chloroform solutions unless otherwise specified. Melting points were obtained on a Uni-Melt Hoover capillary melting point apparatus. Mass spectra were obtained on a Bendix Model 12-100 time-of-flight spectrometer.

1-Methylsulfinylundecan-2-one.—A slurry consisting of 8.6 g of sodium hydride (55% mineral oil suspension; 4.8 g, 0.20 mole, of active sodium hydride) in 300 ml of dried dimethyl sulfoxide was heated at 65° under a nitrogen sweep for 2 hr until gas evolution ceased. The solution was cooled to 20° and maintained at that temperature by an ice-water bath while 18.6 g (0.10 mole) of methyl decanoate was added dropwise. The solution was stirred at room temperature for 30 min, then poured onto 300 g of ice and water containing 52.5 g (0.20 mole) of ammonium chloride. The resultant slurry was extracted with three 500-ml portions of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and the chloroform removed on a rotary evaporator under aspirator vacuum. Residual dimethyl sulfoxide was removed using a vacuum pump. Yield of crude 1-methylsulfinylundecan-2-one was 20.6 g (89%), mp 68–75°. Recrystallization from 300 ml of 60–90° ligroin containing 10 ml of ethanol gave 14.4 g of white crystals, mp 77–78°.

Recrystallized material (0.1 g, 0.00043 mole) was dissolved in 2 ml of ethanol and 8.5 ml (0.00129 mole) of 2,4-dinitrophenylhydrazine reagent solution[12a] was added. The solution was warmed briefly on a steam bath and allowed to cool. The orange precipitate was filtered, washed with 25 ml of ethanol, and air dried, giving 0.16 g of bishydrazone, mp 171°. *Anal.* Calcd for $C_{23}H_{28}N_8O_8$: C, 50,8; H, 4.8; N, 20.7. Found: C, 50.6; H, 4.8; N, 20.7.

Recrystallized sulfoxide (0.1 g, 0.00043 mole) was dissolved in 3 ml of ethanol and about 3 drops of water was added. A 0.142-g (0.00129 mole) quantity of semicarbazide hydrochloride was added and the suspension warmed to reflux. The clear solution was heated at reflux 30 min, then allowed to cool. The precipitate was filtered and washed with 10 ml of water followed by 25 ml of ethanol: yield 0.12 g; mp 230–230.5°. *Anal.* Calcd for $C_{13}H_{26}N_6O_2$: C, 52.5; H, 8.7; O, 10.7. Found: C, 52.6; H, 9.7; O, 11.0.

1,1-Dimethoxyundecan-2-one.—1-Methylsulfinylundecan-2-one (11.6 g, 0.05 mole) was dissolved in 100 ml of methanol containing 8.0 g (0.031 mole) of iodine. The solution was refluxed for 90 min, then allowed to cool. Most of the methanol was removed at room temperature on a rotary evaporator under aspirator vacuum. The dark residual oil was taken up in 50 ml of chloroform and extracted twice with 50-ml portions of saturated sodium thiosulfate solution. The very light yellow chloroform solution was dried with anhydrous magnesium sulfate and solvent removed under vacuum. The residual oil (11.8 g) was subjected to simple distillation through a Vigreux head giving 9.8 g, 85% yield, of a colorless liquid boiling at 85° (0.2 mm). Dimethyl disulfide was identified by its gas chromatographic retention time as the principal component of the lower boiling fraction. Gas chromatography on a 5-ft, $^3/_8$-in. Ucon Polar column showed >95% purity for the keto acetal. Identification by spectral means is described in the Results.

1,1-Dimethoxyundecan-2-one (*in Situ* **Rearrangement**).—Methyl decanoate (18.6 g, 0.10 mole) was added dropwise to a solution of 0.20 mole of methylsulfinyl carbanion in 400 ml of dimethyl sulfoxide (prepared as described above) kept at 15–20° by an ice-water bath. The mixture was stirred at room temperature for 0.5 hr; 400 ml of methanol, 9.8 g (0.10 mole) of sulfuric acid, and 14.0 g (0.055 mole) of iodine were added and the solution was warmed to 60° for 1 hr. The solution was cooled and most of the methanol removed under aspirator vacuum. Sodium thiosulfate, 50 g (0.32 mole) dissolved in 500 ml of water, was added and the resulting cloudy solution extracted with three 300-ml portions of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and the solvent removed under aspirator vacuum. The residual oil was distilled through a simple Vigreux head. That fraction boiling at 85–90° (0.2 mm) was collected and determined by gas chromatography on a 5-ft, $^3/_8$-in. Ucon Polar column to be >98%, 1,1-dimethoxyundecan-2-one: yield 14.5 g (63%) based on methyl decanoate.

Registry No.—**2**, 13133-44-3; **3**, 13133-45-4; **4**, 13133-46-5; **5**, 13133-47-6; **6**, 2813-22-1; **7**, 13133-49-8; **7** (di-DNP), 13133-50-1; **7** (dioxime), 13133-51-2; **7** (disemicarbazone, 13133-52-3; **8**, 13133-53-4; **8** (di-DNP), 13133-54-5; **8** (dioxime), 13133-55-6; **9**, 13133-56-7; **9** (di-DNP), 13133-57-8; **10** (di-DNP), 13133-58-9; **11**, 6956-56-5; **11** (di-DNP), 4881-22-5.

Acknowledgment.—The author wishes to thank Drs. W. I. Lyness, W. W. Bannister, and T. J. Flautt for valuable suggestions and discussions during the course of this work and to acknowledge the technical assistance of R. R. Cvach and J. F. Ward.

Nuclear Magnetic Resonance Spectra of Some Substituted Benzotriptycenes. The Effect of Steric Compression

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The chemical shifts of protons and/or methyl substituents in 5,12-*o*-benzeno-5,12-dihydronaphthacenes (benzotriptycenes) substituted in the 5, 6, 11, and 12 positions with methyl and phenyl groups were determined. The data are interpreted in terms of a steric compression shift by both methyl and phenyl.

The concept of a local magnetic field generated by the interaction of an external magnetic field and the system of π electrons in an aromatic ring has proved very useful in explaining many otherwise anomalous chemical shifts.[1] Some cases exist, however, where the ring current theory fails in even a qualitative sense. For example, the discrepancies between the observed and calculated chemical shifts in the case of 1,4-dialkyl-2,3,9-triphenylanthracenes are approximately 1.5 ppm.[2]

Wilcox and Roberts[3] observed that the bridgehead protons in 2,5-diphenyltriptycene resonate at *lower* field (by 0.3 ppm) than those in triptycene, even though the angle of twist of the phenyl groups was estimated to be such that the ring current theory predicts an *upfield* shift of *ca.* 0.5 ppm. They ascribe this anomaly to the intervention of a "steric" effect previously proposed by Reid[4] and described in more detail by others.[5] An example of this steric effect of classic proportions

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[1] (a) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); **80**, 6697 (1958). (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). (c) A review of ring current anisotropy effects on protons held above the plane of the aromatic ring appears in H. A. P. DeJongh and H. Wynberg, *Tetrahedron*, **21**, 515 (1965).

[2] T. H. Regan and J. B. Miller, *J. Org. Chem.*, **32**, 592 (1967).

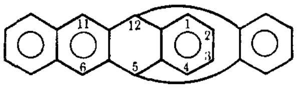
[3] C. F. Wilcox, Jr., and F. D. Roberts, *J. Org. Chem.*, **30**, 1959 (1965).

[4] C. Reid, *J. Am. Chem. Soc.*, **78**, 3225 (1956); *J. Mol. Spectry.*, **1**, 18 (1957).

[5] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963); A. A. Bothner-By, *J. Mol. Spectry.*, **5**, 52 (1960).

TABLE I

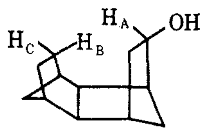
NMR DATA FOR PHENYL- AND METHYL-SUBSTITUTED 5,12-*o*-BENZENO-5,12-DIHYDRONAPHTHACENES



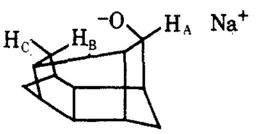
Compd	Substituent at C_5	Substituent at C_6	Substituent at C_{11}	Substituent at C_{12}	δ for substituent at C_5	δ for substituent at C_6	δ for substituent at C_{11}	δ for substituent at C_{12}	σ[a] for substituent at C_5	σ[a] for substituent at C_6	σ[a] for substituent at C_{11}	σ[a] for substituent at C_{12}
3	H	H	H	H	5.48	7.73	7.73	5.48	...	...	...	...
4	H	Ph	H	H	5.33	...	7.97	5.51	+0.18	...	...	...
5	H	CH_3	H	H	5.83	2.77	7.62	5.45	−0.38	...	...	...
6	H	CH_3	CH_3	H	5.84	2.73	2.73	5.84	−0.36	...	...	−0.36
7	CH_3	H	H	CH_3	2.41	7.60	7.60	2.41	...	+0.13	+0.13	...
8	CH_3	Ph	H	CH_3	1.80	...	7.72	2.49	+0.69	...	+0.25	...
9	CH_3	CH_3	H	CH_3	2.76	2.47	...	2.90	−0.35	−0.17	...	...
10	CH_3	CH_3	CH_3	H	2.75	2.80	2.88	5.92	−0.34	−0.15	...	−0.47

[a] The difference between the chemical shift of the specified group and the chemical shift of the analogous group in the appropriate reference compound. A positive value signifies a shift to higher field.

appears in the case of the *endo–endo* fused ring compounds such as **1**,[6] in which H_A is shifted by *ca.* 1 ppm to lower field compared to the analogous proton in the *endo–exo* isomer. For the O-inside half-cage compound **2**, H_B is shifted to lower field to the extent of 4 ppm. These constitute unequivocal examples of chemical shifts owing to steric compression with the consequent alteration of electron densities. Many examples of small shifts ascribed to van der Waals interactions appear in the literature.[7]

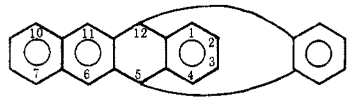


1



2

In the experiments of Wilcox and Roberts,[3] there exists some uncertainty about the twist angle of the phenyl groups in 2,5-diphenyltriptycene, since this was estimated from ultraviolet spectra, and the results of Jaffé and Chalvet[8] cast some doubt on this technique. This uncertainty can be eliminated by working with a system such as 5,12-*o*-benzeno-5,12-dihydronaphthacene (**3**, benzotriptycene), where the steric interaction between a phenyl in the 6 position and the hydrogens at the 5 and 7 positions is severe enough to require that the pendant phenyl be turned perpendicular to the plane of the naphthalene moiety.



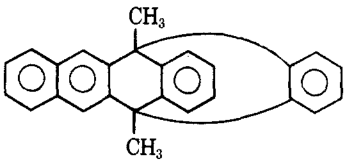
3

Results

The chemical shift of the bridgehead protons in 5,12-*o*-benzeno-5,12-dihydronaphthacene (**3**) is 5.48 ppm; that for the analogous protons in triptycene itself is 5.36 ppm, the difference representing the influence of the additional ring current. In 6-phenyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**4**), two bridgehead proton signals are observed (Table I). The one at 5.51 ppm is assigned to the C_{12} H (not adjacent to phenyl), since this proton should be affected only by the minor inductive perturbation of the naphthalene ring system by the nonconjugated phenyl group. The C_5 H resonates at 5.33 ppm; its signal has been shifted to higher field by 0.18 ppm.[9]

Replacement of phenyl by methyl to give 6-methyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**5**) reduces the anisotropy effect to a minimum and at the same time retains a comparable steric interaction between the bridgehead proton and the adjacent methyl. The two bridgehead proton signals in **5** fall at 5.45 ppm, assigned to the C_{12} H and at 5.83 ppm, assigned to the C_5 H. In compound **6**, 6,11-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene, the two equivalent bridgehead protons fall at 5.84 ppm. Thus an appreciable low-field shift is observed (0.38 ppm) owing to the interaction of methyl and hydrogen. The same phenomenon exists in triptycene itself. The 9,10 protons in 2,5-diphenyltriptycene fall at 5.64 ppm,[3] which is a shift to lower field of *ca.* 0.3 ppm compared to triptycene. The analogous protons in 2,5-dimethyltriptycene resonate at 5.62 ppm, a paramagnetic shift comparable in magnitude.

In an attempt to increase the degree of steric interaction, we studied an analogous set of compounds having methyl instead of hydrogen at the bridgehead position. 5,12-Dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**7**) has its methyl absorption at 2.41 ppm. In the spectrum of 6-phenyl-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**8**), the two methyl resonances fall at 2.49 ppm, assigned to the C_{12} CH_3, and at 1.80 ppm, assigned to the C_5 CH_3, the shift to higher field of the methyl adjacent to phenyl being 0.69 ppm.



7

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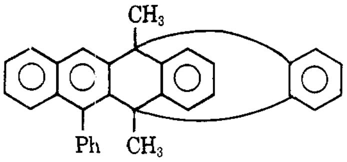
[6] S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

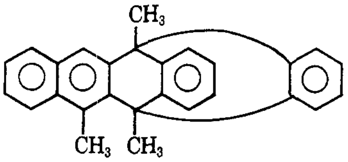
[7] See N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, for some representative samples.

[8] H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

[9] This occurs if the $C_{12}H$ of the same molecule is assumed as a reference point, introducing some uncertainty into the value cited, which, however, must be of the same order as the shift observed in the $C_{12}H$ signal on introduction of phenyl at C_6, *i.e.*, *ca.* 0.03 ppm.

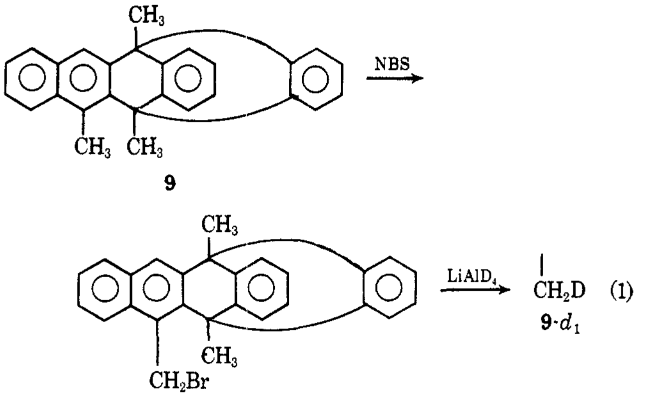


8



9

Replacing the phenyl group in **8** by methyl gives 5,6,12-trimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**9**). The methyl resonances in **9** fall at 2.47 ppm, assigned to the C_{12} CH_3, 2.76 ppm, assigned to the C_5 CH_3, and 2.90 ppm, assigned to the C_6CH_3. The C_6 CH_3 was assigned initially by reference to compound **6** in which the analogous methyls resonate at 2.73 ppm and since the C_6 CH_3 is expected to be shifted to lower field by the bridgehead methyl (at C_5), the signal at 2.90 ppm is the only one which qualifies. This assignment was made unequivocal by the labeling experiment outlined in eq 1. The resultant monodeuterio compound (**9**-d_1) has a spectrum in which the signal at 2.90 is reduced by one-third in intensity with respect to the remaining two methyl signals and appears as a 1:1:1 triplet with the center peak at 2.90 ppm and J_{H-D} = 1.1 cps. Thus the bridgehead methyl experiences a shift to lower field of 0.35 ppm[10] when an adjacent hydrogen is replaced by methyl; the aromatic methyl (at C_6) experiences a downfield shift of only 0.17 ppm.



The analogous shifts were also measured in 5,6,11-trimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**10**), the compound with one bridgehead and two aromatic methyl groups. The three methyl resonances occur at 2.75 ppm (C_5 CH_3), 2.80 ppm (C_{11} CH_3), and 2.88 ppm (C_6 CH_3). The bridgehead methyl (C_5 CH_3) was assigned by analogy with compound **9**; the two aromatic methyls were distinguished on the basis that the one showing a shift to lower field (compared to the analogous methyls in compounds **5** and **6**, Table I) is the one in apposition to the bridgehead methyl. Thus the bridgehead methyl is shifted to lower field by 0.34 ppm, whereas the aromatic methyl (C_6 CH_3) is shifted to lower field by only 0.15 ppm. The bridgehead proton (C_{12} H) is shifted to lower field by 0.47 ppm.

This nonmutuality of the interaction is strikingly demonstrated by the following data. The nonspin-coupled aromatic protons of compounds **3** (C_6 and C_{11} H) and **7** (C_6 and C_{11} H) can be easily seen as sharp singlets above the complex absorption of the remaining aromatic protons and are recorded in Table I. By comparing compounds **3** and **7**, the bridgehead methyl (C_5 CH_3) caused the adjacent *peri* aromatic proton (C_6 H) to shift 0.13 ppm to *higher* field. By comparing compounds **3** and **6**, the aromatic methyl (C_6 CH_3) caused a shift of the bridgehead proton (C_5 H) to *lower* field by 0.36 ppm.

Discussion

The structure of the phenyl-substituted benzotriptycenes is such that the bridgehead substituent lies in the shielding zone of the *peri*-phenyl. The tables of Johnson and Bovey[1b,11] were used to calculate the upfield shift owing to ring current anisotropy expected for the bridgehead substituent. The model used assumes that (1) all bond angles and distances are normal,[12] (2) that the plane of the *peri*-phenyl is normal to the plane of the naphthalene moiety, and (3) that the methyl groups are freely rotating.

A twist angle of the *peri*-phenyl in 2,5-diphenyltriptycene of 60° is consistent with both the ultraviolet spectrum and considerations of van der Waals radii.[3] However, the work of Jaffé and Chalvet[8] suggests that the ultraviolet data tend to underestimate the twist angle since some conjugation, as determined by ultraviolet shifts, exists even in molecules where the twist angle is thought to be 90°. Santhanam and Bard[13] estimate from electrochemical data that the *peri*-phenyls of 9,10-diphenylanthracene are twisted 68° out of the anthracene plane. The benzotriptycenes examined here are considerably more sterically crowded than the examples cited; assumption 2 is made on this basis. Assumption 3 is based on the observation that there is no change in the peak widths of the bridgehead methyl when the hydrogen *peri* to it is replaced by phenyl or methyl.[14]

The use of the Johnson–Bovey tables to calculate ring current shifts has been the subject of criticism[15] on the grounds that it overestimates the shifts owing to ring current anisotropy. In some cases, particularly those where polycyclic aromatics require an allocation of current densities to several rings, the error is very large.[15a] For simple phenyl systems, as much as 30% of the calculated shift may be due to factors other than ring current anisotropy,[16] but the model gives a reason-

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[10] This shift is based on the methyls of compound **7** as a reference point; using the $C_{12}CH_3$ of compound **9** gives a value of 0.29 ppm.

[11] We thank the Minnesota Mining and Manufacturing Co. for a copy of this table.

[12] "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

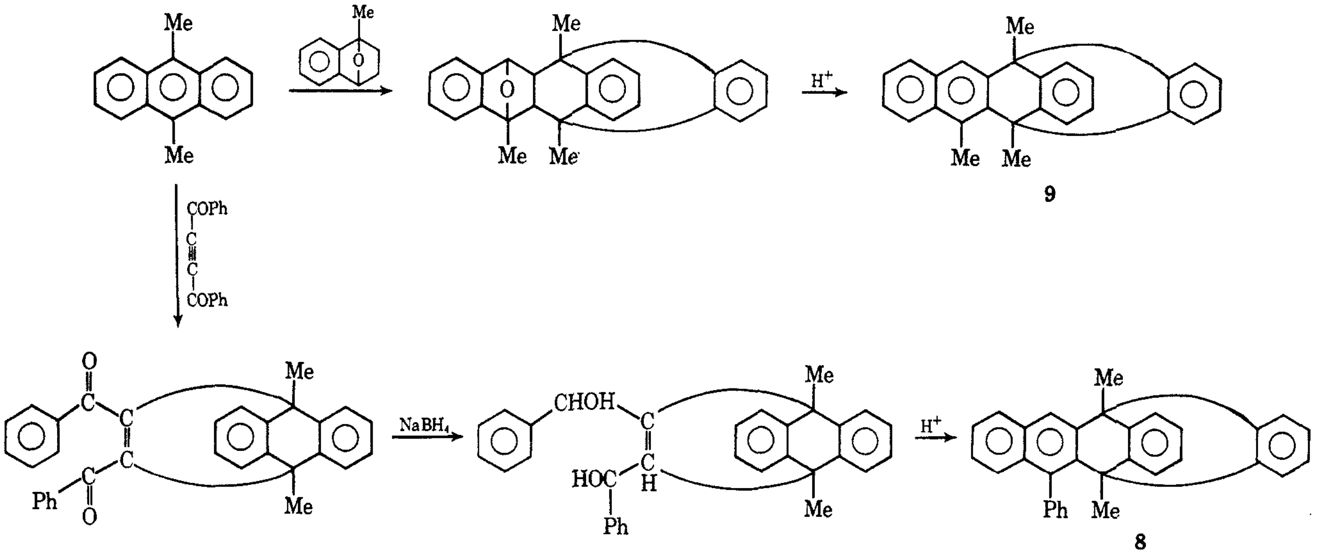
[13] K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

[14] The peak widths of the bridgehead methyls are larger than those of the aromatic methyls in all cases observed here, but this width is independent of the nature of the *peri* substituent.

[15] (a) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962); (b) B. P. Dailey, *ibid.*, **41**, 2304 (1964); (c) J. A. Pople, *ibid.*, **41**, 2559 (1964); (d) A. F. Ferguson and J. A. Pople, *ibid.*, **42**, 1560 (1965).

[16] A. A. Bothner-By and J. A. Pople in "Advances in Physical Chemistry," H. Eyring, Ed., Annual Reviews, Inc., Palo Alto, Calif., 1965, p 64; R. J. Abraham and W. A. Thomas, *J. Chem. Soc., Sect. B*, 127 (1966).

SCHEME I



able order-of-magnitude estimate of the shift expected. Quantitative comparisons showing discrepancies of a few tenths parts per million would be ambiguous, but discrepancies of the order of 1–2 ppm must be accounted for on grounds other than failure of the model.

The discrepancies between the calculated and observed shifts for 6-phenyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (1) and 6-phenyl-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**8**) are 1.8 and 2.0 ppm, respectively. While the shifts of the proton and the methyl are in the direction predicted by ring current anisotropy, the magnitude of the discrepancy argues for the intervention of other effects, the most obvious of which is steric compression.

In an attempt to get a qualitative estimate of the magnitude of this effect, the phenyl was replaced by methyl. There is, of course, no direct comparison between methyl and phenyl with respect to steric bulk, but the complete lack of ring current in methyl permits at least a rough assessment of the steric shift.

The shift to lower field of a bridgehead proton or methyl which occurs when *peri*-hydrogen is replaced by methyl is 0.34–0.47 ppm. An estimate of the extent to which the shift of the C_5 H in **5** could be due to C–CH_3 anisotropy was made using the equation of McConnell[17] and the C–CH_3 bond anisotropy of Zurcher.[18] The resultant value of *ca.* 0.03 ppm to higher field is admittedly based on a series of approximations, but it does suggest that the contribution of this factor is very small, as expected. Therefore we attribute these shifts to the effect of steric compression with the consequent alteration of electron densities around the nuclei in question.[5] The operation of a similar effect in the *peri*-phenyl cases would serve to explain the large discrepancies which exist there.

The nonmutuality of the shift experienced by the bridgehead methyl (or proton) and its aromatic substituted counterpart requires comment. Two factors suggest themselves as possible explanations. First, the degree to which the electron distribution around a substituent is susceptible to distortion by steric compression is very likely a function of the bonding situation; there is no *a priori* reason to expect the bridgehead substituent and the aromatic substituent to be affected to the same extent by a mutual interaction. Second, the steric interaction must result in some relocation of nuclei to accommodate the strain. The aromatic substituent is in a region of high field gradient (the ring current field of the naphthalene system) compared to the bridgehead substituent; an equivalent change in the positions of the two substituents could well lead to a nonequivalent change of field intensity at the different nuclei. In view of this latter argument, the shifts observed for the bridgehead substituent would be a more reliable estimate of the steric compression shift than would those of the aromatic substituent.

A surprising result is that the effect of a C_6 CH_3 is nearly the same for both bridgehead hydrogen and bridgehead methyl, whereas one would expect the steric interaction to be greater in the case of two methyls. This result can be rationalized by considering that the chemical shift of the methyl group is actually the time average of the instantaneous values for each proton of the methyl group. As the methyl rotates about the C–CH_3 bond, the protons are in a position of maximum steric interaction for only a short time and are free of any steric interaction most of the time. To a first approximation, the methyl group protons can be considered to occupy a position along the extension of the C_5 CH_3 bond quite analogous to the bridgehead proton of the C_5 H compound and thus experience a similar steric shift.

Synthesis

Diazotization of anthranilic acid[19] in the presence of 1,4-dimethylanthracene provided 2,5-dimethyltriptycene. Compounds **3**, **5**–**7**, **9**, and **10** were prepared by the procedure reported for the synthesis of 5,12-*o*-benzeno-5,12-dihydronaphthacene.[20] For example, the Diels–Alder adduct of 1,4-epoxy-1-methyl-1,4-dihydronaphthalene and 9,10-dimethylanthracene, on treatment with acid, gives 5,6,12-trimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (Scheme I). Compounds **4**

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[17] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[18] R. F. Zurcher, *ibid.*, **37**, 2421 (1962).

[19] L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

[20] G. Wittig, *et al.*, *Chem. Ber.*, **93**, 951 (1960).

and **8** were prepared by a variation of the synthetic method used to prepare 9-arylanthracenes (Scheme I).[21]

Experimental Section

The nmr spectra were determined on a Varian A-60 spectrometer with the probe at normal operating temperature (~35°). The compounds were examined in $CDCl_3$ solution with tetramethylsilane as a reference ($\delta \equiv 0$).

Compounds 3, 5–7, 9, and 10 (Table II). General Procedure.—The benzyne adducts of furan,[22] 2-methylfuran,[23] and 2,5-dimethylfuran[19] were prepared. Diels–Alder reactions of these adducts with the appropriate anthracenes were carried out in refluxing xylene for 16 hr. These adducts were not characterized except for 5,5a,6,11,11a,12-hexahydro-6,11-epoxy-5,12-dimethyl-5,12-*o*-benzenonaphthacene. This compound was obtained in 83% yield and was recrystallized from benzene to provide an analytical sample of the benzene solvate, mp 255–258.5° (after losing benzene below 200°).

Anal. Calcd for $C_{26}H_{22}O\cdot C_6H_6$: C, 89.7; H, 6.5. Found: C, 89.6; H, 6.6.

Typically, a mixture of 1.7 g of an anthracene adduct, 25 ml of acetic acid, and 1 ml of concentrated hydrochloric acid was boiled. Sufficient acetic acid was then added to give complete solution at the boiling point. Concentrated hydrochloric acid was then added to the hot solution until solids formed. Cooling, filtering, and washing gave the crude products as fluorescent solids. Compound **7** was purified by recrystallization from acetic acid. Crude **3**, **5**, **6**, and **9** were boiled with excess maleic anhydride in diglyme. The solutions were diluted with water, made basic with 5% sodium hydroxide solution, and filtered. Recrystallization from acetic acid (**3**, **5**, and **6**) or acetic anhydride (**9**) gave pure products as white, nonfluorescent solids. Crude **10** was purified by treating a solution of 9 g of the solid in tetrahydrofuran with excess tetracyanoethylene (TCNE). The solution was stripped and the resulting solid was washed with benzene to yield 3.27 g of nonfluorescent crystals, mp 287–289.5°. Chromatography of the benzene solution on alumina gave 4.23 g of less pure product, mp 277–288°. Recrystallization from acetic anhydride gave pure material.

6-Bromomethyl-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene.—A mixture of 1.57 g (0.0045 mole) of 5,6,12-trimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene (**9**), 0.90 g (0.005 mole) of N-bromosuccinimide, and a trace of benzoyl peroxide in 100 ml of carbon tetrachloride was refluxed overnight. The solution was stripped and the resulting solid was washed with water. The solid was dissolved in benzene, dried, treated with Darco, and filtered. Addition of ligroin (bp 30–60°) gave a precipitate whose infrared spectrum indicated contamination with succinimide. The entire purification procedure was repeated to yield 1.41 g (73%) of pure product, mp 280° dec.

Anal. Calcd for $C_{27}H_{21}Br$: C, 76.2; H, 4.9; Br, 18.8. Found: C, 76.2; H, 5.1; Br, 18.6.

6-Methyl-d_1-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene.—A mixture of 1.6 g (0.0038 mole) of 6-bromomethyl-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene and 0.28 g (0.0067 mole) of lithium aluminum deuteride in 100 ml of tetrahydrofuran was refluxed for 41 hr. The reaction mixture, when treated with ethyl acetate followed by 5% hydrochloric acid, gave a crude product which yielded a pure title compound after three recrystallizations from acetic anhydride, mp 284–286°. The analysis for deuterium substitution was carried out by mass spectrometry. The sample was introduced through a Teflon glass inlet system[24] heated at 235°.

Nondeuterated 5,6,12-trimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene gave a molecular ion at *m/e* 346 (495 arbitrary intensity units) with C^{13} isotope peaks at *m/e* 347 (intensity 145) and *m/e* 348 (intensity 25). Significantly, there was *no* peak at *m/e* 345 corresponding to an M − 1 ion. The deuterated material gave molecular ion at *m/e* 347 (intensity 1000) with C^{13} isotope peaks at *m/e* 348 (intensity 300) and *m/e* 349 (intensity 50). There was no peak at *m/e* 346. The absence of a *m/e* 346 peak verifies that no nondeuterated species was present; the nearly exact correspondence between the intensity ratios of the M, M + 1, and M + 2 peaks demonstrates that no more than a trace of di- or higher deuterated matrials could be present. The fragmentation patterns of both compounds were consistent with the assigned structures.

11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes (11).—A mixture of 6.67 g (0.037 mole) of anthracene and 5.85 g (0.025 mole) of dibenzoylacetylene was heated at 200° until a homogeneous melt was obtained. The solid obtained on cooling was recrystallized from a large volume of benzene to yield a trace of anthracene. The mother liquor, on dilution with ligroin (bp 30–60°), gave 8.52 g (83%) of product, mp 199–206°. Recrystallization from acetic acid and drying at 140° provided an analytical sample, mp 209.5–212.5° (lit.[25] mp 212–212.5°).

Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.4; H, 4.9. Found: C, 87.4; H, 5.3.

11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (12).—A mixture of 4.12 g (0.02 mole) of 9,10-dimethylanthracene and 4.68 g (0.02 mole) of dibenzoylacetylene was heated at 200°. This gave initially a red melt which then crystallized. Boiling with 50 ml of ethanol, cooling, and filtering gave 7.66 g (87%) of an off-white solid, mp 263–266.5°. A 2-g sample recrystallized from acetic acid provided 1.78 g of an analytical sample, mp 263.5–265.6°.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.3; H, 5.5. Found: C, 86.9; H, 5.7.

Preparation of Compounds 4 and 8.—A mixture of **11** (or **12**), sodium borohydride, and diglyme in the ratio 1 mole of **11** (or **12**) to 2 moles of sodium borohydride/5 l. of diglyme was boiled. Cooling and dilution with water gave a gum which was dried overnight in a desiccator. The gum was then boiled with acetic acid and 30% hydrogen bromide in acetic acid (1200 ml of each based on 1 mole of **11** (or **12**)). Additional acetic acid was then added until the mixture was homogeneous at the boiling point. Water was then added to the hot mixture until solids formed. Cooling gave the crude product which was then recrystallized from acetic acid to provide the analytical samples (see Table II).

TABLE II

PREPARATION OF 5,12-*o*-BENZENO-5,12-DIHYDRONAPHTHACENES

Compd	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
4	30 (crude)[a] 19 (pure)[a]	271–272.5	94.7	94.9	5.3	5.0
5	51 (crude)[b]	258.5–260	94.3	93.9	5.7	5.9
6	28 (pure)[b]	283.5–285.5	94.0	93.7	6.0	6.3
7	72 (crude)[b] 25 (pure)[b]	229–234.5	94.0	93.9	6.0	6.4
8	91 (crude)[c] 80 (pure)[c]	262.5–265	94.1	94.1	5.9	6.0
9	81 (crude)[b] 48 (pure)[b]	290–292	93.6	93.5	6.4	6.4
10	50 (crude)[b] 28 (pure)[b]	288.5–290.5	93.6	93.4	6.4	6.5

[a] Based on **11**. [b] Based on the appropriate anthracene used. [c] Based on **12**.

2,5-Dimethyltriptycene.—To a refluxing solution of 2.06 g (0.01 mole) of 1,4-dimethylanthracene in 20 ml of 1,2-dimethoxyethane was added simultaneously solutions of 1.51 g (0.011 mole) of anthranilic acid in 20 ml of 1,2-dimethoxyethane and 1.5 ml of isoamyl nitrate in 20 ml of the same solvent. Addition required 5 min and the mixture was then refluxed for 1.5 hr. The mixture was cooled, made basic with 5% sodium hydroxide solution, and then diluted with water to yield an orange solid. A solution of TCNE in tetrahydrofuran was added dropwise to a solution of the orange solid in the same solvent until further addition produced no transient color. Stripping gave a solid which was slurried with benzene and filtered. This gave 1.99 g of a crystalline compound which was identified as the TCNE adduct of 1,4-dimethylanthracene. The benzene filtrate was chromatographed on alumina with benzene as a developer. The effluent when stripped gave a solid which was washed with methanol to yield 0.42 g of white crystals, mp 252–255.5°. A nonfluorescent analytical sample was obtained by recrystallization from acetic acid, mp 253–255.5°.

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Anal. Calcd for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.6.

Registry No.—**3**, 13395-89-6; **4**, 13395-90-9; **5**, 13395-91-0; **6**, 13395-92-1; **7**, 13428-04-1; **8**, 13428-05-2; **9**, 13395-93-2; **9**-d_1, 13395-94-3; **10**, 13395-95-4; **11**, 13391-20-3; **12**, 13396-00-4; 5,5a,6,11,11a,12-hexahydro-6,11-epoxy-5,12-dimethyl-5,12-*o*-benzenonaphthacene, 13395-96-5; 6-bromomethyl-5,12-dimethyl-5,12-*o*-benzeno-5,12-dihydronaphthacene, 13395-97-6; 2,5-dimethyltriptycene, 13395-98-7.

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The Lithium-Ammonia Reduction of Benzofurans

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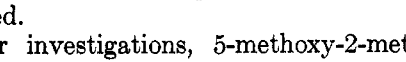
The reduction of 5-methoxy-2-methylbenzofuran (**4**), 5-methoxybenzofuran (**5**), 2,3-dihydro-5-methoxy-2-methylbenzofuran (**6**), and 2,3-dihydro-5-methoxybenzofuran (**7**) with lithium-liquid ammonia systems is described. Furan ring opening was observed in the reduction of **4** or **5** when a limited amount of alcohol was present in the ammonia solution. With excess alcohol, the corresponding 5-methoxy-2,3,4,7-tetrahydrobenzofuran was formed from each substrate. A side product from the reduction of **6** was 2,3,4,5,6,7-hexahydro-2-methylbenzofuran (**3**).

Metal-ammonia reductions of benzenoid systems often provide a key to unlock functional groups which have lain dormant during crucial stages of a synthetic study. In the course of our investigations into the synthesis of natural products, we sought to obtain a derivative of cyclohexane-1,4-dione which could be acted upon selectively. We believed this could be accomplished through tetrahydrobenzofuran derivatives. An obvious route to these compounds would be the metal-ammonia reduction of a benzofuran or of 2,3-dihydrobenzofuran.

Treatment of 2-substituted benzofuran and 2,3-dihydro-2-methylbenzofuran (**1**) with sodium in liquid ammonia had been shown by Hurd to give products of furan ring cleavage.[2] More recently, Brust and Tarbell reported the reduction of **1** with lithium-ammonia and alcohol in which 2-methyl-2,3,4,7-tetrahydrofuran (**2**) and 2,3,4,5,6,7-hexahydro-2-methylbenzofuran (**3**) were formed.[3] While the latter conditions were undoubtedly vigorous enough to cause some isomerization of **2**, base cleavage[2] or electron cleavage[4] of the dihydrobenzofuran was averted.



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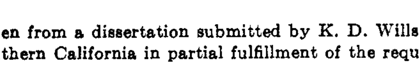
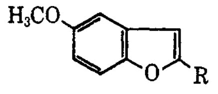
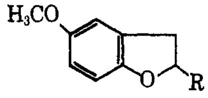


2 **3**

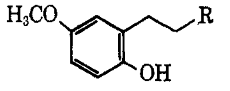
For our investigations, 5-methoxy-2-methylbenzofuran[5] (**4**) and 5-methoxybenzofuran[6] (**5**) were synthesized according to published procedures. The general method of acid-catalyzed ring closure of 2-allylphenols was used to prepare 2,3-dihydro-5-methoxy-2-methylbenzofuran (**6**).[7] Hydrogenation of **5** over 10% palladium on charcoal provided 2,3-dihydro-5-methoxybenzofuran (**7**). Reduction of the benzofurans **4** and **5** with lithium in ammonia would be expected to give the corresponding phenols **8** and **9**.[2]



4, R = CH_3
5, R = H



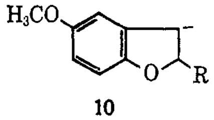
6, R = CH_3
7, R = H



8, R = CH_3
9, R = H

Thus the reduction of **5** with 2 equiv of lithium gave nearly equal amounts of **9** and **5**. The reaction appears to be much faster than previously[2] indicated, however.

Benzofuran cleavage may occur as a direct result of electron addition to give carbanion **10** and not as a subsequent amide-promoted β elimination. This may occur even though the benzyl carbanion is known to be protonated by ammonia.[2,8] β elimination of acetate ion has been reported during the lithium-ammonia reduction of an octalone[9] even though the tertiary carbanion formed in similar reductions has been shown to



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