Benzotriptycenes (*o*-Benzenobenzanthracenes). A Proton Magnetic Resonance Study

By **Russell Godfrey**,† School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

^{1}H N.m.r. spectra at 100 MHz are reported for five different benzotriptycenes (*o*-benzenobenzanthracenes) (II)—(VI) and three model compounds, measured in CCl_4 solution. Calculated coupling constants are given, and no transannular resonance or polarization effect between the chromophores is detectable. Experimental τ values for the cage bridgehead protons are compared to those of other reported compounds by means of both the Johnson–Bovey and McWeeny ' aromatic ring current ' models. The chromophores in (I)—(VI) are evidently under bond angle strain caused by the cage. This causes partial double bond fixation, and reduces the aromatic ring current to about half of that expected in each ring.

THE normal van der Waals distance of constrained and parallel aromatic rings is *ca.* 340 pm.[1] The consequences of constraining such π-systems at distances and geometric orientations other than the van der Waals optimum have

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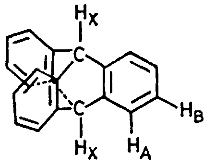
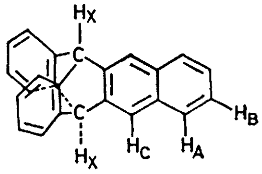
† *Present address:* Sackville School, Lewes Road, East Grinstead, Sussex RH19 3TY.

[1] J. M. Robertson, ' Organic Crystals and Molecules,' Cornell University Press, Ithaca, 1953.

been extensively studied. For example, chemical and spectroscopic methods have demonstrated transannular interaction for biphenylene,[2] the paracyclophanes,[3-5] the paracyclonaphthanes,[6,7] the phenyl substituents at the *cis*- and vicinal positions of three-[8,9] or five-membered[8,10] rings, and at the *peri*-positions of naphthalene[11] and anthracene.[12]



(I)



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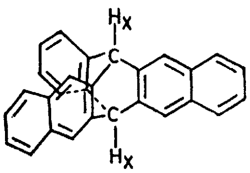

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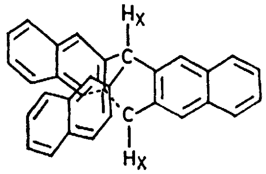

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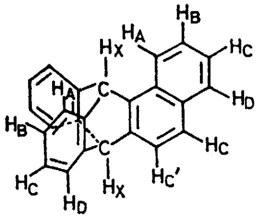
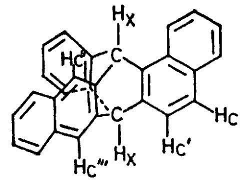


(V)



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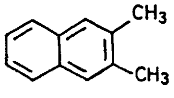
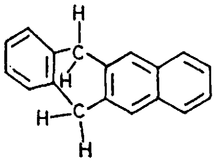
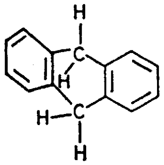


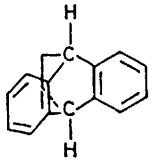
(VII)



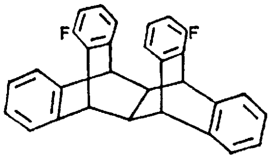
(VIII)



(IX)



(X)



(XI)

The series of molecules (I)—(IV) are of interest in part because of the symmetry of their ground states {triptycene (I) and 6,13-*o*-naphthacenodibenz[*b*,*i*]anthracene (IV), are D_{3h} and benzo[*b*]triptycene (II) and dibenzo[*b*,*i*]triptycene (III) are C_{2v}} and because they comprise planar benzene and naphthalene aromatic systems in well defined orientations to one another. For these reasons, the above series, and their isomeric analogues benzo[*a*]triptycene (V) and dibenzo[*a*,*i*]triptycene (VI) have been selected and synthesised.[13]

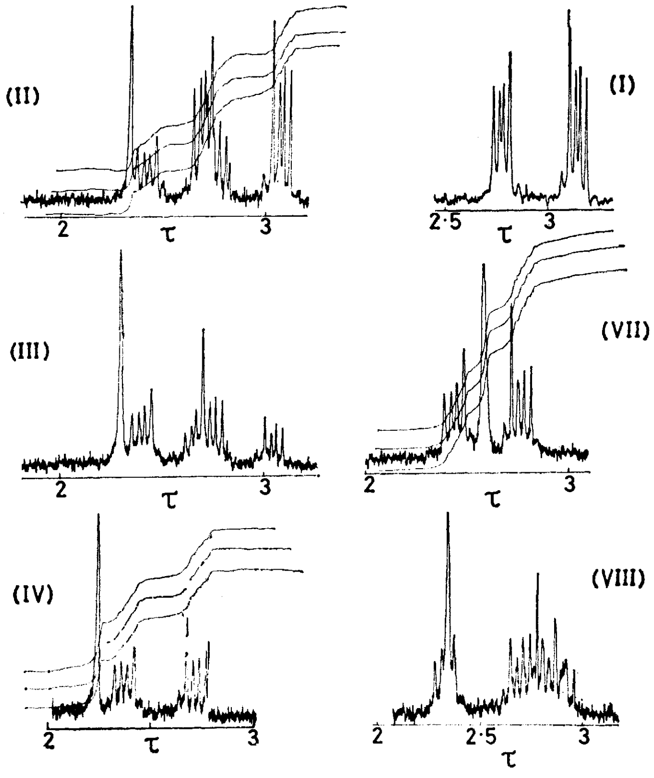


FIGURE 1 ^{1}H N.m.r. spectra of compounds (I)—(IV), (VII), and (VIII)

RESULTS AND DISCUSSION

Figure 1 presents the ^{1}H n.m.r. spectra for the aromatic protons of triptycenes (I)—(IV), along with those of 2,3-dimethylnaphthalene (VII) and 5,12-dihydrotetra-

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[2] W. Baker and J. F. W. McOmie, ' Non-benzenoid Aromatic Compounds,' ed. D. Ginsberg, Interscience, New York, 1959, ch. 2.

[3] D. J. Cram and L. A. Singer, *J. Amer. Chem. Soc.*, 1963, **85**, 1084.

[4] D. J. Cram and R. C. Helgeson, *J. Amer. Chem. Soc.*, 1966, **88**, 3515.

[5] R. Filler and F. W. Choe, *J. Amer. Chem. Soc.*, 1969, **91**, 1862.

[6] D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, 1963, **85**, 1088.

[7] H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, 1969, **91**, 2374.

[8] D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, 1961, **83**, 4838.

[9] M. H. Gianni, E. L. Stogryn, and C. M. Orlando, *J. Phys. Chem.*, 1963, **67**, 1385.

[10] D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 6132.

[11] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, 1963, **28**, 2403.

[12] S. C. Dickerman, D. De Souza, and P. Wolf, *J. Org. Chem.*, 1963, **30**, 1981.

[13] R. Godfrey, Ph.D. Thesis, University of East Anglia, 1970.

cene (VIII) as suitable model compounds. Similarly Figure 2 gives the spectra of (V) and (VI). These spectra have been scanned once at 100 MHz under similar conditions, using tetrachloromethane as solvent. Each spectrum has been duplicated and when necessary triplicated in order to improve the signal to noise ratio.

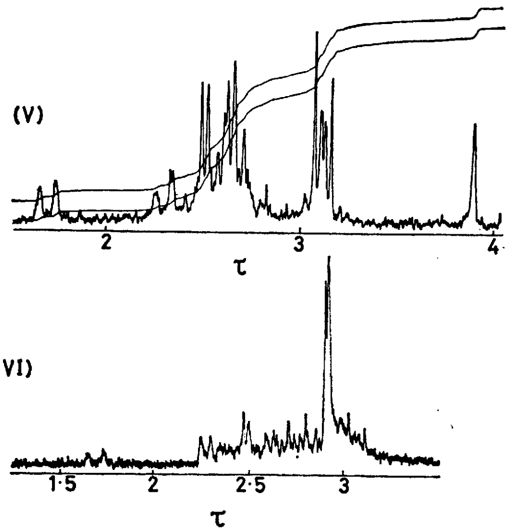

FIGURE 2 ^{1}H N.m.r. spectra of compounds (V) and (VI)

The aliphatic and bridgehead protons, H_X, always appear as sharp singlets, including those of (VIII) where the ring flip is not resolvable on the n.m.r. time scale at the probe temperature of 35 °C. Neglecting inter-ring coupling,[14-16] it can be seen from Figure 1 that the rest of the spectra should contain singlets H_C from the naphthalene chromophores, and also naphthalene $(AB)_2$ and/or benzene $(AB)_2$ spin coupled systems. Similarly, the bridgehead protons of (V) and (VI) appear as two singlets H_X and $H_{X'}$ and from Figure 2 the rest of the spectra should contain the naphthalene AB system (from protons H_C and $H_{C'}$) and also both naphthalene and benzene ABCD spin coupled systems.

The $(AB)_2$ coupling constants were calculated,[17,18] and the resulting data and chemical shifts from the spectra in Figures 1 and 2 given in Tables 1 and 2 respectively. Also added to Table 1 are data from the ^{1}H n.m.r. spectrum of 9,10-dihydroanthracene (IX) determined under similar conditions.

It has been suggested [19-22] that a transannular resonance or polarization interaction may operate in triptycene (I) itself. A comparison of compounds (I), (IX), and *o*-xylene by n.m.r.[23] has found no such detectable interaction. However a similar comparison of dibenzobicyclo[2.2.2]octadiene (X) with the ' double triptycene '

TABLE 1

^{1}H N.m.r. data for compounds (I)—(IV) and (VII)—(IX)

Compound	Aromatic $(AB)_2$ multiplets Chemical shift τ	AB/Hz	J_{AB}/Hz	J_{BB}/Hz	$J_{AB'}$/Hz	J_{AA}/Hz	H_C Chemical shift τ	H_X Chemical shift τ
(IX)	2.90 (8 H, Ph)	8.43						6.15 (4 H, s)
(I)	2.99 (12 H, Ph)	40.3	7.34	7.60	1.07	0.50		4.83 (2 H, s)
(VII)	2.60 (4 H, NAP)	32.5	8.25	6.67	1.75	0.22	2.58 (2 H, s)	7.70 (6 H, s)
(VIII)	2.51 (4 H, NAP)	37.1	8.06	6.90	1.19	0.60	2.34 (2 H, s)	6.01 (4 H, s)
(II)	2.55 (4 H, NAP)	26.5	7.15	6.14	1.85	0.37	2.33 (2 H, s)	4.65 (2 H, s)
(II)	2.93 (8 H, Ph)	32.0	6.95	7.61	0.55	0.59		
(III)	2.53 (8 H, NAP)	26.5	7.70	6.63	1.30	1.00	2.29 (4 H, s)	4.51 (2 H, s)
(III)	2.91 (4 H, Ph)	29.3	7.45	7.45	1.10	0.2		
(IV)	2.54 (12 H, NAP)	35.9	9.10	6.54	1.30	0.30	2.24 (6 H, s)	4.40 (2 H, s)

Ph = Phenyl, NAP = naphthalene.

TABLE 2

^{1}H N.m.r. data for compounds (V) and (VI)

Compound	Benzene $(AB)_2$ multiplet Chemical shift τ	AB/Hz	J_{AB}/Hz	J_{BB}/Hz	$J_{AB'}$/Hz	J_{AA}/Hz	H_C Chemical shift τ	H_X Chemical shift τ
(V)	2.98 (8 H)	31.4	7.78	8.03	0.73	0.25	1.69, 1.78 H_C (1 H ,d) 2.28, 2.37 $H_{C'}$ (1 H, d) $J_{CC'}$ 9 Hz	3.90 (1 H, s, H_X) 4.59 (H s, $H_{X'}$)
(VI)	2.91 (4 H)						1.64, 1.73 H_C (1 H, d) 2.23, 2.32 $H_{C'}$ (1 H, d) $J_{CC'}$ 9 Hz 2.24 $H_{C''}$ (1 H, s) 2.30 $H_{C'''}$ (1 H, s)	3.75 (1 H, s, H_X) 4.42 (H s, $H_{X'}$)

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[14] H. J. Bernstein, W. G. Sneider, and J. A. Pople, *J. Chem. Phys.*, 1957, **26**, 957.

[15] N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.

[16] T. H. Regan and J. B. Miller, *J. Org. Chem.*, 1967, **32**, 2789.

[17] B. Dischler and W. Maier, *Z. Naturforsch.*, 1961, **16a**, 318.

[18] T. K. Lim, A. Taurins, and M. A. Whitehead, *Canad. J. Chem.*, 1966, **44**, 1211.

[19] P. D. Bartlett and E. S. Lewis, *J. Amer. Chem. Soc.*, 1950, **72**, 1005.

[20] C. F. Wilcox, jun., *J. Chem. Phys.*, 1960, **33**, 1874.

[21] C. F. Wilcox, jun., and A. C. Graig, *J. Org. Chem.*, 1961, **26**, 2491.

[22] H. B. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1961, 1224.

[23] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, 1965, **69**, 2022.

molecule janusene (XI)[24] found that the two face rings absorbed at τ 3.40 and the other two rings at τ *ca.* 3.05. This apparently strong evidence for transannular interaction is complicated by the fact that the two face rings in (XI) are separated by only *ca.* 250 pm *i.e.* well within the van der Waals optimum distance.

All studies of this type assumes negligible energy transfer between the chromophores *via* an inductive effect along the joining saturated bonds. This has in fact been found to be the case in two independent studies,[25,26] of the reactivity of groups substituted on the triptycene bridgehead carbon atom.

The molecules in the series (I)—(IV) contain planar π systems held in well defined orientations to each other, but separated by distances greater than the van der Waals optimum. This last criterion is desirable in order to avoid physical contact of the p–π orbitals. There is however some strain [27-29] in these molecules, which was found to be constant along the series (I)—(IV) [see equation (7)].

The suggestions that the apparently anomalous chemical shift of the bridgehead H_X protons of triptycene could be attributed to an ' around the barrel ' flow of π electrons[23] can readily be discounted because the magnitude required by such an electron flow would need to be impossibly large,[30] and also more to the point, because a consideration of the symmetry of the p–π orbitals in relation to the three-fold rotation axis reveals unfavourable overlap.[31]

TABLE 3

Calculated and observed chemical shifts (with respect to benzene) of the aliphatic bridgehead protons (H_X) using the semi-empirical Johnson–Bovey method [32]

Compound	$(\Delta\sigma_{sc}^{benzene} - \Delta\sigma_{sc})$	$(\tau_{obs} - \tau_{obs}^{benzene})$	Ref.[a]
(I)	−1.875	2.10	13
(II)	−2.026	1.92	13
(III)	−2.177	1.78	13
(IV)	−2.328	1.67	13
(XII)	−0	2.58	*b*
(XIII)	−0.625	2.47	*c*
(XIV)	−1.250	2.27	*d*
(XV)	−1.401	2.09	*e*
(XVI)	−1.955	1.86	*e*
(V)			
(hindered proton H_X)	−2.345	1.17	13
(unhindered proton $H_{X'}$)	−2.000	1.86	13
(VI)			
(hindered proton H_X)	−2.496	1.02	13
(unhindered proton $H_{X'}$)	−2.151	1.69	13

[a] Using the value $\tau_{obs}^{benzene}$ 2.73 (C. W. Haigh and R. B. Mallion, *Mol. Phys.*, 1970, **18**, 740). [b] H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, 1964, **86**, 1434. [c] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1798; K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1963, 1597. [d] J.-C. Muller and J. Vergne, *Compt. rend.*, 1966, **263**, 1452. [e] B. H. Klanderman and T. R. Criswell, *J. Org. Chem.*, 1969, **34**, 3426.

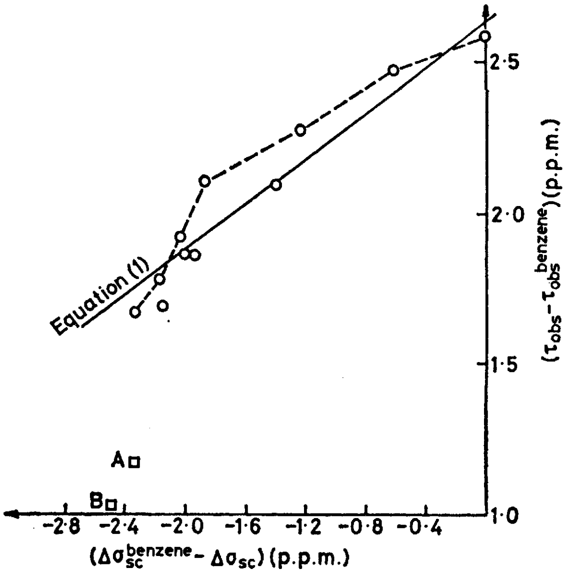
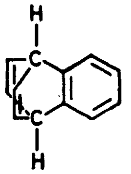
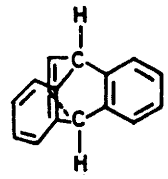


FIGURE 3 Johnson–Bovey plot [32] for the H_X bridgehead protons from Table 3

The Johnson and Bovey semi-classical diagmagnetic ring current theory [32] has been applied to the data for the aliphatic bridgehead protons (H_X) in Tables 1 and 2, for the triptycenes (I)—(VI). Because of the molecular


(XII)


(XIII)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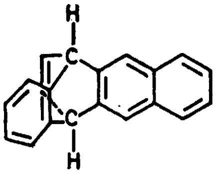
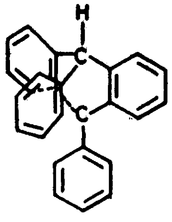

(XV)


(XVI)

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[24] S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, 1967, **89**, 1476.

[25] K. Bowden and D. C. Parkin, *Canad. J. Chem.*, 1969, **47**, 177.

[26] S. F. Nelson and E. F. Travecedo, *J. Org. Chem.*, 1969, **34**, 3651.

[27] W. Theilacker, K. Albrecht, and H. Uffman, *Chem. Ber.*, 1965, **98**, 428.

[28] M. Avram, G. D. Mateescu, and I. I. Pogani, *Rev. Chim. Acad. Rep. Populaire Roumaine*, 1962, **7**, 665 (*Chem. Abs.*, 1962, **61**, 4183d).

[29] K. Anzenhofer and E. de Boer, *Z. Krist.*, 1970, **131**, 103.

[30] K. G. Kidd, G. Kotowycz, and T. Schaefer, *Canad. J. Chem.*, 1967, **45**, 2155.

[31] B. H. Klanderman and W. C. Perkins, *J. Org. Chem.*, 1969, **34**, 630.

[32] (*a*) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; (*b*) F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, London and New York, 1969.

symmetry, these H_X protons should be in the plane of all three aromatic π systems.

The results are given in Table 3 and Figure 3, and included are data for the aliphatic bridgehead protons of some similar model compounds, *viz.* bicyclo[2.2.2]octatriene (barrelene) (XII), 1,4-ethenonaphthalene (XIII), 9,10-ethenoanthracene (XIV), 5,12-ethenonaphthacene (XV), and 9-phenyltriptycene (XVI).

The two points marked as A and B on Figure 3 represent the over-crowded aliphatic bridgehead protons (H_X) of the unsymmetrical triptycenes (V) and (VI). These protons are within the van der Waals radius of the H_A protons on the adjacent naphthalene π-system, and the molecular symmetry is hence locally distorted by bond strain.

The remaining eleven points in Figure 3 fit the regression line (1). The correlation coefficient is 0.855

$$(\tau_{obs} - \tau_{obs}^{benzene}) = 0.38(\Delta\sigma_{sc}^{benzene} - \Delta\sigma_{sc}) + 2.63 \qquad (1)$$

and the standard error in $(\tau_{obs} - \tau_{obs}^{benzene})$ is 0.21 p.p.m. $\Delta\sigma_{sc}$ is the calculated shielding of the proton by the local magnetic field of the π-system using the semiclassical Johnson–Bovey method.

If one considers the points on Figure 3 represented by compounds (XII), (XIII), (XIV), (I), (II), (III), and (IV) taken in sequence (represented by the dashed line in this Figure) then the distribution about the regression line is not random, but instead reveals the bridgehead proton of triptycene as resonating at too high a field. The regular perturbation difference between benzene and naphthalene chromophores clearly leads to a poor correlation.

A completely quantum mechanical approach to the ring current effect in planar condensed, benzenoid hydrocarbons, has been developed by McWeeny [33] by applying molecular orbital theory to the evaluation of magnetic shielding constants. The secondary field H' at a proton in the plane of the ring is given by equation (2) where β

$$H' = 2\beta\left(\frac{2\pi e}{hc}\right)^2\frac{S^2H}{a^3}\left\{\sum_i J_i[-K(r_i)]\right\} = \text{constant} \times \sum_i J_i[-K(r_i)] \qquad (2)$$

is the normal Hückel resonance integral, S and a are the area and C–C bond length respectively of a benzene ring, H the applied external magnetic field, e, h, and c are standard constants, and r_i is the distance of the proton from the ring centre in units of the C–C bond length. J_i is the current density factor and measures the moment of the induced magnetic shell, which corresponds therefore to the ring current in the Johnson–Bovey model,[32] but differs from the latter in taking into account bond orders and polarizabilities. The value of J_i is therefore dependant upon the particular ring under consideration. $-K(r_i)$ is a purely geometric factor.

In the case of benzene, equation (2) reduces to (3) whilst in the case of naphthalene equation (2) reduces to (4). In order to take account of averaging of the

$$H' = \text{constant} \times -K(r)/9 \qquad (3)$$

$$H' = \text{constant} \times [(-0.1214) - K(r) + (-0.1214) - K(r_2)] \qquad (4)$$

secondary field over all molecular orientations,[33] it is necessary to divide the right hand side of equation (2) by 3, however, on taking the ratio $(H' : H'_{benzene})$, the so called ' sigma ratio ', all constant terms disappear.

In the final McWeeny equation for the field, the terms σ_1 and σ_2 are defined as in equation (5), where P_{ij} is the

$$\sigma_1 = \sum_{ij} P_{ij}s_{ij}^2k_{ij} \qquad (5a)$$

$$\sigma_2 = \sum_{ij}\sum_{kl}\beta\pi_{(ij)(kl)}s_{ij}s_{kl}\left(\frac{k_{ij}+k_{kl}}{2}\right) \qquad (5b)$$

bond order between atoms i and j in the ring, $S_{ij} = s_{ij}S$ where S_{ij} is the area of the triangle formed between the proton under study and the C–C bond, i, j, $k_{ij} = 1/r_i^3 + 1/r_j^3$, and $\pi_{(ij)(kl)}$ is the mutual bond polarizability. Hence, equation (6) follows where s_{12} $(= s_{61}) =$

$$9(\sigma_1 + \sigma_2) = 4[s_1^2k_1 + s_2^2k_2 + s_3^2k_3 + s_1s_2(k_1 + k_2) + s_2s_3(k_2 + k_3) + s_1s_3(k_1 + k_3)] = K(r) \qquad (6)$$

s_1 and k_{12} $(= k_{61}) = k_1$, *etc.* $K(r)$ in equation (6) represents the geometric factor for any planar condensed benzenoid ring. For benzene and naphthalene π-systems, it is necessary to substitute for $K(r)$ from equation (6) into equations (3) and (4) respectively to determine the secondary field H'. The sigma ratios $(H' : H'_{benzene})$ have been calculated for the aliphatic bridgehead protons (H_X) of the triptycenes and *model* compounds in Tables 1—3 and the results presented in Table 4 and Figure 4.

TABLE 4

Calculated and observed chemical shifts of the aliphatic bridgehead protons (H_X) using the McWeeny method [33]

Compound	$\sum_i J_i[-K(r_i)]$	$H' : H'_{benzene}$	τ_{obs} [a]	Ref.
Benzene	0.1439	1	2.73	*d*
(I)	0.2023	1.406	4.83	13
(II)	0.2444	1.699	4.65	13
(III)	0.2866	1.992	4.51	13
(IV)	0.3287	2.285	4.40	13
(XII)	0	0	5.31 [b]	*e*
(XIII)	0.0674	0.469	5.2	*f*
(XIV)	0.1349	0.937	5.0 [b]	*g*
(XV)	0.1770	1.230	4.82 [c]	*h*
(XVI)	0.2289	1.591	4.59 [c]	*h*
(V)				
(hindered proton H_X)	0.2710	1.883	3.90	13
(unhindered proton $H_{X'}$)	0.2420	1.682	4.59	13
(VI)				
(hindered proton H_X)	0.3131	2.176	3.75	13
(unhindered proton $H_{X'}$)	0.2841	1.975	4.42	13

[a] All τ_{obs} values obtained in CCl_4 solvent, unless otherwise stated. [b] Solvent not stated. [c] Solvent $CDCl_3$. [d] Note *a*, Table 3. [e] Note *b*, Table 3. [f] Note *c*, Table 3. [g] Note *d*, Table 3. [h] Note *e*, Table 3.

The data for the 11 points in Figure 4 fit the regression

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[33] R. McWeeny, *Mol. Phys.*, 1958, **1**, 311.

line (7). The correlation coefficient is −0.985 and the standard error in τ_{obs} is 0.04 p.p.m. All the required

$$\tau_{obs} = -0.45(H' : H'_{benzene}) + 5.36 \qquad (7)$$

$K(r)$ factors for the sigma ratios were calculated directly from the McWeeny equation (6) by a program written for the University of London CDC 6600 computer.

Equation (2) was also used [34] to analyse the n.m.r. data from 66 non-sterically hindered planar aromatic protons from 16 compounds in CCl_4 solution. The published regression line is unfortunately incorrect as it makes use of the incorrect expansion in *r* from ref. 33 (see Appendix). However, if the sigma values from ref. 34 are recalculated, then the corrected regression line is (8). Equations

$$\tau_{obs} = -0.82(H' : H'_{benzene}) + 3.6 \qquad (8)$$

(7) and (8) are directly comparable and show important differences in both slope and intercept. The effect of adding fused aromatic rings to the barrelene cage [compound (XII)] is to produce a downfield chemical shift on the bridgehead protons, H_X. However, the magnitude of this shift is almost half that expected, *i.e.* these protons are being shielded by some mechanism from the deshielding expected from the aromatic rings.

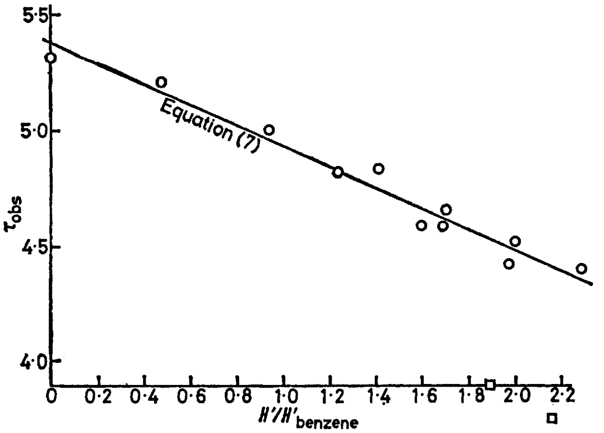
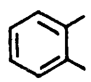


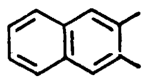
FIGURE 4 Plot of τ_{obs} against $H' : H'_{benzene}$ for the H_X bridgehead protons from Table 4

Conclusions.—Figure 4 is a more linear graph than Figure 3, and has a much higher correlation coefficient. This (1) verifies the practical value of the completely quantum mechanical approach,[33] compared to the semi-classical diamagnetic ring current approach [32] and (2) shows that the strain in the barrelene cage is approximately constant for the series of molecules in Table 4 and Figure 4.

This strain factor in the cage (analogous to the Mills–Nixon effect [35]) gives rise to some distortion of bond angles and a preferential Kekulé structure of (A) or (B), *i.e.* partial single-bond fixation between the cage and the chromophore. The result is a partial bond fixation throughout the whole chromophore and a concurrent decrease of the aromatic ring current. This reduces the magnitude of the J_i terms in equation (2) and also effects the P_{ij} and $\pi_{(ij)(kl)}$ terms in equation (5).



(A)



(B)

This interpretation agrees with the i.r.[28] and *X*-ray crystallographic [29] evidence, as well as the kinetic nitration study [13] of these compounds.

A comparison of equations (7) and (8) would indicate that in the present work, the aromatic ring current term J_i, in equation (2), has been reduced by a factor of *ca.* 2 by the bond angle strain in the cage.

EXPERIMENTAL

Compounds (I), (VII), and (IX) were obtained from Koch–Light Ltd., and each was twice recrystallised from spectroscopic grade cyclohexane before use. Pure samples of compounds (VIII),[36] (V), and (VI) [37] were synthesised by Dr. J. T. Gleghorn. Pure samples of compounds (II) and (IV) were synthesised by the methods of Regan *et al.*[16] and Wittig *et al.*[38] respectively. The mass spectrum of (IV) has *m/e* 404 (M^+), *m*/2*e* 202 (M^+), and *m*/3*e* 135 (M^+). [A similar phenomenon has been observed for compound (I).[39]]

Dibenzo[b,i]*triptycene* (III).—Refluxing xylene (40 cm^3; AnalaR; B.D.H. Ltd.) was slowly purged with dry nitrogen gas. Tetracene (0.3 g) was added, and when fully dissolved this was followed by 1,4-epoxy-1,4-dihydronaphthalene (1.3 g).[40] After 16 h xylene was removed on a rotary evaporator to yield a light brown Diels–Alder adduct. This was not characterised, but was hydrolysed directly to (III) by boiling in acetic acid (5 cm^3) and concentrated hydrochloric acid (0.5 cm^3). The product (350 mg) was obtained by adding concentrated hydrochloric acid to the hot solution, cooling, filtering, washing with water, and drying. Purification by t.l.c. [silica gel; light petroleum (b.p. 60—80°); R_F 0.1] and crystallisation from cyclohexane gave a granular, crystalline *solid* (64 mg), m.p. 273 °C (Found: C, 94.75; H, 5.3. $C_{28}H_{18}$ requires C, 94.9; H, 5.1%); *m/e* 354 (M^+), *m*/2*e* 177 (M^+), *m*/3*e* 118 (M^+);[36] $\lambda_{max.}$ (C_6H_{12}; Cary 14; 22 °C) 324 (ε 4 975), 321 (1 681), 316 (1 412), 310 (2 360), 302 (1 267), 289 (8 420), 278 (18 717), 269 (24 630), 250 (101 637), 243 (63 529), and 229 nm (112 876); $\nu_{max.}$ (Perkin-Elmer 125; CCl_4) 3 054, 3 010, 2 955, 1 499, 1 477, 1 458, 1 449, 1 438, 1 266, 1 142, 1 018, 948, 886, 875, 627, 581, and 559 cm^{-1}.

APPENDIX

An alternative to computing the secondary field *H'* at a proton in the plane of a benzenoid hydrocarbon by means of equation (6), is to expand equation (6) in terms of *r* by substituting for s_1, s_2, *etc.* and k_1, k_2, *etc.* The resulting expansion is very convenient for calculating $K(r)$. How-

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[34] C. W. Haigh and R. B. Mallion, *Mol. Phys.*, 1970, **18**, 751.

[35] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 1930, 2510.

[36] C. Marshalk, *Bull. Soc. chim. France*, 1937, 1381, 1547.

[37] C. D. Hurd and L. H. Juel, *J. Amer. Chem. Soc.*, 1955, **77**, 601.

[38] G. Wittig, H. Harle, E. Krauss, and K. Niethammer, *Chem. Ber.*, 1960, **93**, 951.

[39] M. I. Bruce, *Chem. Comm.*, 1967, 593.

[40] L. F. Fieser and M. J. Haddadin, *Canad. J. Chem.*, 1965, **43**, 1599.

ever the expansion in r is a long algebraic exercise, and unfortunately the result published in ref. 37 is incorrect.

Since this latter result has been quoted [41] and .used elsewhere,[34,42] the correct expansion will be given. The required substitutions in equation (6) are:

$$s_1^2 = \frac{1}{36}(r^2 - 2r + 1),\ k_1 = \frac{1}{r_1^3} + \frac{1}{r_2^3},\ r_1 = r - 1$$

$$s_2^2 = \frac{1}{36} \qquad ,\ k_2 = \frac{1}{r_2^3} + \frac{1}{r_3^3},\ r_2 = \sqrt{r^2 - r + 1}$$

$$s_3^2 = \frac{1}{36}(r^2 + 2r + 1),\ k_3 = \frac{1}{r_3^3} + \frac{1}{r_4^3},\ r_3 = \sqrt{r^2 + r + 1}$$

$$s_1s_2 = \frac{1}{36}(r - 1)$$

$$s_2s_3 = \frac{1}{36}(r + 1)$$

$$s_1s_3 = \frac{1}{36}(r^2 - 1)$$

Thus the expansion for $K(r)$ up to and including the terms in $1/r^8$ (*i.e.* the first eleven terms) is given by equation (9). As a comparison of the approximation of equation (9) to the exact equation (6), for r 2, equation (9) yields $K(r)$ 0.945 and equation (6) yields $K(r)$ 0.962; similarly for r 5,

$$K(r) = 9(\sigma_1 + \sigma_2)$$

$$= \frac{1}{r^3}\left[\frac{8r^2}{9} = \frac{8r}{9} + \frac{19}{18} + \frac{7}{12r} + \frac{193}{96r^2} - \frac{5}{192r^2} + \frac{8\,639}{2\,304r^4} + \frac{13\,825}{4608r^5} + \frac{260\,131}{73\,728r^6} + \frac{275\,193}{147\,456r^7} + \frac{273\,938\,1}{589\,824r^8} \cdots\right] \quad (9)$$

equation (9) yields $K(r)$ 0.223 37 and equation (6) yields $K(r)$ 0.223 98. At large values of r, equation (9) becomes an increasingly better approximation to equation (6).

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[7/1329 *Received*, 25*th July*, 1977]

[41] D. E. O'Reilly, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 1.

[42] J. D. Memory, G. W. Parker, and J. C. Halsey, *J. Chem. Phys.*, 1966, **45**, 3567.