method used for compound III.

(6) Compound III was prepared by a modification of the method of G. Peters, *J. Org. Chem.*, **27**, 2198 (1962).

(7) Purified wheat germ acid phosphatase catalyzes the hydrolysis of the corresponding phosphonate esters as reported by M. E. Hickey, P. P. Waymack, and R. L. Van Etten, *Arch. Biochem. Biophys.*, **172**, 439 (1976).

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Dicyclooctatetraeno[1,2:4,5]benzene Dianion and Tetraanion. Experimental Assessment of Extended Paratropic vs. Restricted Diatropic π-Electron Delocalization

Sir:

Although our perception of aromatic stabilization and destabilization has been greatly extended in recent years, it is not yet possible to predict on an a priori basis the ground-state electronic character of molecules capable of adopting either a diatropic or paratropic ring current. Systems having two fused $4n$ π rings and therefore $[4n + 2]$ π electrons have commanded the greatest experimental and theoretical scrutiny.[1] In general, such compounds appear not to be strongly stabilized, in keeping with the antiaromatic character of their monocyclic components. For several reasons, one would anticipate that diamagnetic π-electron delocalization should dominate in those molecules where the simpler structural unit is $[4n + 2]$ and the larger $4n$. However, this need not be so if the species is charged, and particularly multiply charged, since repulsive electron-electron interactions must now also be considered. Very little is known about the extent to which these counterproductive energetic factors might be offset.[2] In this communication, we report the preparation and direct observation (by NMR spectroscopy) of the dicyclooctatetraeno[1,2:4,5]benzene dianion and present a detailed analysis of its structure. Were this system to adopt a paramagnetic (20 π electron) ring current as in **1**, planarity might be approached (both eight-membered rings would thereby become equivalent) and negative charge would become distributed over the entire framework at one time. This would suggest that electrostatic repulsion between the pair of electrons is adequate to overcome both the compressional strain energy associated with flattening the medium-sized rings and the "antiaromatic" component of the ring current. On the other hand, the existence of this dianion in two interconverting equivalent nonplanar diamagnetic (14 π electron) forms (**2a** ⇌ **2b**) would indicate that dispersal of negative charge is less important than resonance stabilization.


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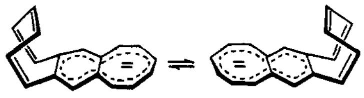
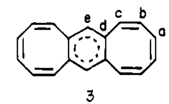

2a 2b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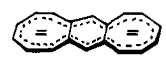
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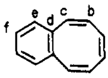
For completeness, we have also examined the 4-electron reduction of neutral parent hydrocarbon **3**[3] to tetraanion **4**, the most highly charged analogue of anthracene presently known.

Initially, the electrochemical behavior of **3** in anhydrous HMPA (vacuum line conditions; oxygen and moisture excluded) was discovered to differ meaningfully in several ways from that of closely related benzocyclooctatetraenes (Table I). Thus, not only is **3** uniquely reduced with greater facility than the parent COT (by 135 mV), but it is the only system which exhibits full chemical reversibility (cyclic voltammetry experiments) at 100-mV/s scan rates (I_{pa}/I_{pc} = 100%). Secondly, because the diffusion current constant (I_p) exhibited by **3** is nearly twice that of COT, rarely precedented[2,5,6] synchronous 2ϵ uptake or closely spaced transfer of two single electrons is occurring.[7] As expected, additional reduction of the dianionic species to the tetraanion was not seen prior to onset of solvent breakdown. Like COT itself, electron transfer to **3** is non-Nernstian as indicated by the scan rate dependency of the peak current constant.[7,8] These characteristics serve to securely classify **3** as a molecule particularly susceptible to dianion formation.[9]

Generation of $\mathbf{3}^{2-}$ either by electrochemical methods or by exposure to Na-K alloy in anhydrous THF-d_8 produced stable dark emerald green solutions displaying ^{1}H NMR signals at δ 6.67 (s, 2), 5.57–5.34 (m, 4), and 4.93 (narrow m, 8).[10] Comparison of this spectrum with that of neutral **3** in THF-d_8 (6.49 (s, H_e), 6.41 (d, J = 12 Hz, H_c), 5.92 (dd, J = 12 and 2 Hz, H_b), and 5.80 (d, J = 2 Hz, H_a)) reveals the benzenoid protons to be downfield shifted ($\Delta\delta$ = −0.18 ppm) but H_a–H_c to be substantially shielded ($\Delta\delta$ = +0.87, 0.99, and 0.84–1.07 ppm, respectively). These characteristics differ from those observed for benzo-COT[11] (**5**, $\delta_{TMS}{}^{THF\text{-}d_8}$ 7.13 (dd, 2, H_f), 6.90 (dd, 2, H_e), 6.51 (d, J = 12 Hz, H_c), 5.94 (dd, J = 12 and 2 Hz, H_b), and 5.82 (d, J = 2 Hz, H_a)) and its well-delocalized 14 π electron dianion[11,12] (**6**, $\delta_{TMS}{}^{THF\text{-}d_8}$ 7.74 (dd, H_e), 6.70 (d, H_c), and 6.41–5.84 (m, H_a, H_b, and H_f)). Here the realization of a diamagnetic ring current more than cancels the "charge effect"[13] and causes all protons except H_f (now additionally shielded owing to the increase in π-electron density



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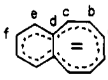

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Table I. Cyclic Voltammetry of Several Benzocyclooctatetraenes at a Platinum Electrode in Anhydrous Hexamethylphosphoramide (0.1 M in $(n\text{-Bu})_4N^+ClO4^-$)[a]

Compd	$E_{1/2}$[b]	$E_{1/2}{}^1 - E_{1/2}{}^1$ (COT), mV	$E_{C_1} - E_{A_1}$, mV	$E_{C_2} - E_{A_2}$, mV	I_P	n_{app}
COT	−1.606		118[c,d]	60	0.42	1
	−1.921				0.40[e,f]	1
Benzo-COT (**5**)	−1.724	−118	64[c,d]	54[e]	0.50	1
	−1.948				0.30[g]	1
sym-Dibenzo-COT	−1.896	−290	58[d,e]	64[e]	0.45	1
	−2.016		–		0.43[g]	1
3	−1.471	+135	60[c,d]		0.73	2

[a] Reference 4. [b] In volts vs. SCE. [c] At 100-mV scan rate. [d] Scan rate dependent. [e] Scan rate independent. [f] I_p measured as I_{pA_2}, but second cathodic wave is scan independent. [g] Measured as second anodic wave at 100 mV s^{-1}.

Table II. Calculated π-Electron Densities for Various Species[a]

	Molecular entity				
Atom	**1**	**2**^{b,c}	**2**^{c,d}	**4**	**6**
a	1.125	1.121	1.119	1.26	1.24
b	1.125	1.088	1.099	1.18	1.18
c	1.125	1.252	1.145	1.34	1.30
d	1.125	1.104	1.108	1.13	1.120
e	1.00	1.068	1.056	1.17	1.07
f					1.09

[a] Reference 15. [b] The overlap integrals across the single bonds in the nondelocalized ring arbitrarily set at 0. [c] The given values represent an average weighting of the two possible environments where applicable. [d] The overlap integrals across the single bonds in the nondelocalized ring arbitrarily set at 0.50.

Table III. ^{13}C NMR Data[a]

Benzo-COT, **5**	Benzo-COT^{2-}, **6**	*sym*-Dibenzo-COT	*sym*-Dibenzo-COT^{2-}	**3**	**3**$^{2-}$
138.12[b]	134.14[c] (147.7)	137.32[b]	137.79[c] (146.5)	137.00[b]	155.88[c] (146.5)
133.75 (156.3)	110.45[b]	133.22 (157.5)	108.40[b]	133.28[d] (158.1)	117.52 (151.3)
131.27[d] (153.8)	107.27 (153.8)	129.07 (161.7)	107.97 (154.4)	131.30 (156)	111.96[b]
130.95[d] (153.8)	94.38 (146.5)	126.69 (161.7)	94.81 (144.6)	131.23 (156)	109.48[d] (145.0)
129.65 (157.5)	90.60[d] (145.3)	(COT, 133 (15t))		130.84 (156)	105.06[d] (150.2)
127.01 (161.1)	89.41[d] (147.7)	(COT^{2-}, 85.3 (145))			

[a] THF-d_8 for anions, CDCl$_3$ for neutral species, 22.6 MHz, in parts per million. Values in parentheses are the ^{13}C–H coupling constants. [b] Quaternary benzenoid carbon d C$_d$. [c] Benzenoid carbon e. [d] Olefinic carbons a or b.

(Table II) and lack of *added* diatropism) to be displayed downfield of their original positions. Interestingly, if one applies to **3**$^{2-}$ the standard correlation, $\Delta\delta q = (10.7\ \Delta q_r)$ ppm,[14] for charged-induced chemical shifts, then those for H$_a$–H$_c$ are seen *not* to be in good agreement with the calculated shifts based on Hückel MO π-electron densities for **2** (Table II).[15] Because this correlation presupposes a diamagnetic ring current, it cannot be applied to **1**. Nonetheless, the lack of correspondence and the obvious pronounced shielding of all the olefinic protons (compare **6**) signal the absence of that diamagnetic ring current demanded by formula **2** even on a time-averaged basis. Therefore, the dicyclooctatetraeno[1,2:4,5]benzene dianion is seen not to be an equilibrating restricted 14 π electron system (**2**). Is it best viewed as an extended planar 20 π paratropic species?

Although this question is rather more difficult to answer, additional information is available from ^{13}C NMR data (Table III) where the shieldings are now primarily dependent upon the local π-electron density at each atom.[16] In particular, we note the spectral parameters for **3**$^{2-}$ to be those of a symmetrical entity on the NMR time scale at +30 °C, differing appreciably from the pair of structurally related dianions in the level of shielding. Further, cooling of solutions of **3**$^{2-}$ to −100 °C caused no obvious spectral changes. Thus, the $\Delta G^{\ddagger}$ of the rapid exchange **2a** $\rightleftharpoons$ **2b**, were it operative, would necessarily be <6 kcal/mol,[17] but ^{1}H NMR has already made further consideration of the equilibrium possibility unnecessary.

It has long been known that ^{13}C–H coupling constants are sensitive to the state of hybridization at carbon, polarization effects, and the presence of charge.[18] The effect of local anisotropic contributions, if any, is not as well understood.[19] As reflected in the COT, benzo-COT, and *sym*-dibenzo-COT examples, conversion to the corresponding dianions causes olefinic carbons a and b to become upfield shifted by 40–50 ppm and to experience a decrease in J_{CH} to 145–147 Hz. In **3**$^{2-}$, the shielding contribution to the chemical shift is expectedly decreased (to ~25 ppm), but the magnitude of J_{CH} remains entirely comparable (Table III). Because it has not proven possible to determine the level of planarity in **3**$^{2-}$ by standard techniques,[10] the factors contributing to this reduction in spin-spin interaction are not known. However, the findings are entirely compatible with structural assignment **1**.

The substantive downfield shifting of C$_e$ in **3**$^{2-}$ is seen to be exceptional for the series of dianions examined and denotes that this dianion is electronically unique. We interpret this sizable deshielding to be the combined result of the low π-electron density calculated to prevail at this site ($\rho_{\mathrm{C_e}} = 1.00$, Table I) and the powerful electron-withdrawing influence of both singly charged cyclooctatetraenyl rings as they strive to gain individual "aromatic character". More detailed theoretical assessments of this phenomenon are pending.

Treatment of THF-d_8 solutions of **1** with additional Na-K alloy led to further reduction with formation of a stable red tetraanion assigned structure **4**. As in the case of **1**, samples of this substance gave no evidence of radical-anion character (ESR studies). Unfortunately, the solubility of **4** was too low to permit spectral examination.[20] Exposure of **4** to air caused immediate reoxidation to **1** in a process which was entirely reversible. Quenching of **4** with methanol resulted in the formation of C$_{18}$H$_{18}$ isomers (*m/e* 234.1412, calcd 234.1408);[21] comparable protonation of **1** provided a mixture of dihydro products (*m/e* 232.1248, calcd for C$_{18}$H$_{16}$ 232.1252).

It is therefore apparent that charge repulsion can be successfully overcome and tetraanion formation achieved in a modestly sized cyclooctatetraene system which is perforce constrained to an essentially planar annulene perimeter. The present results further demonstrate that a tendency toward complete delocalization of double negative charge can indeed override the preservation of "aromatic" character.

Acknowledgment. The authors thank the National Science Foundation for financial support, Dr. C. Cottrell and Dr. J. M. Geckle for the NMR measurements and helpful discussions, and Professor L. Anderson for the use of his electrochemical apparatus.

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(1) R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975), and references cited therein; F. A. Kaplan and B. W. Roberts, *ibid.*, **99**, 513, 518 (1977).

(2) (a) The two rings which comprise the bicyclooctatetraenyl tetraanion are not mutually interactive and likely adopt a perpendicular or near perpendicular geometric relationship: L. A. Paquette, G. D. Ewing, and S. G. Traynor, *J. Am. Chem. Soc.*, **98**, 279 (1976). (b) An unsuccessful attempt to prepare the dicyclooctatetraeno[1,2:3,4]cyclobutadiene dianion has been briefly discussed: S. W. Staley, G. M. Cramer, and A. W. Orvedal, *J. Am. Chem. Soc.*, **96**, 7433 (1974).

(3) (a) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 962 (1970). (b) The molecular geometry and bond energies of **3** have been assessed theoretically by the LCAO–MO–SCF–PP [$\pi + \sigma$] method: D. H. Lo and M. A. Whitehead, *J. Am. Chem. Soc.*, **91**, 238 (1969).

(4) With HMPA as solvent, it is possible to reduce benzo-COT and *sym*-dibenzo-COT to their dianions; compare L. B. Anderson and L. A. Paquette, *J. Am. Chem. Soc.*, **94**, 4915 (1972), and L. A. Paquette, C. D. Wright III, S. G. Traynor, D. L. Taggart, and G. D. Ewing, *Tetrahedron*, **32**, 1885 (1976).

(5) R. D. Rieke and R. A. Copenhafer, *Electroanal. Chem. Interfacial Electrochem.*, **56**, 409 (1974).

(6) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *J. Am. Chem. Soc.*, **93**, 161 (1971); L. A. Paquette, J. F. Hansen, and T. Kakihana, *ibid.*, **93**, 168 (1971).

(7) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); D. S. Polcyn and I. Shain, *ibid.*, **38**, 370 (1966).

(8) This conclusion is further substantiated by the observed changes in E_{C},

$- E_{A_1}$ with scan rate (see R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, p 137). These features contrast markedly with the behavior of biscyclooctatetraene.[2]

(9) Molecular orbital calculations on planar **3** using the Hückel approximation predict its energy levels to be $\alpha + 2.39\beta$, $\alpha + 2.00\beta$, $\alpha + 1.70$, $\alpha + 1.59\beta$, $\alpha + 1.41\beta$ (doubly degenerate), $\alpha + 0.86\beta$, $\alpha + 0.36\beta$, and α (doubly degenerate). Consequently, the first two additional electrons enter a nonbonding level.

(10) Extensive effort was made to extract proton–proton coupling constants from the 90- and 300-MHz spectra of this dianion using the INTRCAL program.[12] However, there proved to be too few resolved lines to allow obtention of an acceptable computer-generated least-squares fit.

(11) All assignments have been made with consideration of the earlier work of (a) G. W. Buchanan and A. R. McCarville, *Can. J. Chem.*, **51**, 177 (1973), and (b) H. Günther, A. Shyoukh, D. Cremer, and K. H. Frisch, *Tetrahedron Lett.*, 781 (1974). (c) A. G. Anastassiou and E. Reichmanis, *Angew. Chem., Int. Ed. Engl.*, **13**, 404 (1974).

(12) The benzo portion of the spectrum of **6** has previously been analyzed.[11b] The chemical shifts and coupling constants of the olefinic protons in **6** were herein determined by computer fitting the 300-MHz spectrum with the Nicolet ITRCAL program (which implements the LAOCN3 algorithm on a minicomputer): δ 6.677 (H_c, $H_{c'}$), 6.300 (H_b, $H_{b'}$), and 5.929 (H_a, $H_{a'}$) ($J_{b,c} = J_{b',c'} = 11.89$ Hz, $J_{a,c} = J_{a',c'} = 0.11$ Hz, $J_{a',c} = J_{a,c'} = 0.19$ Hz, $J_{b',c} = J_{b,c'} = 0.07$ Hz, $J_{c,c'} = 0.02$ Hz, $J_{a,b} = J_{a',b'} = 10.89$ Hz, $J_{a',b} = J_{a,b'} = 0.80$ Hz, $J_{b,b'} = 0.24$ Hz, $J_{a,a'} = 9.63$ Hz).

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(14) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(15) The Hückel program by J. R. Howles and R. D. Gilliom (QCPE 70) as revised by B. R. Gilson and J. E. Bloor for the IBM 1620 computer was employed.

(16) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972; P. Lazzeretti and F. Taddei, *Org. Magn. Res.*, **3**, 283 (1971); G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975); G. A. Olah, J. S. Staral, and L. A. Paquette, *ibid.*, **98**, 1267 (1976).

(17) This value of $\Delta G^{\ddagger}$ was calculated through use of the equations $1/\tau = \pi^2(\nu_B - \nu_A)^2 [(1/T_2)\text{ exch} - (1/T_2)^0]^{-1}$ and $T_2 = 1/\pi\nu_{1/2}$ (L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, p 57). The experimentally determined widths at half-height were $\nu_{1/2}$ (300 K) = 8.3 Hz and $\nu_{1/2}$ (173 K) = 25 Hz.

(18) J. B. Stothers, "Carbon 13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 91.

(19) In the present study, we have also examined the ^{13}C–H coupling constants in the benzotropylium cation (δ 162.2 (J = 163 Hz), 159.8 (167), 145.9 (q), 142.3 (166), 139.9 (169), and 138.9 (171)) and the benzotropenide anion (δ 161.9 (q), 151.2 (139), 126.8 (158), 121.4 (154), 108.0 (153), and 90.7 (155)). The smaller values in the anion are clearly evident, but the full complement of causative effects remain to be addressed.

(20) Addition of hexamethylphosphoramide or 18-crown-6 for solubilization purposes promoted the decomposition of **4.**

(21) This protonation reaction did not afford $C_{18}H_{18}$ cleanly, but also gave di- and octahydro compounds. Such complications could arise as a consequence of the presence of residual Na–K alloy in the mixture and/or because of disproportionation.

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On the Mechanism of Olefin Metathesis

Sir:

Cyclopropanes are converted into metathesis-related olefins over metathesis catalysts[1] in reactions apparently proceeding through interconverting metallocyclobutanes and metal carbenes.[1a] Certain metal–carbene complexes also react with a variety of olefins yielding cyclopropanes and metathesis-related olefins, and metallocyclobutanes have been suggested as the key intermediates.[2] This body of chemistry would seem to interrelate metal–carbene complexes, metallocyclobutanes, and cyclopropanes with olefin metathesis. Indeed, since the initial reports by Casey,[2] demonstrating that tungsten–carbene complexes would react with olefins yielding metathesis-related olefins and cyclopropanes, a general consensus has emerged embracing metal carbenes and metallocyclobutanes as the key, chain-carrying intermediates in olefin metathesis,[1,2-4,] a mechanism proposed earlier by Chauvin.[5]

There remains, however, a number of results which are not easily explained by the Chauvin mechanism. Gassman, for example, has reported the catalytic conversion of a nonconjugated bicyclodiene into a cyclobutane of lower free energy.[6] It proceeds over a metathesis catalyst with remarkable ease.[7] The Chauvin mechanism cannot explain the conversion of olefins into their respective cyclobutanes. It is, therefore, necessary to invoke other reaction paths to explain the transformation of this unusual diolefin by a well-known metathesis catalyst.

Grubbs has shown that his proposed tungstenocyclopentane decomposes at ambient temperatures to metathesized ethylene, the CH_2 groups scrambled to ~12%.[11] The Chauvin mechanism would require the metallocyclopentane to first transform into a metallocyclobutane, a transformation totally without precedent. Assuming that this transformation does not occur, these results would suggest that the observed metathesis proceeded along a path other than that proposed by Chauvin.

I wish to review here some of the recent work supporting the Chauvin mechanism in the context of certain basic principles of thermodynamics.[12] The interrelationship between metal carbenes, metallocyclobutanes, and cyclopropanes which emerges from this work is found to be incompatible with the Chauvin mechanism of olefin metathesis. To illustrate this interrelationship the following hypothetical equilibrium catalytic scheme is constructed:

$$\begin{tikzcd} & \text{C} + \text{X}' \arrow[d, shift left] & \\ \text{A} + \text{X} \arrow[r, shift left] & {[\text{X}_1 \rightleftarrows \text{X}_i \cdots \text{X}_n]} \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left] & \text{B} + \text{X} \arrow[l, shift left] \end{tikzcd}$$

A and B are sets of metathesis-related olefins and C the set of cyclopropanes, products of reductive elimination from the metallocyclobutanes X_i. We shall further assume that this is an equilibrium catalytic reaction, at least in those steps interconverting A and B, in direct accordance with the Chauvin mechanism of olefin metathesis. The extent to which cyclopropanes C would fall into the scheme, interchanging with A and B through the key Chauvin intermediates $[X_1 \rightleftarrows X_i \ldots X_n]$ would, of course, depend on the respective free energies of A, B, and C, and the relative rate constants connecting these substrates to the chain-carrying catalytic intermediates. The free energies of the catalytic intermediates paly no role in the scheme since, by definition, a catalyst undergoes no net change (i.e., its net free energy change is zero) in a catalytic transformation.[13]

If the respective free energies of A, B, and C are about equal under metathesis conditions, and we find experimentally that the rate of cyclopropane reaction with the metathesis catalyst is comparable to that of the olefin systems A and B, then microscopic reversibility would demand that the rate of cyclopropane formation be proportionately rapid. Thus, if cyclopropanes are observed to react, generating key, chain-carrying intermediates,[1] then olefin metathesis, an equilibrium catalytic system, should, to some observable extent, yield the respective set of cyclopropanes C, approaching an equilibrium mixture of A, B, and C, if the key catalytic intermediates ($[X_1 \rightleftarrows X_i \ldots X_n]$) are those proposed by Chauvin and accepted generally.[3]

At ambient temperatures, the equilibrium constant of the ethylene–cyclopropane system ($3C_2H_4 \rightleftarrows 2C_3H_6$) is ~0.17,[14] corresponding to ~20 mol % cyclopropane at equilibrium. Minor ring substitutions would not be expected to alter the free-energy properties significantly. However, cyclopropanes are not generated over active metathesis catalysts at equilibrium;[8] yet they are reported to react with striking ease.[1a] It is