the methylene C-3 and -5 and of the methyl carbon are distinctly broader than the other bands in the spectrum, as expected from an intermediate rate of exchange.[8]

The value of the equilibrium constant is about 100, corresponding to an *A* value for the methyl group of 1.6 kcal/mol, in good agreement with the accepted value of 1.7 kcal/mol.[1,3c]

The power of room temperature ^{13}C nmr spectroscopy for the study of conformational problems is well established,[4,9] and low-temperature measurements, as in the present paper, should provide valuable insight in many such problems.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM12769) for financial support.

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[8] Because of the large value of the equilibrium constant, the bands of the equatorial form do not broaden greatly as they merge with those of the axial form.

[9] J. I. Krosschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 5927 (1969); G. W. Buchanan, D. A. Ross, and J. B. Stothers, *ibid.*, **88**, 4301 (1966); G. W. Buchanan, J. B. Stothers, and S. Wu, *Can. J. Chem.*, **47**, 3113 (1969); G. W. Buchanan and J. B. Stothers, *ibid.*, 47, 3605 (1969).

[10] National Research Council of Canada Postdoctoral Fellow, 1969–1970.

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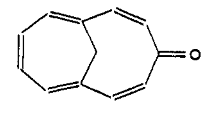
The Synthesis of 4,5-Tetramethylene-2,6,8,14-tetradehydro[15]annulenone, an Aromatic Macrocyclic Ketone. The Demonstration of a Diamagnetic Ring Current in a [4*n* + 3]Annulenone Derivative[1]

Sir:

Planar monocarbocyclic conjugated ketones (annulenones) are expected to be nonaromatic if they contain a (4*n* + 1)-membered ring, due to the electron-withdrawing properties of the oxygen of the carbonyl group. In agreement with this are the properties of the known [5]-,[2,3] [13]-,[4] and [17]annulenone[3,5] derivatives, the nmr spectra of which all show a paramagnetic ring current. Conversely, annulenones containing a (4*n* + 3)-membered ring are expected to be aromatic, and the properties of cyclopropenone (the smallest member) and its derivatives are in agreement with this expectation.[6] However, the properties of cycloheptatrienone (tropone), the next higher (4*n* + 3]annulenone, have been interpreted as being indicative of nonaromaticity,[7] as have those of the very recently described 4,9-methano-[11]annulenone (**1**), a bridged derivative of the next higher member.[8]

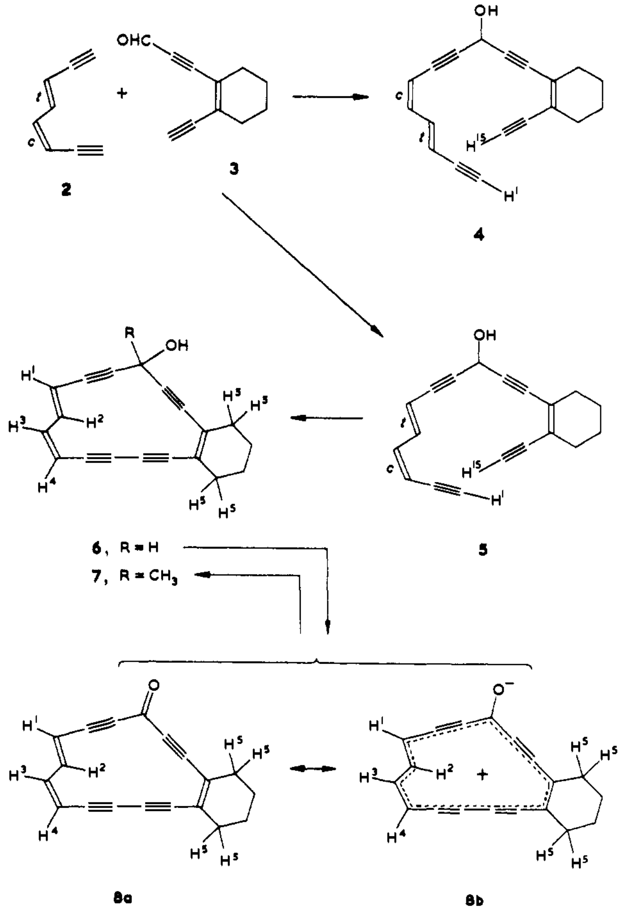


I

In order to gain further information regarding the possible aromaticity of [4*n* + 3]annulenone derivatives, it appeared desirable to make available a macrocyclic member containing inner as well as outer protons, in order that ring-current effects could be more clearly observed by nmr spectrometry. We now describe the realization of this objective, namely the synthesis of 4,5-tetramethylene-2,6,8,14-tetradehydro[15]annulenone (**8**). The nmr spectrum of this substance indeed showed the existence of a diamagnetic ring current, indicative of aromaticity presumably arising from appreciable contribution by the delocalized structure **8b**.

1,2-Diethynylcyclohexene[4] was allowed to react at 20° with 1 mol equiv of EtMgBr in THF and then added to DMF in THF. After 1 hr at 20°, the mixture was poured into dilute H_2SO_4 and stirred for 3 hr.[9] Chromatography on silica gel yielded 25% of the aldehyde **3** as an unstable liquid;[10] $\lambda_{max}^{Et_2O}$ 268 (ϵ 7000), 287 (9600), 298 (12,700), and 312 nm (12,700).[11]

Removal of the protecting groups from the 1,8-bis-(trimethylsilyl) derivative of *cis,trans*-3,5-octadiene-1,7-diyne (**2**)[12] by the silver nitrate–potassium cyanide



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[1] Unsaturated Macrocyclic Compounds. LXXVII. For part LXXVI, see P. J. Garratt, N. E. Rowland, and F. Sondheimer, *Tetrahedron*, in press.

[2] See E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433, 3434 (1966); **91**, 6785 (1969).

[3] G. W. Brown and F. Sondheimer, *ibid.*, **91**, 760 (1969).

[4] G. M. Pilling and F. Sondheimer, *ibid.*, **90**, 5610 (1968).

[5] J. Griffiths and F. Sondheimer, *ibid.*, **91**, 7518 (1969).

[6] *Inter al*, see R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966); R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

[7] D. J. Bertelli and T. G. Andrews, *ibid.*, **91**, 5280 (1969); D. J. Bertelli, T. G. Andrews, and P. O. Crews, *ibid.*, **91**, 5286 (1969).

[8] W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *ibid.*, **92**, 6335 (1970). We thank Professor Vogel for sending us the manuscript prior to publication.

[9] Method of E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 1054 (1958).

[10] The nmr and ir spectra were in accord with the assigned structure, and the substance was chromatographically homogeneous.

[11] The ϵ values represent minimum ones, due to the instability of the substance.

Table I. Nmr Spectra of the Cyclic Conjugated Systems **8–11** Compared with the Model **7**[a,b]

	Entry								
	A **7**	B **8**	C **9**	D **10**[c]	E **11**[d]	F Δ(**8** − **7**)	G Δ(**9** − **7**)	H Δ(**10** − **7**)	I Δ(**11** − **7**)
H-1	4.23	3.55	3.12	4.87		−0.68	−1.11	+0.64	
H-2	3.03	4.99	6.51	−0.31		+1.96	+3.48	−3.34	
H-3	3.17	2.35	1.93	3.88		−0.82	−1.24	+0.71	
H-4	4.43	3.72	3.26	4.95		−0.71	−1.17	+0.52	
H-5	7.50–7.85	7.15–7.50	6.95–7.30		7.85–8.20	−0.35	−0.55		+0.35

[a] All spectra were determined at 100 MHz in $CDCl_3$, except that of **9**, which was determined in CF_3COOD. All values are τ, TMS being used as internal standard. [b] The protons H-1–H-4 could be recognized by their coupling constants; in each case H-1 was a d (J = 16 Hz), H-2 a dd (J = 16 and 12 Hz), H-3 a dd (J = 12 and 10 Hz), and H-4 a d (J = 10 Hz). H-5 was a multiplet in all cases. [c] Reference 3. [d] Reference 4.

method[13] gave the free dienediyne **2** as an unstable liquid;[10] $\lambda_{max}^{Et_2O}$ 273 sh (ϵ 21,300), 282 (29,900), and 295 nm (27,500).[11] Substance **2** was treated directly with 1 mol equiv of EtMgBr in THF at 20°, and then with 0.8 mol equiv of **3** in THF at −40 to 20°. Chromatography on silica gel led to 50% of a $\sim$1:1 mixture of the stereoisomeric alcohols **4** and **5** as an unstable yellow oil;[10] $\lambda_{max}^{Et_2O}$ 265 (ϵ 28,600), 279 (31,200), 291 (37,500), and 304 nm (32,800).[11] The fact that the product was a mixture of **4** and **5** was indicated by the nmr spectrum ($CDCl_3$), which showed two doublets ($\sim$1:1) at τ 6.79 and 6.97 (J = 2 Hz) due to H-1 and two singlets ($\sim$1:1) at 6.84 and 6.90 due to H-15. No attempt at separation was made, since inspection of models indicated that only **5** could form the corresponding cyclic monomer.

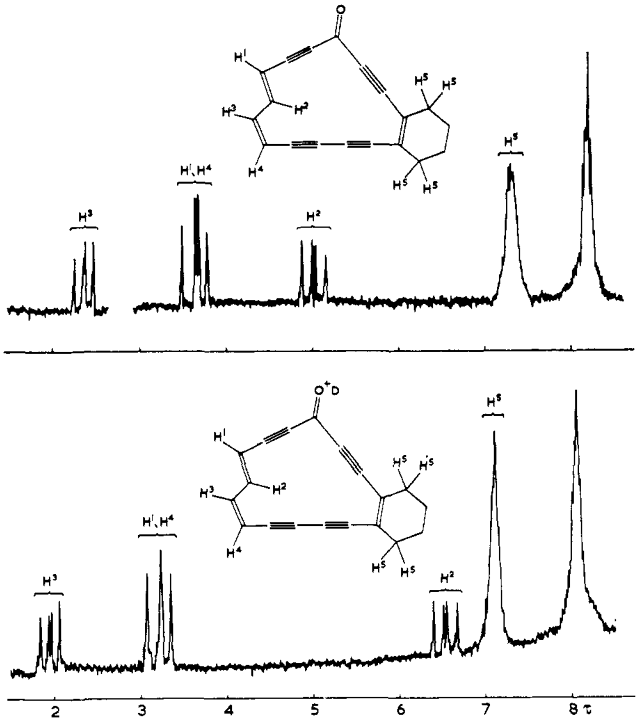

Figure 1. Nmr spectra of 4,5-tetramethylene-2,6,8,14-tetradehydro[15]annulenone (**8**) in $CDCl_3$ (upper curve) and in CF_3COOD (lower curve), determined at 100 MHz, TMS being used as internal standard.

Oxidative coupling of **4** and **5** with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene for 2 hr at 60°[14] led to the 15-membered ring alcohol **6** [$\lambda_{max}^{Et_2O}$ 271 (relative optical density 0.72), 282 (1.00), 366 (0.13), and 392 sh nm (0.10)] as the sole monomeric product, in addition to insoluble polymeric material. The alcohol **6** was exceedingly unstable, and was oxidized directly in ether with MnO_2 for 3 hr at 20°. Chromatography on neutral Al_2O_3 gave the annulenone **8** in $\sim$10% yield (based on **4** and **5**) as orange-yellow needles which decomposed at $\sim$100–120° on attempted melting point determination: $\lambda_{max}^{Et_2O}$ 306 (ϵ 36,000), $\sim$320 sh (26,500), 378 (7800), 396 (7700), 415 sh (4300), and 440 nm (2300); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2180 m, 2170 m (C≡C), 1610 s (C=O), 1580 w, and 1550 m (C=C); mass spectrum, m/e 256 (M) and 226 (M − 30, 100%). The carbon skeleton of **8** was confirmed by catalytic hydrogenation in EtOAc–AcOH over Pt, followed by Jones oxidation, which gave a mixture of the corresponding saturated bicyclic ketone [mass spectrum, m/e 278 (M)] and hydrocarbon [mass spectrum, m/e 264 (M)]. The annulenone **8** was considerably more stable than its precursors; *e.g.*, the crystals suffered only $\sim$10% decomposition after 20 hr in light and air.

The nmr spectrum of **8** (Table I, entry B, and Figure 1, upper curve) indicated the existence of a diamagnetic ring current, since the inner H-2 proton resonated at considerably higher field than the outer H-1, H-3, and H-4 protons. In order to obtain a suitable cyclic model lacking a ring current, **8** was treated with an excess of MeLi in ether at −78 to 20°. Preparative tlc led to $\sim$20% of the tertiary alcohol **7**, an unstable yellow oil;[10] $\lambda_{max}^{Et_2O}$ 271 (relative optical density 0.77), 281 (1.00), 363 (0.20), and 387 nm (0.16); nmr spectrum, see Table I, entry A. Compared with **7**, each of the outer H-1, H-3, and H-4 protons in **8** (Table I, entry F) are shifted downfield by $\tau \sim$ 0.7, and the inner H-2 proton is shifted upfield by $\tau \sim$ 2.0. This is clear evidence for a diamagnetic ring current in **8**.

As expected, the diamagnetic ring current is increased when **8** is protonated. Thus, when **8** is dissolved in CF_3COOD, the nmr spectrum (presumably of the deuteronated species **9**; see Table I, entries C and G, and Figure 1, lower curve) shows downfield shifts for the outer protons of $\tau \sim$ 1.2, and an upfield shift for the inner proton of $\tau \sim$ 3.5 as compared with **7**.

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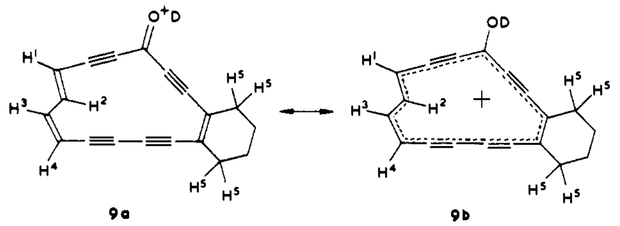
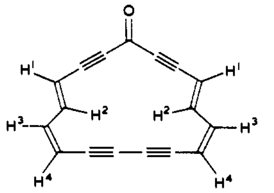
(12) G. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **91**, 7520 (1969).

(13) J. F. Arens and H. M. Schmidt, *Recl. Trav. Chim. Pays-Bas*, **86**, 1138 (1967).

(14) See R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965).



9a **9b**



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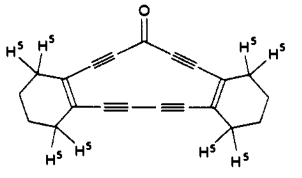

11

It is also of interest to compare the nmr spectrum of the tetradehydro[17]annulenone **10**[3] with that of the model **7**. It can be seen (Table I, entries D and H) that now the outer protons are shifted *upfield* by $\tau \sim 0.6$, and the inner protons *downfield* by $\tau \sim 3.3$, clearly confirming the existence of a paramagnetic ring current in **10**.

Finally, the nmr data show that the allylic H-5 protons are also affected by the ring currents. Thus, in the aromatic **8** and **9** they are shifted *downfield* by τ 0.35 and 0.55, respectively, as compared with **7** (Table I, entries F and G), while in the nonaromatic tetradehydro[13]-annulenone **11**[4] they are shifted *upfield* by τ 0.35 (Table I, entries E and I).[15]

Acknowledgments. We are indebted to the Science Research Council for financial support (to G. P. C. and G. H. M.), and to New Hall, Cambridge, for the award of a Junior Fellowship (to G. M. P.).

(15) The small upfield shift of the allylic protons in the nmr spectrum of **11** had already tentatively been ascribed to the presence of a paramagnetic ring current,[4] but this evidence was not conclusive in the absence of the observation of an opposite shift in compounds possessing a diamagnetic ring current.

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Small Carborane Metallocene Analogs. Iron π Complexes Containing the Formal *nido*-$C_2B_4H_6^{2-}$ and *cyclo*-$C_2B_3H_7^{2-}$ Ligands

Sir:

The recent synthesis[1] of (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$ in the vapor-phase reaction of 2-$CH_3C_3B_3H_6$ with $Mn_2(CO)_{10}$, and also in the reaction[2] of the 2-$CH_3C_3B_3H_5^-$ ion with $BrMn(CO)_5$, has suggested the probable existence of other small carborane–transition metal complexes. Attention was directed to 2,3-dicarbahexaborane(8), $C_2B_4H_8$, which in contrast to the $C_3B_3H_7$ derivatives is a readily obtainable carborane.[3] In theory, removal of the two bridge protons from 2,3-$C_2B_4H_8$ should generate a pyramidal $C_2B_4H_6^{2-}$ anion whose five-membered basal ring contains six delocalized electrons, analogous to $C_5H_5^-$. Although this ion apparently has not been prepared as such,[4] its formal existence in the known polyhedral 1-$CH_3GaC_2B_4H_6$[5] and 1-$CH_3InC_2B_4H_6$[6] species suggested that π complexes of formal $C_2B_4H_6^{2-}$ might be prepared directly from 2,3-$C_2B_4H_8$ and appropriate transition metal carbonyls. Accordingly, a mixture of $C_2B_4H_8$ and excess $Fe(CO)_5$ was heated to 240° in a Pyrex tube, the lower end of which was maintained at 25°. Removal of excess $Fe(CO)_5$ and $C_2B_4H_8$ by distillation at −45° yielded two products which were nonvolatile at that temperature, but which could be separated from each other by repeated fractionation through a trap at −23°.

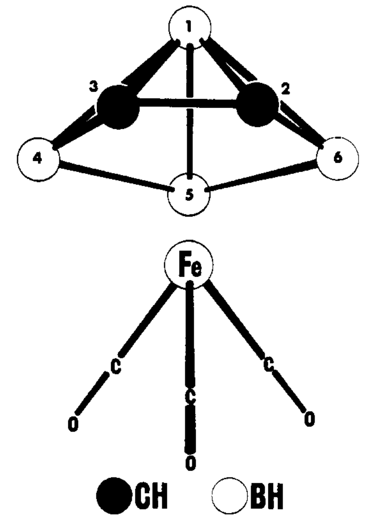

Figure 1. Proposed structure of (π-$C_2B_4H_6$)$Fe(CO)_3$.

The less volatile material, a deep orange liquid, was characterized as (π-$C_2B_4H_6$)$Fe(CO)_3$ (I), shown in Figure 1. The mass spectrum contains a sharp cutoff at *m/e* 214, corresponding to the parent ion, and the profile in the parent region corresponds virtually exactly with the calculated intensities based on natural isotopic distributions.[7] The presence of three carbonyl groups is clearly indicated by strong groupings at *m/e* 186, 158, and 130, corresponding to the loss of one, two, and three CO units, respectively. The 32.2-MHz ^{11}B nmr spectrum of I in CCl_4 solution exhibits three broad, well-separated doublets in a 1:2:1 area ratio, at δ −18.9 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, J = 160 cps; δ −5.16, J = 150; and δ +17.7, J = 160, assigned to B(5)–H, B(4,6)–H, and B(1)–H, respectively.[8] The

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(1) J. W. Howard and R. N. Grimes, *J. Amer. Chem. Soc.*, **91**, 6499 (1969).

(2) J. W. Howard, Ph.D. Dissertation, University of Virginia, 1970.

(3) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(4) Treatment of 2,3-$C_2B_4H_8$ with excess NaH removes only one bridge proton, forming the $C_2B_4H_7^-$ ion: T. Onak and G. B. Dunks, *ibid.*, **5**, 439 (1966).

(5) R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, **91**, 6498 (1969).

(6) R. N. Grimes and W. J. Rademaker, manuscript in preparation.

(7) Hydrogen loss in the parent region is negligible owing to the much more facile cleavage of CO groups from the molecule.

(8) Assignments of the B(5)–H and B(1)–H resonances, which conceivably could be interchanged, are based on the observation that apex B–H resonances of related carboranes and metallocarboranes (*e.g.*, 2,3-$C_2B_4H_8$,[3] 2,4-$C_2B_5H_7$,[9,10] 2-$CH_3C_3B_3H_5Mn(CO)_3$,[1] 1-$CH_3GaC_2B_4H_6$[5]) are found at high field.

(9) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Amer. Chem. Soc.*, **88**, 4622 (1966).