(11) (a) The negative sign of $a(H_7)$ of IV conflicts with the work of Kochi, Bakuzis, and Krusic,[1b] in which $a(H_7)$ of IV was suggested to be positive to explain its unusual temperature dependence. However, the temperature dependence of $a(H_7)$ of IV (with negative sign) may be explained (1) by assuming a broad anharmonic single-minimum potential for the out-of-plane vibration of the C_7H_7 bond or (2)[11b] by assuming an asymmetrical broad double-minimum potential with a low barrier to the inversion of the C_7–H_7 bond; (b) suggested by P. J. Krusic.

(12) Cf. T. Kawamura, T. Koyama, and T. Yonezawa, *J. Am. Chem. Soc.*, **95**, 3220 (1973), and also ref 10.

(13) This interchanges the assignment suggested by Kochi, Bakuzis, and Krusic[1b] of the vinylene and bridgehead protons of IV. We suggest the assignments of $a(H_2)$ = 1.20 and $a(H_1)$ = 1.54 G for IV.

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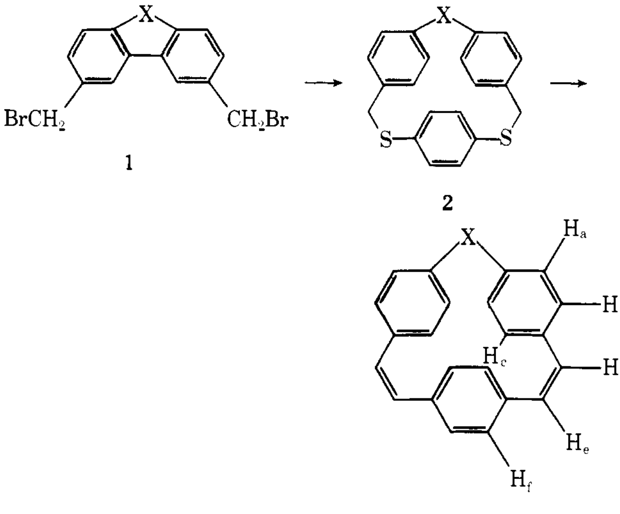
Bridged [18]Annulenes. Dependency of the Ring Current Contribution to Chemical Shift on the Contour of the Annulene Perimeter[1]

Sir:

The discovery that $4n + 2$ annulenes are diatropic, whereas $4n$ annulenes are paratropic has had a profound impact on the assessment of aromatic character.[2] Commonly, qualitative conclusions about the aromaticity of a newly synthesized molecule are made simply on the basis of the observed proton chemical shifts. In a significant development in this regard, Haddon has proposed that analyses of ring current contributions to proton chemical shifts can provide a quantitative measure of aromaticity.[3] In the use of proton chemical shift data, it is important, therefore, to understand as well as possible all of the factors affecting ring current contributions to proton chemical shifts. In this communication we provide experimental evidence that, aside from planarity, the contour of the loop of the annulene perimeter plays an important role in determining the magnitude of the ring current contribution.

Recently, we reported a photochemical procedure for preparing bridged [18]annulenes.[4] This method has proved to be general and has provided a number of new bridged [18]annulenes, of which the properties of three—**5**, **6**, and **7**—are important to the present discussion. The stilbene derivatives necessary for the photochemical preparations of **5**, **6**, and **7** were synthesized as follows. The coupling of 3,3′-bis(bromomethyl)biphenyl (**1a**)[5] with 1,4-bis(mercaptomethyl)benzene proceeded in 52% yield to give the dithiacyclophane **2a**, mp 215–216°.[6] Subjection of **2a** to a Stevens rearrangement followed by a Hofmann elimination readily gave **3a**: ^{1}H NMR (CDCl$_3$), a multiplet at τ 2.6–3.0 (6 H, Ar*H*), a singlet at 2.72 (4 H, H$_f$), doublets at 2.90 and 3.37 (4 H, H$_d$ and H$_e$, $J_{d,e}$ = 12 Hz), and a singlet at 3.26 (2 H, H$_c$).[7]

For the synthesis of **1b**, treatment of 5,5′-bis(carbomethoxy)-2,2′-dimethylbiphenyl[8] with *N*-bromosuccinimide in boiling carbon tetrachloride for 5 hr gave 5,5′-bis(carbomethoxy)-2,2′-bis(bromomethyl)biphenyl, mp 131–133°, in 30% yield. The reduction of this diester with diisobutylaluminum hydride in benzene followed directly by addition of phenyllithium to the reduction mixture gave 3,6-bis(hydroxymethyl)-9,10-dihydrophenanthrene, mp 95–97°, in 65% yield. Reaction of 3,6-bis(hydroxymethyl)-9,10-dihydrophenanthrene with phosphorus tribromide in ether then led to **1b**, mp 224–226°, in 97% yield. Coupling of **1b** with 1,4-bis(mercaptomethyl)benzene gave **2b** in 86% yield.[6] Again, subjection of **2b** to a Stevens rearrangement followed by a Hofmann elimination led to **3b**: ^{1}H NMR (CDCl$_3$), multiplet at τ 3.11 (4 H, H$_{a,b}$), singlet at 3.21 (2H, H$_c$), doublet at 3.03 (2H, H$_d$, $J_{d,e}$ = 11.5 Hz), doublet at 3.47 (2 H, H$_e$, $J_{d,e}$ = 11.5 Hz), singlet at 2.81 (4 H, H$_f$), and a singlet at 7.20 (4 H, ArCH_2–).[7]



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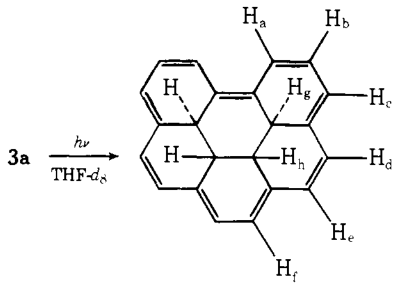
a, X = -H, -H
b, X = -CH$_2$CH$_2$-

The synthesis of **4** (^{1}H NMR (CDCl$_3$), a singlet at τ 3.14 (6 H, -C*H*═C*H*-) and a singlet at 3.26 (12 H, Ar*H*)) was carried out as described by Cram and Dewhirst,[9] who also irradiated **4** in 1959 in an attempt to make **7**.

The irradiations of **3a**, **3b**, and **4** were conducted in each case in carefully degassed perdeuteriotetrahydrofuran solutions held at −80° using a low pressure mercury lamp (2537 Å). After a short period of irradiation, the solutions became colored (orange to red) and new signals appeared in their ^{1}H NMR spectrums, which grew in intensity on prolonged irradiation. In the case of **3a**, the new ^{1}H NMR signals are in accord with the formation of the tetrahydrobenzo[*g,h,i*]perylene derivative **5**. The assignment of the signals for the individual protons are as follows: a doublet at τ 0.90 (2 H, H$_a$, $J_{a,b}$ = 9 Hz), a doublet of doublets at 2.53 (2 H, H$_b$, $J_{a,b}$ = 9 Hz; $J_{b,c}$ = 7 Hz), a doublet at 2.14 (2 H, H$_c$, $J_{b,c}$ = 7 Hz), a multiplet at 2.06 (4 H, H$_d$ and H$_e$), a singlet at 2.32 (2 H, H$_f$), a multiplet at 12.58 (2 H, H$_g$), and a multiplet at 12.86 (2 H, H$_h$). In the case of the irradiation of **3b**, the photoproduct has the analogous structure **6** with the proton chemical shift assignments being a doublet at τ 2.79 (2 H, H$_b$, $J_{b,c}$ = 7 Hz), a doublet at 2.25 (2 H, H$_c$, $J_{b,c}$ = 7 Hz), a broad singlet at 2.14 (4 H, H$_d$ and H$_e$), a singlet at 2.42 (2 H, H$_f$), a multiplet at 7.26 (4 H, H$_a$), a multiplet at 12.53 (2 H, H$_g$), and a multiplet at 12.88 (2 H, H$_h$). Thus **5** and **6** have very similar ^{1}H NMR spectra. Since both conjugated systems have the same benzo[*g,h,i*]perylene-shaped perimeter, this is as expected. As compared to their precursor dienes (**3a** and **3b**), both **5** and **6** show a shift of the signals for the external protons to lower field and a sharp shift of the signals for the internal protons to high field. This is in accord with the formation of the $4n + 2$ bridged [18]annulenes.[10]

In the case of the irradiation of **4**, examination of molecular models suggests that the photoproduct should have the stereochemistry (C_2 symmetry) shown by **7**. The ^{1}H NMR spectrum of **7** is in accord with this with the assignments being made as follows: the external protons provide an AB quartet at τ 0.60 (4 H, $J_{a,b}$ = 8 Hz) and a singlet at 0.52 (8 H), whereas the internal protons exhibit an AA′BB′CC′ multiplet centered at τ 16.44 (2 H), a doublet of doublets at



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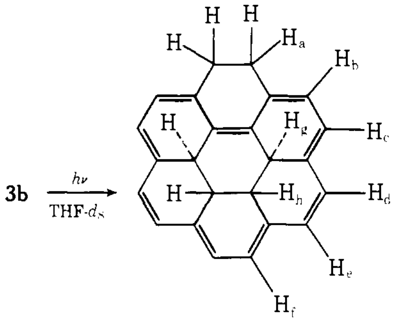

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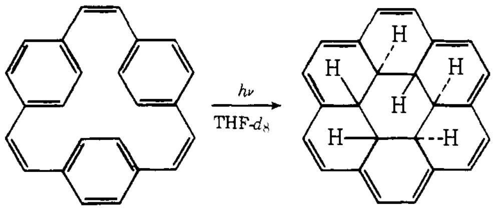

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16.82 (2 H), and a doublet of quartets at 17.88 (2 H). Compound **7**, which has the coronene-shaped perimeter, clearly shows by far the greatest ring current contribution to chemical shift of the three compounds being compared.

As additional evidence for the structural assignments, **6** and **7** were converted to coronene in quantitative yield on exposure to air, whereas **5** gave benzo[*g,h,i*]perylene.

Examination of molecular models of **5**, **6**, and **7** suggests that the annulene perimeter of each should be essentially planar. If we consider the two hexahydrocoronenes, **6** and **7**, the only obvious difference is in the contour of the annulene loop, one following a benzo[*g,h,i*]perylene perimeter and the other a coronene perimeter. From elementary principles, one would expect that the magnetic field for a ring current, which follows a loop that twines back upon itself, as does the benzo[*g,h,i*]perylene perimeter, would be to some extent self-nullifying and this agrees with the smaller ring current contribution of **6** as compared to **7**. What is surprising, though, is the magnitude of the effect, the signals for the internal protons of the molecule with the coronene perimeter appearing at about 5 ppm higher field than the corresponding internal protons where a benzo[*g,h,i*]perylene perimeter is present. Thus, in comparative analyses of ring current contributions to chemical shifts, the contour of the annulene perimeter, aside from its planarity, is clearly an important factor.

Recent calculations of Dewar, Haddon, and Student using a MINDO/3 method predict that [18]annulene itself should be a completely bond alternate hydrocarbon.[11] In our opinion, the strong ring current contributions to chemical shift observed with the bridged [18]annulene **7** contradict that prediction.

References and Notes

(1) We thank the National Science Foundation for their support of this investigation. V. Boekelheide thanks the Alexander von Humboldt Foundation for an award of a Senior Fellowship, 1974–1975.

(2) See F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972), for a review and leading references to the development of this concept.

(3) R. C. Haddon, *Tetrahedron*, **28**, 3613, 3635 (1972).

(4) J. Lawson, R. DuVernet, and V. Boekelheide, *J. Am. Chem. Soc.*, **95**, 956 (1973).

(5) W. Wenner, *J. Org. Chem.*, **17**, 523 (1952).

(6) Satisfactory analyses are available for all new compounds reported except **5**, **6**, and **7**, which were not isolated but only observed in solution. Experimental details for our method of coupling mercaptans and halides to give dithiacyclophanes are reported by R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.* 219 (1975).

(7) Our procedure for converting dithiacyclophanes to cyclophane dienes is given by R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974). In the conversion of **1a** and **1b** to **3a** and **3b**, the intermediate methylsulfonium fluoroborates were formed in essentially quantitative yields using dimethoxycarbonium fluoroborate in dichloromethane at room temperature. The Stevens rearrangement and Hofmann elimination reactions were carried out in each case using potassium *tert*-butoxide in tetrahydrofuran at room temperature. The Stevens rearrangements of **2a** and **2b** occurred in 23 and 21% yields, respectively. The Hofmann eliminations to give **3a** and **3b** proceeded in 13 and 3% yields, respectively.

(8) J. Kenner and E. Witham, *J. Chem. Soc.*, **103**, 237 (1913).

(9) D. J. Cram and K. C. Dewhirst, *J. Am. Chem. Soc.*, **81**, 5963 (1959).

(10) The high field multiplet for the internal protons of **5** and **6** represent in fact an AA'BB'XX' system in which the XX' protons are H_d, as can be shown by double irradiation experiments. A similar analysis has been made for the tetrahydrothiacoronene reported earlier,[4] indicating the photoproduct in this case is also a single isomer rather than a mixture of isomers as previously suggested.[4]

(11) M. J. S. Dewar, R. C. Haddon, and P. J. Student, *J. Chem. Soc., Chem. Commun.*, 569 (1974).

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