eter, and a dropping funnel. In most experiments, the flask containing 0.1 mole of each hydrocarbon was immersed in a thermostated bath and brought to the desired temperature. Then 28.2 ml of 90% nitric acid (about 0.6 mole) was added dropwise, slowly enough to control the exothermic reaction. After all the acid had been added (usually 40–50 min), the mixtures was stirred for an additional 10–20 min and poured onto a mixture of ethanol-free ether and ice to quench the reaction. Products were extracted into the ether layer, which was then washed with a 10% sodium hydroxide and with water, and dried with saturated sodium chloride solution, and the ether was removed in a Rotavapor (Rinco Instrument Co.) at room temperature. The residues were analyzed by gas chromatography.

In the preparative scale experiments larger amounts of reactants (up to 1.0 mole of each hydrocarbon) were used with correspondingly longer reaction times.

Experiments involving tetramthylbenzenes suddenly became violent and got out of control after most of the acid had been added, if the reaction temperature was too high. Such an accident occurred with the *o*-xylene–isodurene pair at 0 to −2°.

Isolation of Cross-Coupled Products. *o*- and *m*-Xylenes.—The crude reaction mixture from the reaction of 1.0 mole of each hydrocarbon at −5 ± 5° was distilled at 0.1 mm. Nitrobixylyls distilled at 145–165°; high-vacuum fractionation of the mixture did not give satisfactory separation. From hexane solution at 0° crystals separated slowly which were recrystallized from ethanol and again from hexane to give pale yellow **2-nitro-2′,4,4′,5-tetramethylbiphenyl** (II, 7.3 g), mp 74.5–76.0°.

Treatment of the mother liquors of the crude II with methanol at 0° yielded crystals. Recrystallization from methanol gave white needles of **2-nitro-2′,3,4,4′-tetramethylbiphenyl** (I), mp 94.0–94.7°.

***o*-Xylene and Mesitylene.**—The crude reaction mixture (209 g) from the reaction of 0.75 mole of each hydrocarbon at −1 ± 2° was distilled at 0.1 mm. The fraction boiling at 167–168° solidified in contact with methanol. Recrystallization from methanol gave off-white crysals of **3-nitro-2,3′,4,4′,6-pentamethylbiphenyl** (III, 14.6 g), mp 103.8–104.8°. The yield of pure product was 8.1% not taking account of the recoverable unreacted hydrocarbon.

***o*-Xylene and Hemimellitene.**—The crude reaction mixture (197 g) from the reaction of 0.75 mole of each hydrocarbon at −5 ± 2° was distilled at 0.1–0.2 mm. The fractions boiling at 172–183° were mixtures of coupled products (46.5 g). Several recrystallizations from ethyl acetate-methanol gave some pure 2-nitro-2′,3,3′,4,4′,5-hexamethylbiphenyl.[1] The major cross-coupled product could not be isolated by fractional crystallization from many solvents. A fraction containing 77.3% of IV, 21.3% 2-nitro-2′,3,3′,4,4′,5-hexamethylbiphenyl, and 1.4% unidentified minor component was used for structure determination by nmr spectroscopy; the peaks owing to 2-nitro-2′,3,3′,4,4′,5-hexamethylbiphenyl[1] were subtracted from the spectrum of the mixture.

The distillation residue was dissolved in hot methanol-acetone, treated with active carbon, and allowed to stand at 0°. After a couple of days crystals separated. These were recrystallized from dioxane to give pure 2,2′-dinitro-3,3′,4,4′,5,5′-hexamethylbiphenyl,[1] mp 281–282°.

***o*-Xylene and Pseudocumene.**—The crude reaction mixture (206 g) from the reaction of 0.75 mole of each hydrocarbon at −8 ± 7° was vacuum distilled at 0.4 mm. The fraction distilling at 163–176° from methanol gave yellow crystals of **2-nitro-2′,4,4′,5,5′-pentamethylbiphenyl** (VI, 10.3 g), mp 114–116°. These were recrystallized from methanol to raise the melting point to 119–120°.

The mother liquors of VI were taken down to dryness and crystallized from hexane at 0°. The impure crop gave colorless **2-nitro-2′,3,4,4′,5′-pentamethylbiphenyl** (V) by recrystallization from methanol (2.1 g), mp 114–116°.

***o*-Xylene and Prehnitene.**—The reaction mixture (79.5 g) from 0.3 mole of each hydrocarbon at −11 to −14° was vacuum distilled at 0.1 mm. The fraction boiling at 171–180° (5.9 g) solidified on cooling. Recrystallization from methanol containing small amounts of ethyl acetate gave colorless crystals of **2-nitro-3,3′,4,4′,5,6-hexamethylbiphenyl** (VII) (or 2-nitro-2′,3,3′,4,4′,-5′-hexamethylbiphenyl (VIIb) in several crops, mp 151–152° (3.5 g).

The solvent was removed from the mother liquors of VII. Syrupy residue from acetic acid gave a few milligrams of colorless crystals, mp 142–144°, 96.1% pure according to gas chromatography. A better recovery of this compound from the solution failed because it tends to form mixed crystals. It has been identified by mass spectroscopy as **octamethyldiphenylmethane.** The reported melting point for octamethyldiphenylmethane is 150°.[8]

Registry No.—I, 7540-83-2; II, 7540-84-3; III, 7540-85-4; IV, 7540-86-5; V, 7540-87-6; VI, 7540-88-7; VII, 7540-89-8; VIII, 7540-90-1; 2,2′-dinitro-3,3′,4,4′-5,5′-hexamethylbiphenyl, 7540-91-2.

Acknowledgments.—The spectroscopic analyses by S. Meyerson, E. M. Banas, and R. R. Hopkins are gratefully acknowledged. M. C. Hoff is thanked for samples of the polymethylbenzenes.

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[8] C. L. Hewett and R. H. Martin, *J. Chem. Soc.*, 1396 (1940); C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 4391 (1951).

The Nuclear Magnetic Resonance Spectra of Some Polyphenyldialkylbenzenes and -anthracenes. Long-Range Shielding by Benzene Rings

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Received October 17, 1966

Several polyphenyldialkylbenzenes and -anthracenes were examined to determine the effect of a phenyl substituent on the nmr absorption of alkyl protons held near the axis perpendicular to the plane of the phenyl group. A set of empirical shielding constants is derived and shown to be generally consistent although anomalies exist. Some of the shielding constants are compared with values calculated on the basis of a previously described theoretical model, and discrepancies between theory and experiment are noted.

The concept of a local magnetic field generated by a ring current arising from the interaction of an externally applied magnetic field and a system of π electrons has been invoked to account for the low-field nuclear magnetic resonance (nmr) absorption of aromatic protons. Theoretical calculations of the magnitude of this effect have been made on the basis of a model invented by Pauling[1] and explicitly stated for the nmr problem by Pople[2] and Waugh and Fessenden,[3] and modified by Johnson and Bovey.[4] Quantitative predictions based on this theory have agreed with experimental values for some simple compounds (ethylbenzene and dibenzyl), but failed to agree for others (diphenylmethane and β-CH_2 of tetralin).[4]

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[1] L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

[2] J. A. Pople, *ibid.*, **24**, 1111 (1956).

[3] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[4] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

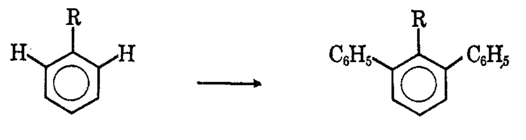
The model predicts that the locally generated magnetic field is divided into two zones: one (termed shielding) in which a proton experiences a decrease in magnetic field intensity and will thus require a higher applied field intensity to make it come into resonance at a given spectrometer frequency; the other (termed deshielding) in which a proton experiences an increase in field intensity and will resonate at a lower applied field. Figure 1 represents the magnetic lines of force generated by the π electrons of a benzene ring and pictures the regions in which a proton is shifted to a lower or higher applied field.

This model has given a satisfactory qualitative explanation for a number of unusual chemical shifts.[5] However, the use of the concept for quantitative predictions has the disadvantage that the net effect of a phenyl substituent is a composite of many factors of which the part owing to ring-current anisotropy may or may not be dominant. This is implicit in the choice by Waugh and Fessenden[3] of a butadienyl system as a starting point from which to compute ring-current shifts. DeJongh and Wynberg,[5] in estimating ring currents in furan and thiophene, attempted to correct their observed shifts for double-bond anisotropy. The mere bulk of the phenyl group probably has an effect owing to distortion of the electron distribution of the shielded group;[6] other effects normally transmitted through bonds, such as electronegativity, will be operative in appropriate circumstances.[7]

We have examined the nmr spectra of a number of 1,4-dialkyl-2,3,5,6-tetraphenylbenzenes and 1,4-dialkyl-2,3,9-triphenylanthracenes in which effects transmitted through bonds are thought to be negligible and the observed shifts thus are due to nonbonded (long-range) interactions. The results show that shielding predicted on the basis of ring-current anisotropy alone is inadequate to account for observed shifts.

Results

The nmr resonances of alkyl groups in 1,4-dialkyl-2,3,5,6-tetraphenylbenzenes fall at a higher field than those of their nonphenyl-substituted analogs. Table I records the pertinent data for several such compounds. Also tabulated for each substituent position is a shielding constant (σ) calculated as the difference between the resonance position of the polyphenyl-substituted compound and its nonphenyl-substituted analog. The σ values thus represent the shielding experienced by an alkyl proton when hydrogen *ortho* to the alkyl group is replaced by phenyl.



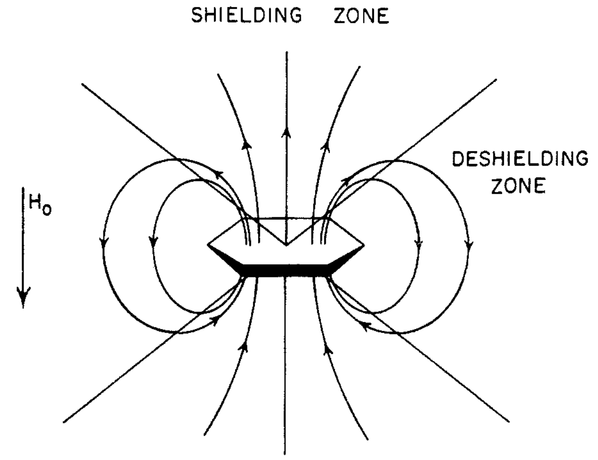
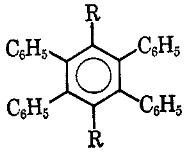


Figure 1.—Magnetic lines of force generated by the interaction of the benzene π electrons and an external magnetic field.

TABLE I

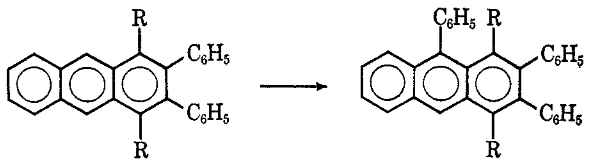
NMR DATA FOR 1,4-DIALKYL-2,3,5,6-TETRAPHENYLBENZENES



		δ, ppm				σ,[a] ppm		
Compd	R	C_6H_5	H_α	H_β	H_γ	H_α	H_β	H_γ
1	CH_3	7.1	1.80	...	...	0.53	...	...
2	C_2H_5	7.1	2.25	0.67	...	0.42	0.56	...
3	n-C_3H_7	7.1	2.13	1.13	0.32	0.43	0.49	0.58
4	CH_2Br	7.1	4.06	...	...	0.32	...	...
5	CH_2OAc	7.1	4.60	...	...	0.48	...	...
6	CH_2I	7.3	4.07	...	...	0.30	...	...

[a] σ = (δ of the tetraphenylbenzene) − (δ of nonphenyl-substituted analog). Based on toluene ($\delta = 2.33$ ppm), ethylbenzene ($\delta_{H\alpha} = 2.67$, $\delta_{H\beta} = 1.23$), n-propylbenzene ($\delta_{H\alpha} = 2.56$, $\delta_{H\beta} = 1.62$, $\delta_{H\gamma} = 0.90$), benzyl bromide ($\delta_{H\alpha} = 4.38$), benzyl iodide ($\delta_{H\alpha} = 4.37$), and benzyl acetate ($\delta_{H\alpha} = 5.08$).

Table II records the pertinent data for several 1,4-dialkyl-2,3,9-triphenylanthracenes. The σ values here are calculated as the difference between the chemical shift of the specified position of the 1-substituted alkyl group and that of the analogous position of the 4-substituted alkyl group. The σ values thus represent the shielding experienced by the alkyl groups in the 1 position when the 9 hydrogen is replaced by phenyl.



In the above-mentioned compounds, the pendant phenyl substituents are held perpendicular to the plane of the central ring system. Table III records the data for some compounds where this is not true, *i.e.*, where at least one of the pendant phenyls is partially free to rotate about the bond joining it to the central benzene ring. Table III also has some miscellaneous compounds included to show that the shielding effect of a pendant phenyl is nearly independent of other substituents on the ring, but is affected to some extent by bulky substituents in the alkyl chain. It also includes

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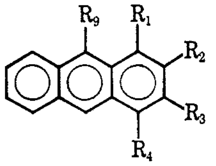
[5] See H. A. P. DeJongh and H. Wynberg, *Tetrahedron*, **21**, 515 (1965), for a discussion of, and leading references to, the subject.

[6] C. Reid, *J. Am. Chem. Soc.*, **78**, 3225 (1956); *J. Mol. Spectry.*, **1**, 18 (1957); 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); 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, Chapters I and II, for a discussion of these factors.

TABLE II

NMR DATA FOR ANTHRACENES[a]



				δ, ppm								$\sigma^{9\text{-}C_6H_5}$,[b] ppm		
Compd	$R_1 = R_4$	$R_2 = R_3$	R_9	R_9	$R_{2,3}$	1-Hα	1-Hβ	1-Hγ	4-Hα	4-Hβ	4-Hγ	1-Hα	1-Hβ	1-Hγ
7	CH_3	H	C_6H_5	7.43	...	1.85	...	...	2.68	...	...	0.83	...	...
8	CH_3	C_6H_5	C_6H_5	7.41	6.97 7.05	1.75	...	...	2.58	...	...	0.83	...	...
9	C_2H_5	C_6H_5	C_6H_5	7.43	6.98 7.05	2.18	0.52	...	3.03	1.27	...	0.85	0.75	...
10[c]	n-C_3H_7	C_6H_5	C_6H_5	7.45	6.97 7.03	2.06	1.08	0.18	2.98	1.78	0.90	0.92	0.70	0.72
11	n-C_3H_7	C_6H_5	H	...	7.03	...	...	...	2.92	1.72	0.88	...	...	...

[a] Preparation of **7–10** was described by J. B. Miller, *J. Org. Chem.*, **31**, 4082 (1966). [b] $\sigma^{9\text{-}C_6H_5}$ is the shielding owing to a 9-phenyl substituent; it represents the difference between δ values for the analogous groups in the 1 and 4 positions. [c] These data were obtained from a 100-Mcps spectrum.

cases where the correlation breaks down for no apparent reason.

Discussion

The degree of steric crowding in the 1,4-dialkyl-2,3,5,6-tetraphenylbenzenes is very large; an estimate of the magnitude of this crowding can be seen by inspecting molecular models which take into account the "thickness" of the benzene ring. Courtald's molecular models use the value of 3.4 A for the van der Waals dimension of the benzene ring in the direction normal to the plane of the ring. It is not possible to construct a model of 1,4-dialkyltetraphenylbenzene with these models even if the maximum degree of angle bending is permitted (*i.e.*, the restraining collars are omitted); it can be seen that the least crowded conformation has the pendant phenyls perpendicular to the central benzene ring and a considerable degree of compression of the π clouds must occur for the molecule to exist. If one of the phenyl groups is left out, the resultant model can be constructed but it is then apparent that the pendant phenyls are severely restricted with respect to torsional motion.

The 1,4-dialkyl groups are thus held close to the faces of the pendant phenyl groups and lie in the shielding zone. It is interesting to note, however, that the steric crowding does not impose a severe restriction to rotation about the methyl–central ring bond in the 1,4-dimethyl compound. The methyl absorption of **1** (1,4-dimethyl) is a sharp singlet, and the methylene of **2** (1,4-diethyl) is a slightly skewed quartet showing only a small second-order contribution, but no evidence for nonequivalence of the methylene protons. The α-methylene of **3** (1,4-di-*n*-propyl) is quite distorted from the expected triplet and can be interpreted in terms of nonequivalence of the α protons analogous to those in hexa-*n*-propyl benzene.[8]

The data in Table I show that, in the 1,4-dialkyl-2,3,5,6-tetraphenylbenzenes, the resonances of the alkyl protons, located as far away from the central ring as the methyl of *n*-propyl, fall at higher field than do those of nonphenyl-substituted analogs. The net shifts observed (σ) are purely empirical parameters, but the most obvious contributing factors are the ring-current anisotropy, double-bond anisotropy, and bulk effects.

The magnitude of the ring-current shift was estimated for the 1,4-dimethyl case by the Johnson–Bovey equation by using a model based on a rapidly rotating methyl group, perpendicular *ortho* phenyls, and all bond distances and angles of normal values.[9] We found that the complete calculation, taking a line integral of the instantaneous shift of the three methyl hydrogens over all possible positions, gave a value (0.33 ppm/phenyl) very close to that estimated from the graphical presentation of Johnson and Bovey (0.34 ppm/phenyl).

This calculated shift, however, must be the minimum expected since the calculation accounts only for ring-current anisotropy; to this should be added the effect of the double-bond anisotropy, which has been found to be as large as 0.2–0.3 ppm/double bond in a closely analogous situation.[10]

The observed value of 0.27 ppm/phenyl is only slightly lower than the calculated value, but we believe it to be significantly lower than what should reasonably be expected from a consideration of all factors.

The shielding effect of perpendicular *ortho* phenyls is dependent to some extent on the nature of the group being shielded. For example, the shielding owing to two *ortho* phenyls decreases from a value of 0.53 ppm for methyl, to 0.42 ppm for alkyl methylene, to 0.3 ppm for bromomethylene and iodomethylene. This can be ascribed, at least in part, to changes in conformational populations when bulky groups are present. Interference to completely free rotation places the α-methylene protons more often in the regions above and below the plane of the central benzene ring (which in itself tends to deshield them) and into that part of the ring-current field of the *ortho* phenyls which is less effective in shielding. The degree of inhibition of rotation and hence the extent to which ring-current effects are changed is difficult to estimate.

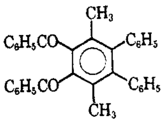
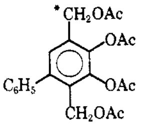
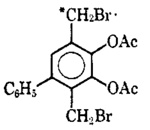
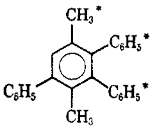
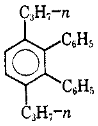
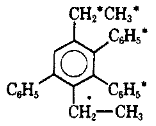
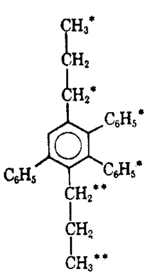
(8) H. Hopff and A. Gati, *Helv. Chim. Acta*, **48**, 509 (1965).

(9) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(10) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 129.

TABLE III

NMR DATA FOR OTHER COMPOUNDS

Compd	δ, ppm		σ, ppm
	Phenyl	Alkyl	
 **12**	7.08	1.87	0.23[a]
 **13** [b]	7.34	5.05* 4.95	0.08–0.10[c]
 **14** [b]	7.40	4.37* 4.27	0.08–0.10[d]
 **15** [e]	7.07* 7.37	2.09* 1.93	0.24[f] 0.40[f]
 **16**	7.00	2.35 (α-CH_2) 0.77 (CH_3)	0.21[g] 0.13[g]
 **17**	7.10* 7.36	2.40 (CH_2* + CH_2) 1.03 (CH_3*) 0.68 (CH_3)	... 0.20[h] 0.55[h]
 **18**	7.02* 7.33	2.37 (CH_2* + CH_2**) 0.75 (CH_3*) 0.40 (CH_3**)	... 0.15[g] 0.50[g]

[a] Calculated on the basis of δ_{CH_3} = 2.10 ppm for 1,4-dimethyl-2,3-dibenzoylbenzene [R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **61**, 2083 (1939)]. [b] D. L. Fields, J. B. Miller, and D. D. Reynolds, *J. Org. Chem.*, **29**, 2640 (1964). [c] Calculated on the basis of δ_{CH_2*OAc} = 5.03 for 1,4-bisacetoxymethyl-2,3-diacetoxybenzene (footnote *b* above) or on the basis of comparison of the 1-acetoxymethyl resonance with that of the 4-acetoxymethyl. [d] Calculated on the basis of δ_{CH_2Br} = 4.35 for 1,4-bisbromomethyl-2,3-diacetoxybenzene or on the basis of the δ_{CH_2Br} for the 1 position compared with that of the 4 position. [e] C. F. H. Allen and J. A. VanAllan, *J. Am. Chem. Soc.*, **64**, 1260 (1942). [f] Calculated from δ_{CH_3} of toluene = 2.33 ppm. [g] Calculated from the analogous resonances of *n*-propylbenzene (see footnote *a* in Table I). [h] Calculated from the analogous resonances of ethylbenzene (see footnote *a* in Table I).

As the chain length of the alkyl substituent increases, the observed shielding increases at least out to the methyl of *n*-propyl. Models indicate that a maximum ring-current effect should occur at the methyl of *n*-butyl; an estimate of the concurrent change of the other factors is not possible.

Compounds **12**, **15**, and **16** (Table III) show that the shielding effect on methyl of a single, perpendicular *ortho* phenyl group is reasonably constant whether the position on the other side of the alkyl group is occupied by H (σ/phenyl = 0.20–0.23 ppm) or by a group (benzoyl) with a large anisotropy of its own (σ/phenyl = 0.24 ppm). Compound **15** also illustrates the two kinds of phenyl substituents. Its aromatic proton resonances fall at 7.07 (area 10 H) assigned to the 2,3-diphenyls, and 7.37 ppm (area 5 H) assigned to the 5-phenyl. The methyl resonances fall at 2.09 assigned to the methyl shielded by only one perpendicular *ortho* phenyl (σ/phenyl = 0.24 ppm) and at 1.93 ppm, assigned to the methyl shielded by two phenyls (σ/phenyl = 0.20 ppm), one perpendicular, the other free to undergo torsional oscillation.

Compounds **17** and **18** are anomalous. Although each shows two kinds of phenyls and two differently shielded methyls, the α-methylene protons on opposite sides of the ring are identical (Table III). We are unable to account for this.

Compounds **13** and **14** illustrate the effect of a single *ortho* phenyl which is free to undergo torsional oscillation. The phenyl resonances at 7.34 and 7.40, respectively, indicate that these phenyls are capable of some degree of approach to planarity; the adjacent methylenes are shielded to the extent of only 0.08–0.10 ppm, whether comparison is made internally (*i.e.*, with the nonshielded methylene in the 1 position) or externally (*i.e.*, with the analogous methylene in a nonphenyl-substituted compound).

In the 1,4-dialkyl-2,3,9-triphenylanthracene series we chose to calculate the shielding constants by comparing analogous protons in the 1- and 4-alkyl substituents. This procedure was justified by the observation that the 4-alkyl resonances are practically unchanged (Δδ of 0.02 to 0.06 for α, β, and γ protons) on going from 1,4-di-*n*-propyl-2,3-diphenylanthracene to 1,4-di-*n*-propyl-2,3,9-triphenylanthracene (Table II).

The 2,3 phenyls in these compounds have aromatic resonances (7.0–7.1 ppm) similar to those found in the tetraphenylbenzene case, characteristic of *ortho* phenyls held face to face and perpendicular to the central ring plane. The 9-phenyl resonance is unique in that its protons fall under the influence of the three rings.

Comparison of compounds **7** and **8** with compounds **1** and **15** shows that introduction of a perpendicular *ortho* phenyl in the 2 position of anthracene has a markedly smaller effect on the 1-alkyl resonance (0.1 ppm) than was found for the analogous substitution in the tetraphenylbenzene case. The origin of this difference is not apparent.

The shielding effect of the 9-phenyl is seen to be very large (0.7–0.9 ppm). The 1-alkyl group is held in a position much closer to the plane and to the perpendicular axis of the *peri* phenyl than are the alkyl groups to the *ortho* phenyls of the tetraphenylbenzenes. Furthermore, the shielding by the 9 and 2 phenyls decreases along the alkyl chains in contrast to the tetraphenylbenzene case. This is reasonable since the α-methylene of the 1 substituent in anthracene occupies the position closest to the perpendicular axis of the 9 phenyl, and in the region very close to this axis and to the plane of the benzene ring the ring-current field is changing very rapidly with distance compared with regions at greater distance.

The ring-current shift for the 1-methyl group of compound **8** estimated from the graphical representation of Johnson and Bovey is 2.5 ppm. The very large difference between this and the observed 0.83 ppm bespeaks the intervention of other effects of magnitude comparable to ring-current shielding and points out the dangers attendant to the use of the ring-current anisotropy model without considering other factors.

Experimental

Spectra.—The nmr spectra were determined on a Varian A-60 spectrometer with the probe at the ambient operating temperature (~35°), except for compound **10** which was determined on a Varian HR-100 spectrometer (*i.e.*, at 100 Mcps). Spectra were determined in deuteriochloroform solution at concentrations ranging from 1 to 10% (w/v), except compound **6** whose very low solubility (unknown concentration) required the use of a Varian C-1024 time-averaging computer. It was shown that there was negligible concentration dependence of the chemical shifts. δ is defined as parts per million (ppm) to lower field from tetramethylsilane. Chemical shifts of the ethyl and *n*-propyl protons were determined by visual estimation of the center of gravity of the appropriate multiplet. Since all of the absorptions except those for the α-CH_2 of the *n*-propyl were close to first order in appearance, as determined by the symmetry of the multiplets, this procedure does not introduce significant error. We estimate the uncertainty of the chemical shifts to be of the order of ±0.01 ppm for the methyl and ethyl compounds and ±0.03 ppm for the propyl compounds.

The chemical shift for the methyls of 1,4-dimethyl-2,3,5,6-tetraphenylbenzene was calculated on an IBM 1620 computer with the equation of Johnson and Bovey and a mathematical model of the compound as described in the text.

Compounds 1–3, 17, and 18.—A mixture of 0.01 mole of the appropriate 2,3-diphenyl-1,4-dialkylcyclopentadienone[11] and 0.01 mole of the appropriate acetylene in 15 ml of *o*-dichlorobenzene was refluxed for 30 min. In the case of solid products, dilution with methanol gave the crude product which was recrystallized from the solvent shown in Table IV.

TABLE IV

1,4-DIALKYLPOLYPHENYLBENZENES

Compd	Mp or bp (μ), °C	Yield, % (recryst solvent)	% C Calcd	% C Found	% H Calcd	% H Found
1	363–365	86 (xylene)	93.6	93.8	6.3	6.8
2	324–326	33 (xylene)	93.2	93.2	7.0	7.1
3	268–272.5	7 (benzene)	92.7	92.9	7.3	7.3
17	173–174.5	55 (*n*-PrOH)	92.8	92.7	7.2	7.6
18	130–131 (5)	79	92.3	91.9	7.7	7.8

In the case of **17**, the solvent was omitted and an excess of phenylacetylene was used. Compound **18** was distilled directly from the reaction mixture and was obtained as an extremely viscous liquid.

1,4-Bis(bromomethyl)-2,3,5,6-tetraphenylbenzene (4).—A suspension of 2 g of **1** in 400 ml of acetic acid containing 3 ml of bromine and a trace of iodine was refluxed for 6 hr. Cooling and filtering gave 2.31 g (83%) of white, crystalline product, mp 314° dec. Recrystallization from xylene and drying at 140° gave a product whose melting point was unchanged. A satisfactory analysis was not obtained and mass spectral examination indicated the presence of small amounts of chlorine and iodine, and this probably accounts for the low bromine content in the analysis.

Anal. Calcd for $C_{32}H_{24}Br_2$: C, 67.6; H, 4.8; Br, 28.2. Found: C, 67.7; H, 4.8; Br, 27.5.

1,4-Bis(acetoxymethyl)-2,3,5,6-tetraphenylbenzene (5).—A mixture of 2.12 g of **4** and 250 ml of acetic acid saturated with sodium acetate was refluxed for 2.5 hr. The mixture was stripped until solids appeared and then diluted with water. Filtration and washing gave 1.78 g (91%) of white, crystalline solid, mp 272–305°. Recrystallization from acetic acid gave a sample with mp 271–306.5° which, after crystallizing from a melt, then had mp 283–306°. Infrared examination of this sample did not indicate solvation, the Beilstein halogen test was negative, and thin layer chromatography gave only one spot.

Anal. Calcd for $C_{36}H_{30}O_4$: C, 82.2; H, 5.7. Found: C, 81.9; H, 5.8.

1,4-Bis(iodomethyl)-2,3,5,6-tetraphenylbenzene (6).—A mixture of 0.78 g of **4**, 0.82 g of sodium iodide, and 50 ml of 1,2-dimethoxyethane was refluxed for 16 hr. Stripping and dilution with water gave pale yellow crystals, mp 248° dec, 0.64 g (70%). A sample recrystallized from xylene showed no change in melting point.

Anal. Calcd for $C_{32}H_{24}I_2$: C, 58.0; H, 3.6; I, 38.4. Found: C, 58.0; H, 4.0; I, 38.0.

1,4-Dipropyl-2,3-diphenylanthracene (11).—The procedure of Fieser and Haddadin[12] for the preparation of 1,2,3,4-tetraphenylanthracene was followed with 3,4-diphenyl-2,5-dipropylcyclopentadienone on an 0.02-mole scale. The crude product was obtained as a red, pasty solid. A benzene solution of this solid was chromatographed on alumina with benzene as the developer. The colorless effluent was stripped to yield an oil which crystallized on trituration with methanol. Filtration gave 3.98 g (48%) of a pale yellow solid, mp 160.5–164°. Recrystallization from acetic acid gave 3.28 g of pure material: mp 161.5–163°; $\lambda_{\max}^{CHCl_3}$ (log ϵ), 272 (4.95), 359 (3.71), 377 (3.87), 397 (3.78).

Anal. Calcd for $C_{32}H_{30}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.4.

1,2-Diphenyl-3,6-dipropylbenzene (16).—The procedure of Fieser and Haddadin[11] for the preparation of 1,2,3,4-tetraphenylbenzene was followed. The adduct of 3,4-diphenyl-2,5-dipropylcyclopentadienone and 1,4-epoxy-1,4-dihydronaphthalene was prepared in 71% yield, mp 154–156°.

A solution of 4.04 g of the adduct in 75 ml of diglyme was refluxed for 17 hr. The mixture was then diluted with water and extracted with chloroform. The chloroform extract was then washed, dried, and stripped to yield a heavy oil. The addition of ligroin precipitated 0.69 g of an amorphous material which was removed by filtration. Distillation gave 1.20 g (43%) of product, bp 80° (4 μ), $n^{25}D$ 1.5772.

Anal. Calcd for $C_{24}H_{26}$: C, 91.8; H, 8.3. Found: C, 91.5; H, 8.2.

Registry No.—**1**, 7541-77-7; 2, 4919-53-3; **3**, 7548-20-1; **4**, 7541-79-9; **5**, 7541-80-2; **6**, 7541-81-3; **7**, 7541-82-4; **8**, 7541-83-5; **9**, 7541-84-6; **10**, 7541-85-7; **11**, 7541-86-8; **12**, 7541-87-9; **13**, 6452-96-6; **14**, 6453-00-5; **15**, 7541-90-4; **16**, 7541-91-5; **17**, 7541-92-6; **18**, 7541-93-7.

Acknowledgment.—We are indebted to Dr. John Figueras, for the computer study of 1, to Mr. R. L. Young, for obtaining the nmr spectra, and to Mrs Jean C. Dignan, for synthetic work. We thank Dr. Wilson Goodlett, of the Tennessee Eastman Co., for the 100-Mcps spectrum.

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(11) Table III, footnote *e*.

(12) L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).