¹³C Nuclear Magnetic Resonance Studies of Methylated Anthracenes

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The 13 C n.m.r. spectra of anthracene and 11 methylated anthracenes have been examined. Analysis of the 1 H spectra allowed unequivocal assignments for most of the protonated carbons by selective proton decoupling. Parameters describing the methyl substituent effects on the aryl carbon shieldings were defined and refined by regression analysis so that the 13 C shieldings were predicted for 67 independent aryl positions in anthracenes without *peri*-methyls with a standard deviation of 0.12 p.p.m. *Peri* methyl-methyl interactions cause considerable deviations from the predicted substituent effects. The relationships of the 13 C shieldings to charge densities calculated by the CNDO/2 method were briefly examined. Syntheses of 2,7,9-trimethyl-, 1,4,5,8- and 1,4,5,9-tetramethyl-, and 1,4,5,8,9-pentamethylanthracene are described.

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On a examiné les spectres de résonance magnétique nucléaire du ¹³C de l'anthracène et de 11 dérivés méthylés de l'anthracène. L'analyse des spectres ¹H permet d'attribuer d'une façon non-équivoque la résonance de la plupart des carbones protonés en faisant appel au découplage sélectif du proton. On a défini des paramètres décrivant les effets d'un substituant méthyle sur le blindage des carbones aromatiques. Ces paramètres ont été affinés par une analyse de régression d'une façon telle que les blindages du ¹³C ont pu être prédits (avec une déviation standard de 0.12 p.p.m.) pour 67 positions aromatiques indépendantes dans des anthracènes sans groupement méthyle en *péri*. Les interactions *péri* méthyle–méthyle causent des déviations considérables par rapport aux effets de substituants qui sont prédits. On a examiné brièvement les relations entre les blindages dus ¹³C par rapport aux densités de charges calculées par la méthode CNDO/2. On décrit la synthèse du triméthyl-2,7,9, des tétraméthyl-1,4,5,8 et 1,4,5,9 et du pentaméthyl-1,4,5,8,9 anthracène.

Introduction

Since the pioneering studies of ${}^{13}C$ spectra by Lauterbur and Burke and Lauterbur (1) in the early sixties, the utility of ${}^{13}C$ shieldings for identification of hydrocarbons (2–4) and assessment of electronic structure (5–6) has been firmly established. There is great interest in the relationships of the chemical reactivities and electronic structures to carcinogenicities of several polynuclear aromatic hydrocarbons (7–9). Thus the potential of ${}^{13}C$ n.m.r. studies to elicit information about the local electronic environments of these compounds has considerable practical as well as theoretical significance.

Detailed interpretation of the ${}^{13}C$ n.m.r. parameters of a group of compounds such as the methylated polycyclic aromatic carcinogens (10) depends to a large extent on an understanding of the influences governing ${}^{13}C$ shieldings in simpler methyl-substituted aryl systems. Methylbenzenes were carefully examined some time ago (3) and recently series of methylnaphthalenes have been examined in two separate studies (11, 12), one of which also included an investigation of the relationships of the ${}^{13}C$ shieldings to calculated charge densities (11).

To aid the further understanding of ¹³C shieldings in aryl systems, in this study the ¹³C spectra of anthracene and 11 methylated anthra-

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cenes were examined. Analyses of the proton n.m.r. spectra allowed unequivocal assignments of the resonances of the proton-bearing carbons by selective proton decoupling. From the measured effects of the methyl substituents on the ¹³C shieldings, a set of parameters describing the effect of methyl substitution at the 1-, 2-, and 9positions was derived. Deviations from the expected substituent effects due to steric interactions of *peri*-methyl groups were found. Charge densities at the carbons calculated by the CNDO/ 2 method were found to correlate roughly with the ¹³C shieldings. Two of the compounds studied, 1,4,5,9-tetramethylanthracene and 1,4,5, 8,9-pentamethylanthracene, have not previously been reported in the literature. Their syntheses are described below.

Results and Discussion

Syntheses of Substrates

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Polysubstituted anthracenes are commonly prepared by cyclodehydration of *o*-benzylacetophenones (13) and *o*-methylbenzophenones (14) or by reduction of the corresponding anthraquinones which are obtained by the cyclodehydration of *o*-benzoylbenzoic acids (15). These cyclodehydrations, which are carried out under vigorous pyrolytic or acid-catalyzed conditions, are subject to phenonium ion rearrangements (16), alkyl group migrations (17), and dealkylations (18). As a result of these and other unspecified side reactions, anthracenes prepared by these cyclodehydration processes are often obtained in low yields as difficult to purify mixtures (19).

In contrast to cyclodehydration leading to anthracenes and anthraquinones, anthrones can be prepared by the cyclodehydration of *o*-benzylbenzoic acids under mild conditions (80% sulfuric acid, 0 °C) and in high yields (>90\%) without rearrangement (20). Anthrones **are** particularly useful synthetic intermediates for the present study since they can be reduced by complex metal hydrides to 9,10-dihydro-9-anthranols which can then be converted to the corresponding anthracenes by mild acid-catalyzed dehydration. This route, summarized in Scheme 1, was used for the synthesis of 1,4,5,8-tetramethylanthracene (**4**).

Anthrones may also be converted conveniently to 9- or 10-alkylated anthracenes by basecatalyzed alkylation at the 10-methylene group followed by reduction and dehydration, or by Grignard addition to the carbonyl group followed





SCHEME 2. Preparation of 1,4,5,8,9-pentamethylanthracene (6).

by dehydration. The former route, outlined in Schemes 2 and 3, was used for the syntheses of 1,4,5,8,9-pentamethylanthracene (6) and 1,4,5,9tetramethylanthracene (12). The latter route, shown in Scheme 4, was followed for the synthesis of 2,7,9-trimethylanthracene (16).

Syntheses of 4 and 16 through the anthrones confirm the structures of these anthracenes, which previously had been prepared via the anthraquinone for 4 (19) and via a modified Bradsher route for 16 (21).

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SCHEME 4. Preparation of 2,7,9-trimethylanthracene (16).

Nuclear Magnetic Resonance Parameters

The proton n.m.r. parameters for anthracene and 11 methylated anthracenes are given in Table 1. The deshielding effect of substitution at the 1-, 4-, 5-, 8-, 9-, or 10-positions on the *peri*-proton resonances is well established (22); thus unambiguous assignments were possible for all the proton resonances, including those giving AA'BB' patterns, with the exception of 2methylanthracene for which there was extensive

overlap of the subspectral patterns and which also had nearly equivalent chemical shifts. Using these proton assignments, selective decoupling experiments allowed assignments of the ¹³C resonances to specific proton-bearing carbons for all the compounds except 2-methylanthracene. Quaternary carbon signals were assigned on the basis of their relative intensities, with the assumption of approximately equal effective rotational correlation times. The nuclear Overhauser

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					Chem	ical shift (a	ò, p.p.m. fi	rom TMS)	I.			
Substitution		СН₃	H-1	н-2	H-3	H-4	H-5	H-6	H-7	H-8	Н-9	H-10
9-Me	3.0	70	8.261	7.482	7.436	7.974	7.974	7.436	7.482	8.261		8.311
9,10-Me2	3.0	86	8.316	7.500	7.500	8.316	8.316	7.500	7.500	8.316		_
1-Me	2.8	:02		7.284	7.341	7.851	7.986	7.439	7.458	8.017	8.517	8.396
1,4-Me ₂	2.7	68		7.174	7.174		8.018	7.456	7.456	8.018	8,520	8.520
1,8-Me ₂	2.8	23		7.303	7.344	7.849	7.849	7.344	7.303		8.597	8.393
1,4,5,8-Me ₄	2.7	83		7.189	7.189	_	_	7.189	7.189		8.591	8,591
1,4,9-Me ₃	2.7	37(4)		7.130	7.130		7.971	7.425	7.472	8.248	_	8.390
,, -	2.9	40(1)										
	3.2	29(9)										
1,4,5,9-Me₄	2.7	72(4)		7.155	7.155		_	7.290	7.383	8.152		8.515
	2.8	19(5)										
	2.9	48(1)										
	3.2	44(9)										
1.4.5.8.9-Mes	2.7	62(4, 5)	_	7.160	7.160			7.160	7.160			8.419
	2.8	72(1, 8)										
	3.0	93(9)										
2-Me	2.5	12	7.708	_	7.271	7.874	7.945	7.399	7.407	7,938	8.269	8.334
2.7.9-Me ₃	2.5	59(2.7)	7.978		7.252	7.850	7.850	7.252	_	7.978	_	8.204
	3.0	09(9)										
·					C	oupling co	nstants (J,	Hz)				
Substitution	1,2	1,3	1,4	2,3	2,4	3,4	5,6	5,7	5,8	6,7	6,8	7,8
9-Me	8.6	0.7	0.3	6.2	1.1	8.5	8.5	1.1	0.3	6.2	0.7	8.6
9,10-Me ₂	8.6	1.4	0.0	5.5	1.4	8.6	8.6	1.4	0.0	5.5	1.4	8.6
1-Me		_		6.9	0.9	8.2	8.6	1.6	0.4	7.0	1.6	8.2
1.4-Me ₂				_			8.5	1.2	0.0	6.6	1.2	8.5
1.8-Me ₂		_	_	6.7	1.1	8.5	8.5	1.1	_	6.7		
1.4.9-Me3						_	8.9	1.0	0.3	6.4	0.5	9.8
1.4.5.9-Me₄								_		8.7	1.4	8.4
2-Me		1.7	~0.0	_	_	8.7	7.6	1.1	0.0	6.2	1.4	9.3
2.7.9-Me ₃	_	0.9	~0.0		_	8.0	8.0		~0.0		0.9	

TABLE 1. Proton n.m.r. parameters of several methylanthracenes*

*Obtained for 5% (w/v) solutions in chloroform-d, using LAOCN3 program. The mean overall rms error is 0.059 Hz, with a range of 0.029-0.178 Hz, except for 2-methylanthracene, for which the r.m.s. error is 0.244 Hz.

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TABLE 2.	^{13}C shieldings of several methylanthracenes*
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Substitution	C-1	C-2	C-3	 C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	Me
 Ni1	127.9	125.1	125.1	127.9	127.9	125.1	125.1	127.9	126.0	126.0	131.5	131.5	131.5	131.5	
-Me	124.3	(124.8)	(124.4)	128.7	128.7	(124.4)	(124.8)	124.3	129.7	124.3	129.8	131.1	131.1	129.8	13.7
0,10-Me₂	125.0	124.4	124.4	125.0	125.0	124.4	124.4	125.0	128.1	128.1	129.6	129.6	129.6	129.6	14.1
-Me	133.9	125.4	124.9	126.5	127.7	125.1	125.0	128.3	122.5	126.6	131.2	131.7	131.4	131.2	19.7
,4-Me2	132.1	125.2	125.2	132.1	128.1	125.1	125.1	128.1	123.0	123.0	131.0	131.0	131.3	131.3	19.7
,8-Me2	134.1	125.4	124.9	126.3	126.3	124.9	125.4	134.1	118.7	127.1	130.9	131.4	131.4	130.9	19.7
,4,5,8-Me₄	132.2	125.2	125.2	132.2	132.2	125.2	125.2	132.2	119.6	119.6	130.6	130.6	130.6	130.6	19.6
4,9-Me3	133.0	128.5	125.1	132.5	128.7	124.7	124.3	124.5	131.5	122.0	131.7	132.1	130.4	131.2	19.6
1,4,5,9-Me4	133.1	128.8	125.0	133.0	134.6	125.3	125.0	123.0	131.72	118.3	131.6 ₈	132.2	130.2	132.0	(4-Me) 20.3 (9-Me) 27.1 (1-Me) 19.9 (4-Me) 20.0 (5-Me) 20.3
,4,5,8,9-Me₅	134.3	128.5	124.8	132.2	132.2	124.8	128.5	134.3	133.4	118.0	132.3	131.0	131.0	132.3	(9-Me) 27.0 (1-Me) 20.0 (4,5-Me) 25.9 (1,8-Me)
-Me ,7,9-Me3	126.3 122.7	134.9 134.3	128.2 126.9	128.0 128.7	128.1 128.7	(124.9) 126.9	(125.2) 134.3	128.2 122.7	125.2 127.5	125.9 124.5	132.1 130.3	130.4 129.4	131.3 129.4	131.9 130.3	26.8 (9-Me) 21.9 13.7 (9-Me) 22.4 (2,7-Me)

*In p.p.m. from internal TMS in CDCl₃ solutions; similar values in parentheses may be interchanged.

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TABLE 3. Methyl substituent effects* on anthracene ¹³C shieldings

										ļ	ļ			l
Substitution	-	C-2	C.3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14
1-Methyl	5.8	0.3	-0.2	-1.5	-0.2	0.0	0.0	0.4	-3.6	0.5	-0.4	0.0	-0.1	-0.3
2-Methyl	-1.5	9.6	2.9	0.0	0.2	-0.3	0.0	0.1	-1.0	0.0	0.4	-1.2	-0.4	0.2
9-Methyl	-3.6	-0.2	-0.6	0.8	0.8	-0.6	-0.2	-3.6	3.7	-1.7	-1.6	-0.3	-0.3	-1.6
*In p.p.m.; positi	ive values deno	te downfield	shifts.											

i-methvl

	TABLE 4. L	Differences	between	predicted ar	nd observed	¹³ C shiel	dings* in n	nethylated	anthrace	thes having	peri-met	hyl group	s	
Substitution	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14
1,4,9-Me ₃	4.4	3.5	0.5	-0.5	-0.2	0.2	-0.6	0.0	4.6	0.8	2.2	1.3	-0.4	2.0
1,4,5,9-Me4	4.7	3.8	0.4	-0.4	-0.1	0.5	0.3	0.0	5.1	0.7	2.3	1.5	-0.2	2.2
1,4,5,8,9-Mes	5.5	3.5	0.2	-1.0	-1.0	0.2	3.5	5.5	9.9	-0.1	3.2	0.6	0.6	3.2

*Observed - calculated (by additivity) values in p.p.m.

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FIG. 1. Observed vs. calculated methyl substituent effects on aryl ¹³C shieldings in several methylated anthracenes. \bigcirc , anthracenes without *peri*-methyl groups; \blacktriangle , anthracenes with *peri*-methyl groups. The line drawn is that for a perfect correlation with slope + 1. The numbers beside groups of data points lying far off the line indicate the positions of those carbons in the anthracene molecule. Some closely clustered points have been omitted for clarity.

enhancements depend on dipolar relaxation by protons, which decreases with increases in the C-H separation, as the inverse sixth power of this separation. Thus the closer the neighboring protons, the more intense the carbon resonances, up to the maximum enhancement, which is obtained for entirely dipolar relaxation (23). The remaining resonances were assigned in a mutually consistent manner, assuming additivity of methyl group effects. The ¹³C shieldings are collected in Table 2.

Using the results for 1-methyl-, 1,4-dimethyl-, 1,8-dimethyl-, and 1,4,5,8-tetramethylanthracene, a set of additive parameters describing the effects of a 1-methyl group on the ¹³C shielding at all aryl positions was derived. Similarly, from the data for 9-methyl- and 9,10-dimethylanthracene, parameters for a 9-methyl substituent were obtained and from these and the data for 2methyl- and 2,7,9-trimethylanthracene, the corresponding parameters for a 2-methyl substituent were found. After refinement of the parameters to provide the best overall fit for the set of all methylated anthracenes lacking peri substituents, the methyl substituent parameters given in Table 3 were obtained. These parameters predict the ¹³C shieldings at all 67 independent aryl positions in the methylanthracenes lacking peri-methyl substitution with a standard error of 0.12 p.p.m. This is illustrated in Fig. 1, which compares the

predicted to the observed methyl substituent effects, where the open circles correspond to data points for non-peri-substituted methylanthracenes. The substituent effects of a 1-methyl group on the anthracene ¹³C shieldings are similar to those previously observed for 1-methylnaphthalenes (11). For positions which are nearly equivalent in the two systems, these agree within 0.2 p.p.m., except for the deshielding effects of the 1-methyl at C-1 and C-2, which are smaller by -0.4 and -0.5 p.p.m. in anthracene. The 2methyl substituent effects in anthracene differ from those in naphthalene by -0.5, 0.0, 0.6, and 0.6 p.p.m., for C-1, C-2, C-3, and C-4, respectively. Although these effects are more pronounced at positions near the substituent in anthracene, at the methyl-substituted carbon C-2, they are identical, 9.6 p.p.m. in both naphthalene and anthracene.

 $\mathcal{M}_{\mathcal{M}}$

A different picture emerges for the anthracenes with *peri* methyl-methyl interactions, 1,4,9trimethyl-, 1,4,5,9-tetramethyl-, and 1,4,5,8,9pentamethylanthracene. These compounds have ¹³C shieldings which differ markedly from those predicted on the basis of the derived substituent parameters and the assumption of additivity. These differences are illustrated by the shaded triangles in Fig. 1 and are listed in Table 4.

In contrast to the increased shielding generally associated with crowded carbons separated by three bonds (24, 25) and observed for the methyl carbons with ortho-dimethyl substitution in naphthalenes (11), steric crowding of carbons separated by four bonds leads to deshielding of the carbons involved. This δ effect, only recently clearly recognized (26), is evident in the deshielding of the 1-methyl and 9-methyl carbons, 7.4 and 6.6 p.p.m., respectively, relative to their ¹³C shieldings in their nonhindered counterparts. Other carbons in the sterically crowded part of the molecule likewise evince this deshielding. Thus at the methyl-substituted carbons, a single peri-methyl interaction results in average deshieldings of 4.9 p.p.m. at C-1 and C-9. In 1,8dimethylnaphthalene (11) this effect was 5.1 p.p.m. at C-1. At positions ortho to the perimethyl groups, C-2, C-11, and C-14, these effects average 3.6, 2.2, and 2.1 p.p.m., respectively. These, too, are similar to those observed in 1,8dimethylnaphthalene, 3.0 p.p.m. at C-2 and 1.2 p.p.m. at C-9. Interestingly, the deshielding δ effects appear to be approximately additive, as is shown by comparison of the differences between

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predicted and observed shieldings (Table 4) for C-9 of 1,4,5,8,9-pentamethylanthracene, which has two peri-methyl interactions, with those differences at the same carbon in 1,4,9-trimethyland 1,4,5,9-tetramethylanthracene, each of which has only one peri-methyl interaction. The 9methyl carbon shieldings in these three compounds exhibit similar behavior, with two perimethyl interactions giving rise to a deshielding of 13.1 p.p.m. and one a deshielding of 6.6 p.p.m. This 6.6 p.p.m. methyl carbon deshielding resulting from one peri-methyl interaction is exactly that observed in 1,8-dimethylnaphthalene (11). It seems likely that the deviations in Table 4 resulting from steric crowding of the methyl groups arise partially from alterations in the aryl carbon -carbon bond orders in the parts of the molecule close to the methyl groups. Other factors cannot, however, be discounted. One contribution to the shielding of a given

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¹³C nucleus results from the electronic charge density at that nucleus (24). Several studies have indicated that charge distributions calculated by the CNDO/2 method (27) correlate reasonably well with experimental trends in ¹³C n.m.r. data (28). To test for such correlations between the observed aryl shieldings and calculated charge densities for the methylated anthracenes, CNDO/2 calculations (29) for anthracene and its 1-methyl, 2-methyl, 9-methyl, 1,4-dimethyl, 1,8-dimethyl, 9,10-dimethyl, 2,7,9-trimethyl, and 1,4,5,8-tetramethyl derivatives were carried out. The results of these calculations are plotted in Fig. 2 vs. the experimental ¹³C shieldings. The points shown are for the total charge density; the π charge density gave a similar plot but the correlation was slightly poorer. It was anticipated from the previous work on methylated naphthalenes (11), that aryl carbons in the β positions (C-2, C-3, C-6, C-7) of unsubstituted rings and these carbons when two bonds removed from the substituted carbon in substituted rings would be more shielded than the general trend for the other carbons, illustrated by the straight line in Fig. 2, would indicate. Data points for these β carbons were clustered tightly about one point, showing no trend in shielding with charge density. The peri effects of 1-methyl groups on the C-9 shieldings are sufficiently large that no discernible correlation of these shieldings with total charge density was found. For all carbons at ring junctions, C-11, -12, -13, and -14, the trends in both π and total charge densities successfully predicted the



FIG. 2. Total charge densities vs. ¹³C shieldings of aryl carbons in methylated anthracenes. \bigcirc , anthracene; \spadesuit , 1-methylanthracene; \triangle , 2-methylanthracene; \spadesuit , 9-methylanthracene; \diamondsuit , 1,4-dimethylanthracene; \blacklozenge , 2,7,9-trimethylanthracene; \bigcirc , 1,4-dimethylanthracene; \spadesuit , 2,7,9-trimethylanthracene; \bigcirc , 1,8-dimethylanthracene; \blacksquare , 1,4,5,8-tetramethylanthracene; \bigtriangledown , 9,10-dimethylanthracene. The total charge is given in units of *e*, the charge on the electron.

ordering of the ¹³C resonances, but extension of these predictions to include all quaternary aryl carbons was unsuccessful, suggesting that the prediction of the ordering of the condensed carbon shieldings was somewhat fortuitous. The observed ¹³C shieldings in the methylated anthracenes are related to the electronic charge distributions, but crudely, and other contributions to these shieldings, including bond orders and possibly as yet ill-defined steric effects, must be considered.

Experimental

Materials

Anthracene and 2-methyl-, 9-methyl-, and 9,10dimethylanthracene of reagent quality were commercially obtained and used without further purification. Literature methods were followed for the syntheses of 1-methylanthracene (30), 1,4-dimethylanthracene (31), 1,8dimethylanthracene (20), and 1,4,9-trimethylanthracene (31).

1,4,5,8,9-Pentamethylanthracene (6)

(a) 2-(2,5-Dimethylbenzyl)-3,6-dimethylbenzoic Acid (2)

To a well-stirred solution of 14.1 g (0.05 mol) of 2-(2,5-dimethylbenzoyl)-3,6-dimethylbenzoic acid (1) in 1500 ml of 10% sodium hydroxide heated at reflux, 50 g of zinc dust was added over a period of 48 h (19). The mixture was refluxed for an additional 24 h and then filtered. The filter cake was washed with 10% sodium hydroxide and with boiling water. The combined filtrates were strongly acidified with hydrochloric acid and extracted with benzene. The benzene extracts were dried, treated with charcoal, concentrated and then diluted with hexane. Crystallization gave 9.5 g (71%) of 2.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.72; H, 7.59.

(b) 1,4,5,8-Tetramethylanthrone (3)

A mixture of 2.68 g (0.01 mol) of finely powdered 2-(2,5-dimethylbenzyl)-3,6-dimethylbenzoic acid (2) and 20 ml of ice-cold concentrated sulfuric acid was stirred for ca. 15 min until all the solid had dissolved to give a clear lemon-yellow solution. This solution was allowed to warm to room temperature over 30 min, then poured onto ice and the resultant colorless solid was filtered and washed with hot water. The crude solid was dissolved in benzene, treated with anhydrous potassium carbonate and char-coal, and recrystallized from benzene-hexane to give 2.26 g (90%) of 3, m.p. 198.5–199 °C.

Anal. Calcd. for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 86.35; H, 7.25.

The ¹H n.m.r. spectrum of 3 in CDCl₃ showed singlets for the 1- and 8-methyl (δ 2.48, 6H), the 4- and 5-methyl (δ 2.73, 6H), and the methylene (δ 3.82, 2H) protons; and an AB quartet (centered at δ 7.185, J = 8 Hz, 4H) for the aromatic protons.

(c) 1,4,5,8,10-Pentamethylanthrone (5)

To a refluxing, vigorously stirred suspension of 1.50 g(5.99 mmol) of 1,4,5,8-tetramethylanthrone (3) in 75 ml of 95% ethanol and 25 ml of methyl iodide, 9 g (0.15 mol) of potassium hydroxide was added over a period of 1 h. The cooled reaction mixture was poured into 1 l of water, filtered, and dried to give 1.61 g of a crude heterogeneous yellow and red solid.

This solid was dissolved in chloroform, treated with anhydrous sodium sulfate and charcoal and crystallized from chloroform – carbon tetrachloride to give 1.43 g (91%) of 5.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.35; H, 7.63. Found: C, 86.28; H, 7.71.

The ¹H n.m.r. spectrum of 5 in CDCl₃ showed singlets for the 1- and 8-methyls (δ 2.44, 6H) and the 4- and 5methyls (δ 2.65, 6H); a doublet for the 10-methyl (δ 1.33, 3H, J = 7 Hz); a quartet for the 10-methine proton (δ 4.40, 1H, J = 7 Hz); and an AB quartet (centered at δ 7.12, 4H, J = 8 Hz) for the aromatic protons. A carbonyl absorption at 1665 cm⁻¹ was observed in the i.r. spectrum of 5 in a KBr pellet.

(d) 1,4,5,8,9-Pentamethylanthracene (6)

To a stirred solution of 1.0 g (26 mmol) of lithium aluminum hydride in 100 ml of absolute ether at 0 °C was added 100 mg (0.38 mmol) of 1,4,5,8,10-pentamethylanthrone (5). The solid dissolved rapidly to give a pale yellow-green solution which turned colorless over 15 min. The reaction was allowed to continue for 1 h at 0 °C. Stirring and cooling was continued while ice was added over a period of 1 h and while anhydrous magnesium sulfate was added over a second 1 h interval. The mixture was filtered and the filtrate evaporated to dryness under a stream of nitrogen to give 104 mg of a colorless mixture of *cis*- and *trans*-1,4,5,8,10-pentamethyl-9-anthranol (> 90% *cis*).

The ¹H n.m.r. spectrum of this alcohol, 100 mg in 0.5 ml dimethyl sulfoxide- d_6 , exhibited singlets for the 1- and 8-methyls (δ 2.38, 6H), the 4- and 5-methyls (δ 2.48, 6H), and the aromatic protons (δ 6.99, 4H); doublets for the 10-methyl (δ 1.42, 3H, J = 7 Hz), the carbinol proton (δ 5.97, 1H, J = 4 Hz) and the hydroxyl proton (δ 5.14, 1H, J = 4 Hz); and a quartet for the 10-methine proton (δ 4.25, 1H, J = 7 Hz).

Dehydration of the alcohol was carried out in the n.m.r. tube by the addition of 0.05 ml of acetic acid- d_4 and heating to 130 °C. After heating for 10 min the spectrum of the alcohol was completely replaced by the spectrum of 1,4,5,8,9-pentamethylanthracene (6), which showed singlet resonances for all protons; the 1- and 8-methyls (δ 2.82, 6H), 4- and 5-methyls (δ 2.70, 6H), and 9-methyl (δ 3.03, 3H); the 2-, 3-, 6-, and 7-aromatic protons (δ 7.16, 4H) and the 10- aromatic proton (δ 8.36, 1H).

1,4,5,8,9-Pentamethylanthracene (6) was isolated by dilution with water and extraction with chloroform as a slightly yellow, blue-green fluorescent solid (81 mg, 87%). Aged samples lost their fluorescence and turned yellow. Due to rapid oxygen incorporation, with formation of a photo-oxide of formula $C_{19}H_{20}O_2$, probably by oxygen addition across the 9,10 or 1,4 positions (32), satisfactory elemental analyses could not be obtained.

Vacuum sublimation of 6 at *ca*. 115 °C and 20 mm Hg gave a yellow crystalline solid, m.p. 140–148 °C. This solid was sublimed at 0.35 mm Hg and the fraction which sublimed between 110 and 150 °C was passed through a silica gel column (Woelm activity grade 1) with 5% benzenehexane. The first-eluting component was concentrated and pumped at room temperature for 45 min at 0.15 mm Hg. The resulting very pale yellow crystalline solid had m.p. 154–157 °C. Its mass spectrum had the anticipated molecular ion at *m*/e 248 and the expected mass fragments for a pentamethylanthracene of formula C₁₉H₂₀. No significant impurities were observed.

1,4,5,8-Tetramethylanthracene (4)

This preparation was similar to the preparation of 6 above, but 1,4,5,8-tetramethylanthrone (3) was the starting material. The 1,4,5,8-tetramethylanthracene, in 87% yield from 3, recrystallized from benzene-hexane and sublimed had m.p. 221-221.5 °C (lit. (19) m.p. 220-221 °C). Anal. Calcd. for C₁₈H₁₈: C, 92.26; H, 7.74. Found: C,

Anal. Cared. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.34; H, 7.60.

1,4,5,9-Tetramethylanthracene (12)

(a) 2-(2,5-Dimethylbenzyl)-6-methylbenzoic Acid (9)

To a cooled, stirred solution of 50 g (0.31 mol) of 3methylphthalic anhydride (33) in 400 ml of p-xylene was added 190 g of anhydrous aluminum chloride. The reaction mixture was heated at 60-65 °C for 4 h, poured onto ice, acidified with hydrochloric acid, and extracted with benzene. The benzene extracts were extracted with 5% sodium hydroxide. This basic solution was treated with charcoal, filtered, and acidified to give, upon filtration and washing with hot water, 56 g (68%) of a mixture of 2-(2,5-dimethylbenzoyl)-3- and 6-methylbenzoic acids (7). This mixture of isomeric acids was dissolved in 31 of 10% sodium hydroxide and heated at reflux for 72 h with 250 g of zinc dust, which was added in portions over the course of the reduction. The hot mixture was filtered and the residue washed with hot 10% sodium hydroxide and hot water. The filtrates were strongly acidified with hydrochloric acid and extracted with benzene. The benzene extract was treated with charcoal, then fractionally recrystallized from benzene-hexane. From the more soluble fractions there was isolated 2.4 g of 2-(2,5-dimethylbenzyl)-6methylbenzoic acid (9), m.p. 103-104.5 °C.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.26.

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From the less soluble fractions there was obtained 15.6 g of 2-(2,5-dimethylbenzyl)-3-methylbenzoic acid (8), m.p. 184–185 °C.

Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.20; H, 7.30.

The structures of the isomeric acids 8 and 9 were determined from the ¹H n.m.r. spectra. The proton *ortho* to the carboxyl group in 8 appeared as a multiplet at δ 7.8, with the remainder of the aromatic protons absorbing at δ 6.8–7.5. With a methyl group *ortho* to the carboxyl group in 9, all of the aromatic proton resonances were at δ 6.8–7.5.

(b) 1,4,8-Trimethylanthrone (10)

A mixture of 1.5 g (5.9 mmol) of 2-(2,5-dimethylbenzyl)-6-methylbenzoic acid (9) and 10 ml of concentrated sulfuric acid was stirred at 0 °C for *ca*. 10 min until a clear yellow solution was obtained. This solution was allowed to stand at room temperature for 30 min, then poured onto ice. Filtration and washing with water followed by recrystallization from benzene-hexane gave 1.15 g (83%) of 10.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.22; H, 6.92.

The ¹H n.m.r. spectrum of **10** in CDCl₃ exhibited singlet absorptions for the 4-methyl (δ 2.36, 3H), the 1and 8-methyls (δ 2.72 and 2.77, 6H), and the methylene (δ 4.06, 2H); and a multiplet for the aromatic protons (centered at δ 7.25, 5H).

(c) 1,4,8,10-Tetramethylanthrone (11)

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To a refluxing solution of 500 mg (2.16 mmol) of 1,4,5trimethylanthrone (10) in 75 ml of ethanol under a nitrogen atmosphere, was added 1.0 g (17 mmol) of potassium hydroxide followed by the slow addition of 14 g (0.1 mol) of methyl iodide. The reaction was heated at reflux for 30 min, cooled to room temperature, diluted with 50 ml of water, and concentrated with a rotary evaporator. Filtering and drying gave 519 mg (98%) of pale yellow 1,4,8,10-tetramethylanthrone (11).

The ¹H n.m.r. spectrum of **11** in CDCl₃ showed singlets for the 4-methyl (δ 2.41, 3H) and the 5- and 8-methyls (δ 2.67 and 2.70, 6H); a doublet for the 10-methyl (δ 1.38, 3H, J = 7 Hz); a quartet for the methine proton (δ 4.22, 1H, J = 7 Hz); and a multiplet for the aromatic protons (centered at δ 7.2, 5H).

Attempts to recrystallize this anthrone **11** from chloroform-pentane caused the formation of a colorless high melting, sparingly soluble product. The same product appeared in aged samples of the anthrone.

(d) 1,4,5,9-Tetramethylanthracene (12)

A fresh sample of 1,4,8,10-tetramethylanthrone (11) was prepared by the above procedure from 100 mg of 1,4,8-trimethylanthrone (10) and without purification was directly subjected to reduction and dehydration. The crude dried 11 was dissolved in 100 ml of ether, to which, at the boiling point, 1.0 g (26 mmol) of lithium aluminum hydride was added. The reaction was stirred at room temperature for 45 min, then poured into a vigorously stirred mixture of 250 ml of ether and 10 ml of water. After 15 min of stirring, the mixture was dried with anhydrous magnesium sulfate. The filtrate was concentrated to 100 ml and then heated at the boiling point with several crystals of *p*-toluenesulfonic acid and 1 ml of water for 10 min. The solution was cooled, dried over anhydrous

potassium carbonate, and evaporated to dryness with a stream of nitrogen to give 81 mg (82%) of pale yellow crystalline 1,4,5,9-tetramethylanthracene (12).

The mass spectrum of 12 gave the expected molecular ion at m/e 234 and fragments consistent with a tetramethylanthracene C₁₈H₁₈. About 7% of the sample was an oxygenated impurity, C₁₈H₁₈O₂, probably the transannular peroxide (32). Since this oxygen adduct formed rapidly in solution, n.m.r. analyses were obtained on the directly prepared product above.

Vacuum sublimation of 2 mg of 12 recovered from the n.m.r. analyses at 115 °C and *ca*. 20 mm Hg gave pale yellow crystals, m.p. 131-135 °C.

2,7,9-Trimethylanthracene (16) (34)

(a) 2-(4-Methylbenzoyl)-5-methylbenzoic Acid (13) To 15 ml of 100% sulfuric acid was added 16.3 g (64.2 mmol) of a mixture of 2-(4-methylbenzoyl)-4- and 5-methylbenzoic acids (35). The bright orange mixture was heated at 50 °C for 49 h.

The resulting deep brown solution was poured with rapid stirring onto a slurry of crushed ice and water. The precipitate was extracted into ether and the ether solution extracted with a saturated solution of sodium bicarbonate. The basic solution was treated with charcoal, acidified with concentrated hydrochloric acid and the precipitated keto acid was extracted into ether. The ether solution was washed with water and a saturated solution of sodium chloride. After the ether solution was dried over magnesium sulfate and evaporated to dryness, 10.6 g of product was recovered, m.p. 127-144 °C. Fractional crystallization from benzene-heptane and chloroform-heptane as alternating solvent systems yielded 1.73 g (16.3%) of 2-(4methylbenzoyl)-5-methylbenzoic acid (13), m.p. 162-163 °C. The i.r. spectrum showed absorption maxima at 760, 830, and 940 cm^{-1} characteristic of 13, with no bands at 778, 842, 858, and 963 cm⁻¹ characteristic of 2-(4methylbenzoyl)-4-methylbenzoic acid.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.69; H, 5.49.

The structure of keto acid 13 was proven by decarboxylation (36) to 4,4'-dimethylbenzophenone. To 19 mg of basic cupric carbonate in a short path distillation apparatus was added 500 mg (1.97 mmol) of keto acid 13. The mixture was heated gently with a free flame until the acid melted and neutralization was complete. Water was removed on a steam bath under reduced pressure. Decarboxylation was accomplished by heating the mixture in a sand bath at 265 °C until evolution of carbon dioxide ceased. Distillation of the residue (0.5 mm) gave 205 mg (49.7%) of a yellow oil. Pale yellow needles, m.p. 91-93 °C, were obtained after a solution of the yellow oil in 95% ethanol was allowed to cool slowly. A mixture melting point of 91-93 °C was obtained for the crystallized product and an authentic sample of 4,4'-dimethylbenzophenone, m.p. 92.5-93.5 °C (lit. (37) 95 °C). The i.r. spectra of the two samples were superimposable.

(b) 2-(4-Methylbenzyl)-5-methylbenzoic Acid (14)

To 50 ml of glacial acetic acid in a Parr bottle was added 4.65 g (18.3 mmol) of keto acid 13 and 0.6 g of 5% palladium-on-carbon. The mixture was hydrogenated on a Parr apparatus under 40 psi of hydrogen at 65 °C for 6 h. The catalyst was filtered off and the acetic acid filtrate diluted with water to give 3.95 g (90%) of 2-(4-methylbenzyl)-5-methylbenzoic acid (14), m.p. 113–115 °C. An analytical sample was prepared by recrystallization from chloroform-benzene, m.p. 116 °C.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.69; H, 7.00.

(c) 2,7-Dimethylanthrone (15)

To 5 ml of 98% sulfuric acid at 0 °C was added 500 mg (2.1 mmol) of 2-(4-methylbenzyl)-5-methylbenzoic acid (14). The orange solution was allowed to warm to room temperature over 30 min, poured onto ice, and filtered. The dried product was recrystallized from chloroform-hexane to give 403 mg (87%) of pale yellow needles, m.p. 153–154 °C.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.60; H, 6.25.

(d) 2,7,9-Trimethylanthracene (16)

To a chilled solution of methylmagnesium bromide (9 mmol) in 15 ml of ether was added 400 mg (1.8 mmol) of 2,7-dimethylanthrone 15. The reaction mixture was vigorously stirred for 2 h while cooled in an ice-water bath. The mixture was then poured into dilute hydrochloric acid and extracted with ether. The ether solution was washed with water, 5% sodium bicarbonate, and saturated sodium chloride and dried over anhydrous magnesium sulfate. The dried ether solution was treated heavily with charcoal and evaporated to dryness. Recrystallization from ethanol gave 286 mg (72%) of 2,7,9-trimethylanthracene 16, m.p. 124–126 °C (lit. 126 °C (21)).

Spectra

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The ¹H n.m.r. spectra were obtained by pulsed Fourier transform operation on a Varian XL-100 spectrometer with internal deuterium lock, using 5% (w/v) solutions in chloroform-d containing 0.5% tetramethylsilane (TMS) at 28 °C. These spectra were examined with methyl protons and other protons decoupled as appropriate to obtain more accurate line positions by removal of line broadening due to small long-range couplings. Additional spectra in other solvents, e.g., benzene- d_6 and acetone- d_6 , were used to aid the interpretation of the overlapping patterns observed for some of the compounds. Analysis of the spectra was done with the aid of the iterative spectral fitting program LAOCN3 (38). Natural abundance ¹³C spectra were obtained similarly, using 10-15% (w/v) solutions in chloroform-d containing a few drops of TMS at 40 °C. The individual aryl carbon shieldings were measured from noise-decoupled spectra. Definitive assignments of the protonated carbon resonances were then made by single frequency proton decoupling at relatively low decoupler power, with the decoupler frequency set at the proper value for each individual proton resonance in turn. The 500 Hz sweep widths used for the ¹³C spectra gave precisions of ± 0.03 p.p.m., however, dilution effects are anticipated to be significant in these systems (11), although probably small at the concentrations employed (10), and the shieldings are therefore reported to ± 0.1 p.p.m., except for very closely lying signals.

Mass spectra were obtained by gas-liquid chromatography coupled with methane chemical ionization and 70 eV electron impact mass spectrometry on a Finnigan Model 1015C mass spectrometer interfaced with a Finnigan model 9500 gas chromatograph and on a Hewlett-Packard 5930 70 eV electron impact mass spectrometer interfaced with a Hewlett-Packard 5700 gas chromatograph. Single components and the expected mass fragments were observed for 1-methyl-, 1,4-dimethyl-, 1,8dimethyl-, and 1,4,5,8-tetramethylanthracene. The 1,4,5,9 compound ($C_{18}H_{18}$) contained less than 7% of an oxygenated impurity ($C_{18}H_{18}O_2$) and the 1,4,5,8,9 compound contained approximately 4% of a similar impurity ($C_{19}H_{20}O_2$). Attempts to prepare acetate derivatives of the concentrated impurities were unsuccessful. These impurities are probably photooxides (32) formed by oxygen addition. To prevent formation of photooxides, the solid methylated anthracenes were stored in the dark in the freezer and solutions for n.m.r. analysis were made up immediately prior to the acquisition of spectra.

CNDO/2 Calculations

Standard bond lengths and bond angles as given by Pople and Beveridge (27) and planar ring systems were assumed. The CNINDO program from QCPE (29) was used without modification. Calculations were done on the IBM 370/165 computer of the Triangle Universities Computation Center.

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