allylic ion, *e.g.*, XX, to a second such ion involving the second cyclopropane ring, *e.g.*, XXI, occurs competitively with solvent attack on the first homoallylic ion. Perhaps a bishomopentadienyl[9] ion such as XXII needs to be considered.

Acknowledgment. We are indebted to Dr. Arthur Diaz for assistance in connection with some of the solvolysis kinetics. We are grateful to Drs. G. Hummel and F. Ebel of the Badische Anilin and Soda Fabrikwerke in Ludwigshafen, Germany, for generous supplies of the necessary cyclooctatetraene starting material.

[9] R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, 2, 423 (1963).

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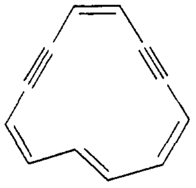
5-Bromo-1,9-bisdehydro[12]annulene. A Verification of an Induced Paramagnetic Ring Current in a 4n π-Electron System

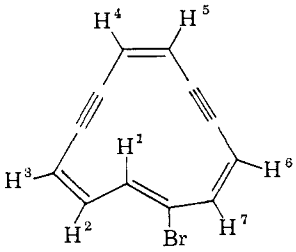
Sir:

Recently we presented a theory[1,2] and some evidence that conjugated cyclic 4n π-electron systems display an induced paramagnetic ring current in a magnetic field, *i.e.*, a ring current opposite in sign from the familiar induced diamagnetic ring current associated with aromatic or 4n + 2 π-electron systems. Since our report, more evidence has been uncovered which lends additional support to this generalized description. The nmr spectra of [16]-,[3] 1,9-bisdehydro[16]-,[4] 1,11-bisdehydro[20]-,[4] and [24]annulenes[5] have now been studied at lower temperatures (where valence and/or conformational interconversions have been slowed or stopped) and found to be qualitatively as expected from the generalized explanation, *i.e.*, inner hydrogens shifted upfield, outer hydrogens downfield for 4n + 2 π-electron systems; inner hydrogens downfield, and outer hydrogens upfield for 4n π-electron systems.

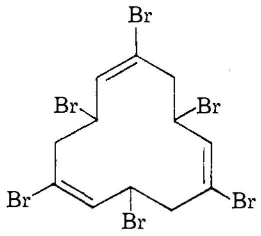
A compound synthesized by Wolovsky and Sondheimer,[6] 1,5-bisdehydro[12]annulene (I), is a particularly interesting 4n π-electron system in regard to induced paramagnetic ring currents because of the unusually low value of the chemical shift (τ scale) observed for the two hydrogens of the *trans* double bond. We have suggested[1] that the nmr signal of these two hydrogens at τ -0.9 is the result of an averaging process caused by interconversion between two equivalent *planar* conformers. The nmr spectrum of I has been found to be temperature dependent and the absorption of the *trans* double bond hydrogens is broadened and shifted downfield by *ca.* 0.4 ppm at $-80°$.[4] Unfortunately, spectra taken at still lower temperatures, wherein the noninterconverting conformer might be observed, are not yet available.


I

We wish to report here the synthesis of a molecule, 5-bromo-1,9-bisdehydro[12]annulene (II), that strikingly verifies the expectations for chemical shifts of hydrogens of 4n π-electron systems based on the idea of an induced paramagnetic ring current. The oily isomeric mixture of 1,3,5,7,9,11-hexabromo-*cis,cis,cis*-1,5,9-cyclododecatriene (III) resulting from the bromination (NBS) of 1,5,9-tribromo-*cis,cis,cis*-1,5,9-cyclododecatriene (IV), after chromatography (SiO$_2$, hexane–CCl$_4$), was separated; the crystalline isomer V, mp 185°, was obtained in *ca.* 15% yield; the oily isomer in *ca.* 60%.[7] The oily hexabromocyclododecatriene with 4 equiv of sodium ethoxide in ethanol (18 hr, room temperature) gave II (17% yield after silicic acid column chromatography) as a reddish brown oil. Mass measurement of the *two* isotopic parent molecular ions dictates the molecular formula for II; calcd for $C_{12}H_7Br$: 229.9732, 231.9712; found: 229.9743, 231.9732. The infrared spectrum of II (liquid film) exhibited absorptions at 3.28 (m), olefinic CH; 4.62 (w), triple bond; 6.24 (m), conjugated double bond; 7.72 (s), *cis* olefinic CH; 12.06 (s), trisubstituted olefinic CH; and 13.37 (vs) μ, disubstituted *cis* double bond.[8] Twelve absorptions correspond very closely to those reported[6b] in the infrared spectrum of I. The ultraviolet spectrum of II is very similar to that of I.[6b] It has absorptions at 244 mμ (sh) (ϵ 33,000), 251 (35,000), 290 (sh) (1150), and 466 (200).[9] The nmr spectrum (Figure 1) provides the added data necessary for the structural assignment of II and reveals the unique absorption of the inner hydrogen of this cyclic 4n π-electron system. The spectrum is partially interpretable by first-order analysis. The low-field absorption due to H^1 (area 1) is a doublet ($J_{12} \simeq 9.4$ cps) with additional splittings; H^2 (area 1) is an apparent triplet; H^3 (area 1) is seen as a doublet ($J_{23} \simeq 10.2$ cps, typical for *cis* olefinic hydrogens) with additional splittings; H^4, H^5 (area 2) and



II



III

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[1] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 88, 4811 (1966).

[2] Essentially the same theoretical conclusions have been independently reached by H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109, and by F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, 22a, 103 (1967).

[3] G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

[4] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75 (privately communicated by F. Sondheimer).

[5] I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).

[6] (a) F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); (b) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, 87, 5720 (1965).

[7] K. G. Untch and D. C. Wysocki, *ibid.*, 88, 2608 (1966).

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[9] The ϵ values may be low since the sample used was not a crystalline compound.

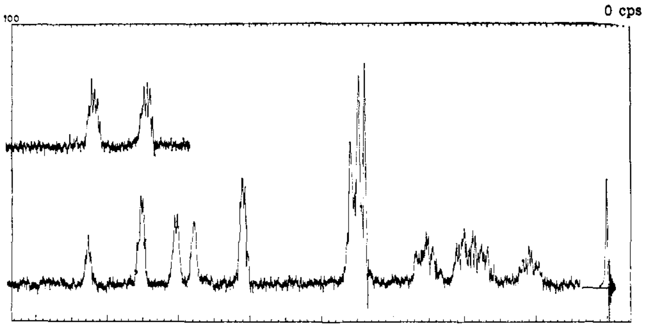

Figure 1. Nmr spectrum of II in carbon tetrachloride (*ca.* 10%) with tetramethylsilane as an internal reference using a Varian A-60 spectrometer. The two scans are 100-cps full scale: the lower is offset 240 cps; the upper, which shows the absorption due to H^1, is offset 900 cps.

H^6, H^7 (area 2) are complex multiplets. That the molecule contains a *trans* double bond with one bromine on it can be deduced from (a) the apparent doublet for H^1 [10] and (b) from the coupling constant J_{12}. The system which includes H^1, H^2, H^3 in II is that found in substituted butadienes. The characteristic range of values for J_{23} (across the formal single bond) in dienes that are in *s-trans* planar conformations is 10.3–12.5 cps.[11] On the other hand, the typical range for sp^2–sp^2 proton coupling across the formal single bond in *cis* dienes is 5–7 cps.[12] The observed value for J_{12} of 9.4 cps corresponds best to a *trans* arrangement for H^1 and H^2 in II.

The most striking feature of the nmr spectrum of II is the chemical shift of the one hydrogen assigned H^1. This hydrogen exhibits an absorption at τ *−6.4* (985 cps downfield from that of tetramethylsilane). Previously we predicted[1] that I was interconverting between two equivalent planar conformers and that the chemical shift of the inner hydrogen of I would be observed at *ca.* τ −6.4[13] for the frozen conformer. In the case of II no such conformational interconversion can occur, since the bromine atom is too large to fit through the ring and thus the nmr spectrum of II is that of a single conformer.

We conclude from these data that II is planar or nearly so and that the value of the chemical shift for H^1 is due to an induced paramagnetic ring current of a $4n$ π-electron cyclic system. It should also be pointed out that local anisotropic effects of the two triple bonds in close proximity to this inner hydrogen would, if operative, cause an upfield shift.

To our knowledge, no hydrogen bonded to carbon in hydrocarbons or simple derivatives has been observed at such a *low-field* value. The only other kind of shift of similar magnitude previously noted is in the $4n + 2$ π-electron annulenes. The largest *upfield* shift among these is found for the inner hydrogens of 1,8-bisdehydro[14]annulene at τ 15.5,[14] a shift of *ca.* 11 ppm compared to cyclic monoolefins, τ 4.4. The same comparison made with the value of the chemical shift for H^1 in II also gives a shift of *ca.* 11 ppm, but in the *opposite* direction, downfield (a difference of *ca. 22* ppm for the inner hydrogens of these two kinds of conjugated cyclic systems).[15]

Such dramatic changes in chemical shifts for corresponding inner hydrogens of $4n + 2$ π-electron systems are compelling. The argument that an induced diamagnetic ring current be a criterion for aromaticity now seems strengthened by this and other demonstrations[4] of induced paramagnetic ring currents in cyclic $4n$ π-electron systems.

Acknowledgment. The authors are grateful to Mr. R. E. Rhodes for obtaining the mass spectrometric measurements and to the National Science Foundation (Grant GP-6612) for partial support of this work.

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[10] If H^1 were flanked by two adjacent hydrogens, its absorption pattern would be more complex, ranging from perhaps a triplet to an ABC pattern with additional long-range couplings.

[11] A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965): butadiene, J_{23} = 10.41 cps; 1,4-dichlorobutadienes, J_{23} = 10.84 ± 0.5 cps.

[12] *E.g.*, 1,3-cyclohexadiene, J_{23} = 5.14 cps; see footnote 8 in ref 7.

[13] This predicted value (τ −6.4) cited in ref 1 is in error. The corrected value is τ − 7.3. The arguments made remain unchanged.

[14] F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Am. Chem. Soc.*, **84**, 4595 (1962).

[15] Consistent with an induced paramagnetic ring current, the outer hydrogens of II are shifted upfield from the olefinic value to τ 4.6–5.7.

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Protonation of Norbornadienetricarbonyliron

Sir:

Norbornadienetricarbonyliron (**1**), in contrast to norbornadiene itself, can be recovered unchanged from sulfuric acid solution.[1] We have undertaken an nmr study of **1** in strongly acidic media and find that, unlike tricarbonyliron derivatives of conjugated dienes,[2] it undergoes protonation on iron.

The nmr spectrum of **1** in liquid sulfur dioxide is simple, reflecting its apparent C_{2v} symmetry. The hydrogens at C_7 appear as a triplet at τ 8.75 while the olefinic and bridgehead protons appear as an overlapping triplet (τ 6.85)[3] and multiplet (τ 6.65), respectively. Addition of fluorosulfonic acid to the deep red solution of **1** in sulfur dioxide at −70° changes the color to pale yellow-green and gives the nmr spectrum shown in Figure 1. A triplet (1 H, J = 13 Hz) has appeared at τ 17.3 while below TMS all signals have been shifted to lower fields, and the symmetry of the spectrum has been reduced considerably. The two triplets separated by 13 Hz are caused by two equivalent hydrogens coupled by 13 Hz to the high-field hydrogen. Experiments at 60 and 100 Mc show that this splitting (in hertz) is field independent and therefore caused by spin–spin coupling. The spectrum of **1** in D_2SO_4 is the same as that in FSO_3H–SO_2 except that the high-field proton is missing, and the two triplets have collapsed to a single multiplet. Compound **1** can be recovered unchanged from these strongly acidic solutions by pouring into ice water and subsequent ether extraction. Nmr integration of recovered **1** establishes that no incorporation of deuterium into the norbornadiene ligand occurred in the D_2SO_4 solution.

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[1] R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[2] G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

[3] Attachment of a transition metal to a double bond causes a large upfield shift of the olefinic hydrogens: M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).