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THE CARBON-13 NMR SPECTRA OF BENZANTHRONE AND ITS DERIVATIVES

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SUMMARY

The normal and noise-decoupled ^{13}C n.m.r. spectra of benzanthrone and its derivatives are recorded. The spectra are analysed by single-proton decoupling and compared with spectra of its simple derivatives.

1. INTRODUCTION

Benzanthrone (7H-benz(de)anthracen-7-one) and its derivatives are considered anthraquinone dye intermediates of importance because of the valuable tinctorial properties of their more complex analogues. In spite of the considerable variety of chemical compounds studied by ^{13}C n.m.r., ^{13}C investigations of polycyclic aromatic quinones[1] are surprisingly lacking; these data contribute to the general understanding of the systems. Carbon-13 n.m.r. chemical shifts of polycyclic aromatics are shown to provide useful information about the substitution pattern in the system.

2. EXPERIMENTAL

Samples of benzanthrone (**3**), 2-chlorobenzanthrone (**4**), 3-chlorobenzanthrone (**5**), 3-bromobenzanthrone (**6**), 3-nitrobenzanthrone (**7**), 11-nitrobenzanthrone (**8**), 3-methoxybenzanthrone (**9**) and 4-methylbenzanthrone (**10**) were obtained from ICI Organics Division, Grangemouth, Great Britain, and purified by simple crystallisation from chloroform–petroleum ether (40–60 °C). Their purity was checked by t.l.c. and melting point.

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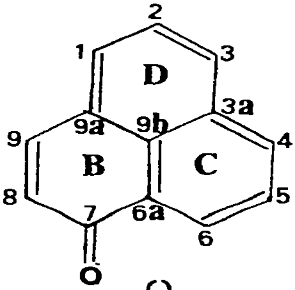
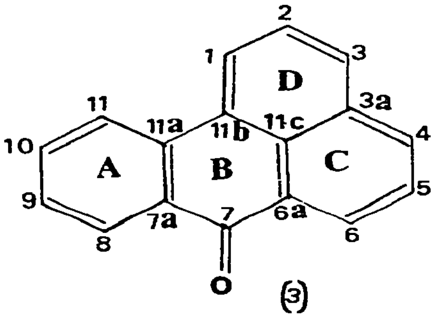
The ^{13}C spectra of the compounds were obtained by the pulsed Fourier transform technique at 45·28 MHz on a Bruker WH180 WB spectrometer. Samples were studied in tubes of 12 mm outer diameter with concentrations at 0·24 M in $CDCl_3$. The deuterium of the solvent was used as a field-frequency lock and all chemical shifts are expressed on a δ-scale downfield from internal tetramethylsilane (TMS). Proton irradiation was carried out for benzanthrone and its derivatives at low decoupler power no-noise modulation at various frequencies on a Jeol FX 90Q instrument.

3. RESULTS AND DISCUSSION

The ^{13}C chemical shifts of model compounds phenalenone (**1**) and its 3-methoxy derivative[2] are included. The numbering scheme and structures for phenalenone (**1**) and benzanthrone (**3**) are illustrated.



(1)



(3)

Assignments of resonances were accomplished using several methods. Initially, reduced intensities of all quaternary centres were evident, permitting ready distinction between these resonances and those due to carbons bearing hydrogen. Increased relative intensities for quaternary carbons were observed by the addition of the relaxation reagent $Cr(acac)_3$ which is known to attenuate greatly the spin-lattice relaxation times.[3]

The decoupled spectrum of benzanthrone can be divided into two groups of peaks, namely those from ten ^1H-bearing carbons and those from seven quaternary carbons. The ^{13}C chemical shifts of benzanthrone fall within a fairly narrow range (δ 122–136). The ^{13}C chemical shifts of phenalenone (**1**), 3-methoxyphenalenone (**2**) and benzanthrone (**3**) and its derivatives (**4**–**10**) are given in Table 1, and substituent chemical shifts for benzanthrone are given in Table 2.

Rama Rao and Vaidyanathan[4] have reported the proton nuclear magnetic resonance spectrum of benzanthrone. All the aromatic protons appeared in the region 7·5–9·0 and could be assigned by a simple first-order analysis. The spectrum

TABLE 1

CARBON-13 CHEMICAL SHIFTS FOR PHENALENONE AND BENZANTHRONE DERIVATIVES IN $CDCl_3$ (PPM)

Compound	*C-1*	*C-2*	*C-3*	*C-3a*	*C-4*	*C-5*	*C-6*	*C-6a*	*C-7*	*C-7a*	*C-8*	*C-9*	*C-9a*	*C-9b*	*C-10*	*C-11*	*C-11a*	*C-11b*	*C-11c*
1[a]	131·0	126·4	131·6	131·9	134·5	126·7	129·8	129·3	185·0	—	128·9	141·3	127·5	127·3	—	—	—	—	—
2[a]	133·3	104·5	150·7	124·8	126·3	129·1	130·6	129·4	185·6	—	126·3	141·9	120·8	128·40	—	—	—	—	—
3	123·95	126·44	129·99	132·89	134·93	126·44	129·60	128·48	183·65	131·11	128·02	128·15	—	—	133·15	122·96	136·11	127·82	126·77
4	124·67	132·69	129·01	133·48	134·07	127·63	129·75	128·48	183·26	131·18	128·22	128·22	—	—	133·58	123·16	134·86	128·81	126·18
5	123·55	126·58	134·27	130·19	131·11	127·17	131·32	128·59	182·93	130·39	128·01	128·42	—	—	133·48	122·76	135·19	125·72	128·59
6	123·94	130·43	125·43	131·38	130·57	127·51	133·95	128·83	182·93	130·32	128·05	128·51	—	—	133·41	122·87	135·33	126·51	128·56
7[b]	122·30	124·22	147·51	125·07	130·37	130·22	130·99	128·94	183·16	133·09	129·68	129·68	—	—	134·11	124·28	134·63	131·11	128·67
8	126·40	128·10	131·38	133·50	136·13	126·93	130·55	128·68	181·69	133·17	132·02	128·45	—	—	128·01	149·37	122·06	128·01	127·68
9	125·33	104·58	157·61	125·11	125·59	126·97	130·06	128·75	183·91	130·06	127·96	129·10	—	—	133·09	122·30	136·44	119·28	128·22
10	123·75	126·05	127·93	132·02	143·02	126·05	129·60	128·09	183·52	131·97	127·89	127·96	—	—	133·02	122·96	136·24	127·10	126·18

[a] Values from ref. 2.

[b] Recorded at 100·63 Hz on a Bruker WH 400 spectrometer.

TABLE 2

CARBON-13 SUBSTITUENT CHEMICAL SHIFTS FOR BENZANTHRONE, $\Delta\delta$ (*ppm*)[a]

Substituent	*C-1*	*C-2*	*C-3*	*C-3a*	*C-4*	*C-5*	*C-6*	*C-6a*	*C-7*	*C-7a*	*C-8*	*C-9*	*C-10*	*C-11*	*C-11a*	*C-11b*	*C-11c*
2-chloro	+0·72	+6·25	−0·98	+0·59	−0·86	+1·19	+0·15	0·0	−0·39	+0·07	+0·20	+0·07	+0·43	+0·20	−1·25	+0·99	−0·59
3-chloro	−0·40	+0·14	+4·28	−2·70	−3·82	+0·73	+1·72	+0·11	−0·72	−0·72	−0·01	+0·27	+0·33	−0·20	−0·92	−2·10	+1·82
3-bromo	−0·10	+3·99	−4·56	−1·51	−4·36	+1·07	+4·35	+0·35	−0·72	−0·79	+0·03	+0·36	+0·26	−0·09	−0·78	−1·31	+1·79
3-nitro	−1·65	−2·22	+17·52	−7·82	−4·56	+3·78	+1·39	+0·46	−0·49	+1·98	+1·66	+1·53	+0·96	+1·32	−1·48	+3·29	+1·90
11-nitro	+2·45	+1·66	+1·39	+0·61	+1·20	+0·49	+0·95	+0·20	−1·96	+2·06	+4·0	+0·30	−5·14	+26·41	−14·05	+0·19	+0·91
3-methoxy	+1·38	−21·86	+27·62	−7·78	−9·34	−0·53	+0·46	+0·27	+0·26	−1·05	−0·06	+0·95	−0·06	−0·66	+0·33	−8·54	+1·45
4-methyl	−0·20	−0·39	−2·06	−0·87	+8·09	−0·39	—	−0·39	−0·13	+0·86	−0·13	−0·19	−0·13	0·0	+0·13	−0·72	−0·59

[a] Plus sign denotes a downfield shift and minus an upfield shift.

of the compound could be divided into two regions. The region 8·66–7·86 corresponds to six protons (6-H, 8-H, 1-H, 11-H, 4-H and 3-H) appearing as doublets or doublets of doublets and the remaining four protons (5-H, 10-H, 2-H and 9-H) appeared in the region 7·67–7·47 as doublets of triplets.

3.1. ^1H bearing carbons

The protons at C-6 and C-8 are expected to absorb at lower field (8·4–8·70) due to proximity of the C=O group, and H-6 appears downfield (8·68) compared with H-8. Selective ^{1}H decoupling at 8·50 sharpens the signal at 129·60 and hence C-6 has been assigned this value. Similarly selective irradiation at 8·25 sharpens the carbon signal at 128·02, and this has been assigned to C-8.

Rings A, B and D constitute a phenanthrene unit and protons at C-1 and C-11 appear at low field (8·20–8·30) as they come under ring current effects. Selective ^{1}H decoupling at 8·20 sharpens the carbon signals at 122·96 and 123·95, which are shielded from the well-known 'γ' steric effect.[6] Since H-11 appears upfield (8·21) when compared with H-1, the peak at 122·96 has been assigned to C-11.

The protons at C-2 and C-9 appear at higher field (7·49–7·56). Irradiation at 7·00 sharpens the peak at 128·15. Since H-9 appears at the highest field in the proton spectrum, C-9 has been assigned 128·15. Irradiation at 7·50 sharpens peaks at 126·44 and 128·15. Since H-2 appears downfield when compared with H-9, the peak at 126·44 has been assigned to C-2.

Rings C and D constitute a naphthalene unit and the carbons at peri-positions (C-3 and C-4) are expected to appear at low field. Irradiation at 7·80 sharpens the peak at 129·99 since H-3 appears upfield (7·86) when compared with H-4, the peak at 129·99 has been assigned to C-3.

In addition to selective decoupling, changes in chemical shifts due to substituents in the ring have been used to confirm the assignments. The B, C and D rings of benzanthrone constitute a phenalenone (**1**) ring, and the values for C-2, C-3, C-4 and C-6 for benzanthrone (**3**) and 3-methoxybenzanthrone (**9**) are in agreement with the values obtained for phenalenone (**1**) and 3-methoxyphenalenone (**2**) respectively.

3.2. Quaternary carbons

The assignment of the carbonyl shift (C-7) is quite obvious, but assignments of the remaining quaternary carbons remain speculative. The chemical shift of the carbonyl resonance in compounds (**4**–**10**) is dependent on the substitution pattern in the benzanthrone ring.

The tentative designations of the remaining quaternary carbons in benzanthrone are based upon the differences that are observed in the chemical shifts of the quaternary carbons of its derivatives. As in the case of other polycyclic aromatic compounds,[7] C-11b and C-11c will be the most shielded of those arising from quaternary centres, and C-3a and C-11a will be least shielded. C-3a, C-6a, C-11b and C-11c are assigned, based on the values obtained for phenalenone (**1**). The chemical shift of C-11a remains unchanged in compounds (**9**) and (**10**). Hence C-11a has been assigned 136·11.

3.3. Substituent effects

Carbon-13 chemical shifts primarily reflect the electronic charges at the carbon, and substituent-induced chemical shifts (SCS) have similarly been shown to reflect the distribution of charge caused by the substituent. The distribution of charges can be influenced by many factors—mesomeric, inductive, steric or direct electric field effects in addition to magnetic anisotropy effects. Substituent effects in naphthalenes and anthracenes are parallel to those found in substituted benzenes, and substituent chemical shift values are remarkably additive. These generalisations are also applicable to benzanthrone derivatives. Since rings C and D constitute a naphthalene unit, substitution in the ring C or D mainly affects the chemical shifts of carbons in rings C and D.

In the case of 3-chlorobenzanthrone (**5**), the carbon attached to the halogen group is shifted downfield by 4·28 ppm and the carbon (C-4) at the peri-position is shifted upfield (3·82 ppm). The highfield shift of C-4 is due to the γ (*gauche*)-effect. As expected, C-6 is also shifted downfield (1·62 ppm). A chloro substituent at the 2 position, as in the case of 2-chlorobenzanthrone (**4**), shifts C-2 downfield by 6·25 ppm. C-3 and C-4 are shifted downfield by less than 1 ppm, and C-6 is subjected to a downfield shift of 0·15 ppm. This is in keeping with the observation that substituent chemical shifts in 2-chloronaphthalene closely resemble those in benzene. In the case of 3-bromobenzanthrone (**6**), C-3 is shifted upfield by 4·56 ppm, and this is explained on the basis of a 'heavy atom effect'; a downfield shift of C-2 (3·99 ppm) is also observed.

The introduction of a nitro group in the 3-position, as in the case of 3-nitrobenzanthrone (**7**), results in the downfield shift of C-3 by 17·52 ppm; C-1 and C-2 are shifted upfield and C-4 is moved upfield by 4·56 ppm. The highfield shift of carbons *ortho* to a nitro group in naphthalene derivatives is due to direct electric field effects.[1] In the case of 11-nitrobenzanthrone C-11 is shifted downfield by 26·41 ppm, which is 8·89 ppm higher than the shift observed in the 3-nitro derivative. This is because substituent chemical shifts in ring A resemble those observed in benzene derivatives. Hence C-10 is moved upfield by 5·14 ppm and C-9 downfield by 0·30 ppm, whereas C-2 and C-1 in compound (**7**) are moved upfield by 2·22 ppm and 1·65 ppm respectively.

A methoxy substituent at the 3-position in 3-methoxybenzanthrone (**9**) causes a somewhat larger downfield shift of C-2 (27·62 ppm) than that of a chloro, bromo or methyl substituent. This is attributed to the carbon of the methoxy group having the same effect as a β-carbon relative to C-3.[8] The oxygen atom is regarded here as an 'α-C' to C-3. The γ-effect (upfield shift) on C-2 (21·86 ppm) can be explained by similar reasoning.

The introduction of a methyl substituent at the 4-position as in 4-methylbenzanthrone (**10**) causes only a slight upfield shift (0·39 ppm) at C-5. The carbon attached to the methyl group is moved downfield by 8·09 ppm. The highfield shift of C-3 has been attributed to polarization of the CH bond caused by steric interactions.

It is possible to predict the substitution pattern in benzanthrone derivatives with the help of ^{13}C n.m.r. spectroscopy. It has been found that the substitution in the ring C or D affects only the chemical shifts of carbons in rings C and D and the substituent chemical shifts are similar to those observed in naphthalene derivatives and are additive. Substituent chemical shifts in ring A resemble those observed in benzene derivatives.

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