e] |
| A | 6.40 | 146.49 | 143.3 | 1.91 | 6.14 | 131.5 | 135 | 1.90 |
| B | | | | | 4.63 | 106.3 | 151 | 1.94 |
| C | 2.56 | 73.73 | 144.3 | 4.12 | 3.06 | 75.3 | 159 | 4.22 |
| D | 3.78 | 61.51 | 128.5 | 1.96 | 2.31 | 36.3 | 122 | 1.94 |

[a] $Li_2C_8H_8$ at −38 °C in dimethyl-$d_6$ ether at 80 MHz; $Li_2C_{10}H_{10}$ at −20 °C in 1,2-dimethoxyethane-$d_{10}$ at 90 MHz.[1] [b] Relative to benzene in dimethyl ether at $\delta_H = 7.30$. [c] Relative to (1:2) $Me_4Si$ in the appropriate ether at $\delta_H$ 0.00. [d] In Hz. [e] Proton areas normalized to the appropriate sum. [f] Relative to $CHD_2O(CD_2)_2OCD_3$ at $\delta_H$ 3.31.



**4** **5** **6**

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[†] Dedicated to Professor W. von E. Doering on the occasion of his 65th birthday.

[‡] Presented in part at the Fourth International Symposium on the Chemistry of Novel Aromatic Compounds, Jerusalem, Sept 1, 1981.

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(5) The current fashion is equally oblivious to the dianion, **2**. Its synthesis and characterization apparently excaped the otherwise extensive literature surveys of ref 4b–l.

0002-7863/82/1504-2669$01.25/0

Table II. NMR Spectra of Dilithium Semibullvalenide and Bicyclo[3.3.2]decatrienide at Low Temperature[a] in Dimethyl-$d_6$ Ether

| | $Li_2C_8H_8$ | | | | | | | | $Li_2C_{10}H_{10}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | major component | | | | minor component | | | | | |
| nucleus | $\delta_H$ | $\delta_C$ | $J_{CH}$[b] | $A_H$[c] | $\delta_H$ | $\delta_C$ | $J_{CH}$[b] | $A_H$[c] | $\delta_H$ | $A_H$[c] |
| A | 6.24 | 144.84 | 142.4 | 1.76 | 6.60 | 149.61 | 140.6 | 2.03 | 6.13 | 2.10 |
| B | | | | | | | | | 4.70 | 1.74 |
| C1 | 3.89 | 93.21 | 156.2 | *d* | | 86.40 | 148.0 | | | |
| | | | | | 2.44 | | | *e* | 3.05 | *f* |
| C2 | 1.06 | 52.46 | 129.5 | 2.19 | | 61.44 | 124.1 | | | |
| D | 3.80 | 62.32 | 127.6 | *d* | 3.42 | 56.69 | 128.4 | 1.98 | 2.31 | 2.15 |

[a] $^1H$ NMR spectra at −143 °C, 270 MHz, $\delta_H$ relative to benzene in dimethyl ether at $\delta$ 7.37; $^{13}C$ NMR spectra at −153 °C, 75.47 MHz, $\delta_C$ relative to (1:2) $Me_4Si$:dimethyl ether at $\delta$ 0.00. [b] In Hz. [c] Proton areas normalized to the appropriate sum. [d] $A_H = 4.05$ for C1 + D. [e] Unreliable; a dynamically broadened singlet. [f] Unreliable; solvent overlap.

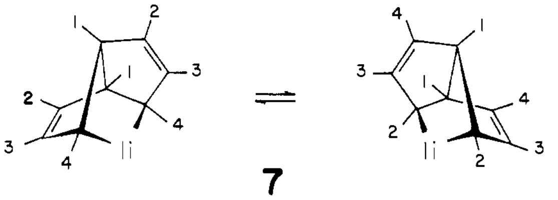
[3.3.0] dianion (**5**) should then appear, though perhaps only transiently. A symmetry-allowed and thermodynamically attractive cyclodissociation to the cyclooctatetraenyl dianion (**6**) would be difficult to resist.

The homoaromatic model predicts otherwise. It recognizes that **5** should be destabilized, like **3**, and so it expects other results.

We now report that these results satisfy the expectations of the homoaromatic model in a structurally unanticipated way. The reduction product of semibullvalene is qualitatively different from that of bullvalene, both spectroscopically and in its chemical reactions.

Semibullvalene[6] is easily reduced by lithium, in tetrahydrofuran or dimethyl ether solution, even at −78 °C. The resulting $^{13}C\{^1H\}$ NMR spectra reveal two reversible temperature-dependent processes (Figure 1). The first is a dynamic process, rapid on the NMR time scale only at high temperatures; at lower temperatures, the C peak is resolved into its components, C1 and C2. The second process then also becomes apparent: the appearance and growing importance of a minor component. Its equilibration with the major one is uniformly slow on the NMR time scale. This component, too, exhibits four $^{13}C$ signals: A′, C1′, C2′, and D′. They resemble the corresponding signals of the major component in their chemical shifts, coupling constants, and equilibration of C carbon atoms. Tables I and II compare these data with the corresponding temperature-insensitive parameters of the bicyclo[3.3.2]decatrienyl dianion (**2**).[1]

The observation of *four* $^{13}C$ NMR signals unambiguously excludes the $C_{2v}$ structure (**5**), for both the major and minor components. An attractive structural hypothesis (**7**) further presupposes the absence of accidental degeneracies in the $^{13}C$ NMR spectra and the presence of a common $C_8H_8$ ligand in both components. It thus identifies the dynamic process as a racemization that may or may not be concerted.



**7**

In either case, the distinct chemical environments of carbon atoms 1 and 3 (peaks D and A) are conserved, while those of 2 and 4 (peaks C1 and C2) are permuted. Such structural assignments reflect the general concordance of literature data[7] with those reported in Table II; we think the assignments plausible, rather than necessary.[8]

The symbol "li" is used to represent a residual structural problem without specifying a particular solution. At −140 °C, the $^6Li$ NMR spectra, obtained from 96% enriched material, reveal four peaks: $\delta_{Li}^{Me_2O}$ 1.139, 0.801, 0.605, 0.332[9] in the area ratios 0.34:0.34:0.17:0.16. These ratios correspond to the 2:1 $^1H$ NMR area ratios of the major and minor components at that temperature. Each component is therefore an aggregate that contains equal numbers of lithium atoms in two structurally different environments.[10a] At higher temperatures, the peaks merge into one ($\delta_{Li}^{Me_2O}$ 0.702 at −30 °C). As expected, the lithium salt of the bicyclo[3.3.2]decatrienyl dianion (**2**) reveals only a single peak ($\delta_{Li}^{Me_2O}$ 0.261 at −140 °C, 0.459 at −40 °C), different from those of either semibullvalenide aggregate. The relative $^1H$ NMR areas of these aggregates change by less than a factor of 1.25 over a 27-fold range of dilution; they must therefore be isomers. They may be stereoisomeric covalent organolithium clusters.[10b]

Two of these properties are quite rare in organolithium chemistry: isomerism[11] and the possession of (at least) two structurally distinct lithium atoms.[12] A third is unprecedented: $\eta^1$ rather than $\eta^3$ bonding to a sterically unbiased allyl ligand.[13]

Chemical characterization was achieved with methanol, methanol-*d*, and carbon dioxide. The first provided the hydrocarbons (X = H; 49% **8** and 22% **9**).[14] The second introduced 1.77 (2) and 1.85 (1) atoms of deuterium into **8** and **9** (X = D), and with somewhat greater stereospecificity in **8**-$d_2$ (62% exo) than in **9**-$d_2$ (50% exo). Carboxylation provided **8** (X = $CO_2H$) regiospecifically in 95% yield, the derived dimethyl ester being a 1:1:1 mixture of *stereo*isomers by gas chromatographic analysis.[15] Sodium methoxide in refluxing methanol uneventfully transformed this mixture to the conjugated isomer (**10**).[16,17] We note that the corresponding tautomerization in the [3.3.2] series (to produce **11**[16,18]) could be achieved under unusually mild conditions:

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[6] Conveniently prepared according to the following: Turro, N. J.; Liu, J.-M.; Zimmerman, H. E.; Factor, R. E. *J. Org. Chem.* **1980**, *45*, 3511–3512.

[7] (a) van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Rec. Trav. Chim. Pays Bas* **1974**, *93*, 29–32. (b) Bywater, S.; Lachance, P.; Worsfold, D. J. *J. Phys. Chem.* **1975**, *79*, 2148–2153.

[8] Otherwise useful correlations of $\delta$ and/or $J$ with electron-density and ring-current models cannot reliably be extended to new topologies.[1]

[9] Positive $\delta_{Li}$ values (at 44.165 MHz) are *downfield* from 1 M aqueous lithium chloride at 27 °C.

[10] (a) Cf.: Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1976; Chapter 1. (b) Weiss, E.; Lucken, E. A. C.; *J. Organomet. Chem.* **1964**, *2*, 197–205. Köster, H.; Thoennes, D.; Weiss, E. *Ibid.* **1978**, *160*, 1–5. Zerger, F.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048–6055. Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681–689. Dietrich, H. *J. Organomet. Chem.* **1981**, *205*, 291–299.

[11] Lithioisobutyrophenone tetramer: Jackman, L. M.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 3687–3692. Jackman, L. M.; Szeverenyi, N. M. *Ibid.* **1977**, *99*, 4954–4962.

[12] Hexamethylneopentylcyclohexadienyllithium dimer: Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657–5664.

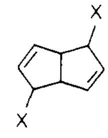
[13] (a) Allyllithium: Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459–5464. Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *198*, C1–C3. Brownstein, S.; Bywater, B.; Worsfold, D. J. *Ibid.* **1980**, *199*, 1–8. (b) 1-*tert*-Butylallyllithium: Glaze, W. H.; Jones, P. C. *J. Chem. Soc. D* **1969**, 1434–1436.

[14] (a) Identified by comparison of $^1H$ NMR spectra with those reported for authentic samples[14b,c] and by diimide reduction to bicyclo[3.3.0]octane of $\delta_C^{CDCl_3}$ (20.02 MHz) 43.16 (1.8 C), 34.18 (4.0 C), 26.32 (2.2 C). (b) Freeman, P. K.; Ziebarth, T. D. *J. Org. Chem.* **1973**, *38*, 3635–3637. (c) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715–737.

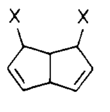
[15] $\delta_C^{THF}$ (20.02 MHz) (a) 174.05, 135.12, 128.68, 58.28, 52.03, 47.50; (b) 173.91, 137.00, 128.13, 55.75, 52.64, 52.00; (c) 173.81, 173.00, 135.64, 134.19, 129.09, 128.67, 56.75, 53.53, 52.52, 51.93, 51.43 (the last peak twice as intense as the others).

[16] C and H analyses agreed with expectation to within ±0.3%.

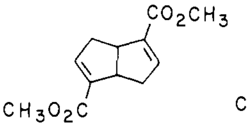
[17] **10**: mp 111.2 °C; IR ($CDCl_3$) 1720 cm$^{-1}$; $\delta_H^{CDCl_3}$ 6.72 (1.8 H, m), 3.74 (8.1 H, s within m), 3.17–2.33 (4.1 H, m); $\delta_C^{CDCl_3}$ 165.27, 142.62, 137.93, 51.41, 47.25, 38.56.



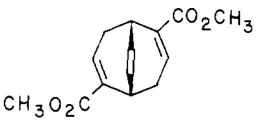
**8**



**9**



**10**



**11**

aqueous potassium carbonate at ambient temperature. Perhaps this reflects the greater anionic stabilization to be expected in the longicyclic environment.

A sharper distinction results from the addition of 12-crown-4[19] to tetrahydrofuran solutions of the ionic [3.3.2] and the covalent [3.3.0] organolithium compounds at −78 °C. Subsequent deuteronation of the [3.3.2] solution introduced 1.97 (2) atoms of deuterium, indistinguishable from the 1.95 (4) atoms acquired in the absence of crown ether.[1] Subsequent deuteronation of the [3.3.0] solution, however, introduced only 0.80 (5) atoms of deuterium, half as much as in the absence of crown ether. We assume that this difference reflects, first, the ability of the crown ether to displace the destabilized bicyclo[3.3.0]octadienyl ligand (**5**) from the coordination sphere of lithium, and, second, the unusual basicity of the free ligand. It apparently deprotonates the solvent and/or crown ethers to provide the allylically stabilized bicyclo[3.3.0]octenyl anion. Only one deuteron can then be acquired.

If that be so, **5** cannot be an intermediate in the thermal rearrangement of dilithium semibullvalenide to the cyclooctatetraenyl dianion, a reaction that proceeds with $10^5k^{0\,°\mathrm{C}} = 9.0$ (1)[20] and without detectable byproducts. As expected, the stabilized bicyclo[3.3.2]decatrienyl dianion (**2**) is quite inert under these same conditions.

These results suggest that the binary predictions of qualitative models[2,3]—stabilized or destabilized—might more generally be reflected in the binary properties of organolithium compounds—ionic or covalent. Previous failures to detect anionic manifestations of the homoaromatic model[4a–d,h] have many possible origins. Perhaps these new results will encourage a more critical reexamination of the older data and their interpretations. The failures of ab initio STO-4G calculations to detect "through-space" overlap, in homoaromatic and longicyclic anions,[4k,l] are easier to understand. Such minimal basis-set models are notoriously unreliable guides to the thermodynamic properties of gas-phase carbanions.[21,22] We are encouraged that one group has since turned to quantitatively more realistic models,[23] and we wish them well.

**Acknowledgment.** We are grateful to N. J. Turro and H. E. Zimmerman for a preprint of ref 6 in advance of publication and to the National Science Foundation for its support of the research (CHE77-26482) and of NMR facilities (Varian CFT-20, CHE76-05884, and Bruker WM-300, CHE79-04825, at Cornell, and Bruker HX-270, CHE79-16210, at the Southern New England NMR Facility).

**Registry No. 1**, 1005-51-2; **2**, 81408-59-5; **4**, 6909-37-1; **5**, 81408-60-8; **8** (x = H), 17618-97-2; **8** (X = $CO_2H$), 81408-61-9; **9** (X = H), 7863-35-8; **10**, 81408-62-0; **11**, 81408-63-1.

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[18] **11**: mp 100.5 °C; IR ($CCl_4$) 1715 cm$^{-1}$; $\delta_H^{CDCl_3}$ 7.08 (1.9 H, t, $J$ = 4 Hz), 6.07 (1.9 H, dd, $J$ = 4, 6 Hz), 3.7 (8.1 H, s within m), 2.58 (4.1 H, m).

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## A Trimeric Iron(III) Heme–Copper(II) Complex: Support for an Alternate Explanation of the "EPR Silent" Iron–Copper Pair in Cytochrome *c* Oxidase

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One of the major enigmas associated with the active site of cytochrome *c* oxidase is the so-called "missing" or "EPR silent" ferric heme–copper pair in the resting enzyme. Recently, the prevalent view has been that the absence of an observable EPR signal from both the iron and copper is best explained by proposing a high-spin ($S = {}^5/_2$) ferric heme strongly antiferromagnetically coupled to the ($S = {}^1/_2$) copper.[1,2] This model is consistent not only with EPR results but with the bulk magnetic susceptibility, which is significantly lower than what would be expected for the same system with isolated spins.[3–6]

The major problem with this model is that in order for it to explain the lack of an observed temperature dependence in the magnetic moment, an exceptionally large coupling constant, $-J > 200$ cm$^{-1}$, must exist.[1,2,4–6] The problem is further complicated by the recent proposal of a detailed active-site structure based on EXAFS data for the enzyme.[7] In that study the coupled Fe/Cu pair is described as being bridged by a cysteine-like thiolate. If this structural representation is correct, the uncomfortable fact remains that a sulfur-mediated coupling of the order of magnitude of −200 cm$^{-1}$ is completely unprecedented.[8] The preparation of structurally appropriate iron–copper-containing model complexes is important to further the understanding of the physical and chemical properties of the enzyme, especially those intimately related to spin states.

Using simple monomeric metal complexes, we have taken advantage of established properties of iron hemes and prepared a unique complex that incorporates two irons (porphyrins) and one copper into a single trimeric moiety. Treatment of *meso*-tetraphenylporphyrinatoiron(II) ($Fe^{II}TPP$) with a stoichiometric equivalent of tetrabutylammonium bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)cuprate(III) ($TBA^+Cu^{III}MNT_2^-$) in dry benzene under $N_2$ results in a reaction having the following stoichiometry:

$$\mathrm{Fe^{II}TPP + TBA^+Cu^{III}MNT_2^- \rightarrow {}^1/_2(TBA^+)_2Cu^{II}MNT_2^{2-} + {}^1/_2Fe^{III}TPP\cdot[Cu^{II}MNT_2]\cdot Fe^{III}TPP}$$

**1**

Compound **1** is isolated as black crystals or as a purple-black powder. (Anal. Calcd for $C_{96}H_{56}N_{12}S_4Fe_2Cu$: C, 68.59; H, 3.36; N, 10.00. Found: C, 68.52; H, 3.33; N, 9.78). Molecular weights

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