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^{13}C NMR Study of Derivatives of Dibenzobarrelene, Anthraquinone and Anthracene

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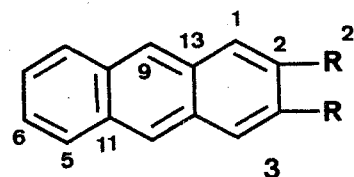
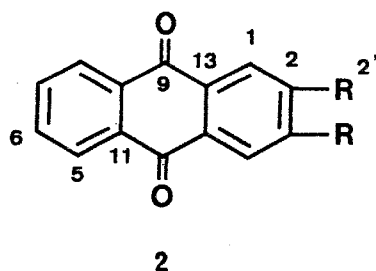
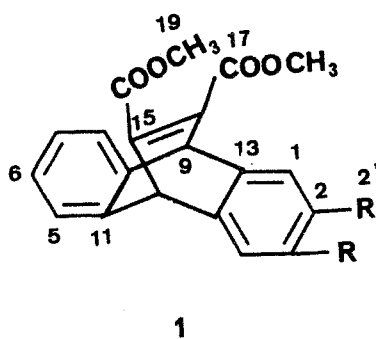
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Carbon-13 chemical shifts of 22 derivatives of dibenzobarrelene, anthraquinone and anthracene are reported, each of which includes a symmetrical *ortho*-benzene moiety. The assignment of the chemical shifts of the aromatic carbons of these derivatives was achieved by correlation with the corresponding ^{13}C chemical shifts of *ortho*-disubstituted benzenes.

KEY WORDS ^{13}C NMR 2,3-Di-X'-11,12-carbomethoxydibenzobarrelenes 2,3-Di-X'-9,10-anthraquinones
2,3-Di-X'-anthracenes

INTRODUCTION

Although there have been several ^{13}C NMR investigations dealing with the recording and assignment of *para* and *meta*-disubstituted benzene derivatives having two like or two different substituents,¹ there has hitherto, to my knowledge, been no systematic report on symmetrically disubstituted benzene derivatives. The ^{13}C NMR spectra of symmetrically substituted *ortho*-disubstituted aromatic compounds are only sporadically found in the literature within the series of 1,2-di-X'-benzenes² and 2,3-di-X'-naphthalenes.³ This work provides, for the first time, ^{13}C NMR chemical shift data for several classes of compounds, namely 2,3-di-X'-carbomethoxydibenzobarrelenes (1), 2,3-di-X'-9,10-anthraquinones (2) and 2,3-di-X'-anthracenes (3).



RESULTS AND DISCUSSION

The chemical shifts of the 2,3-di-X'-dicarbomethoxydibenzobarrelenes (1) are presented in Table 1. The chemical shifts of the 2,3-di-X'-9,10-anthraquinones (2) are presented in Table 2 together with those of the parent compound anthraquinone, the chemical shifts of which have already been published.⁴ The chemical shifts of the 2,3-di-X'-anthracenes (3) are given in Table 3 together with those of the parent compound anthracene, the chemical shifts of which have already been published.⁵

The assignment of the chemical shifts of the aromatic carbons of the substituted moiety of the compounds mentioned above, and presented in Tables 1-3, was achieved by correlation with the corresponding chemical shifts of the 1,2-di-X'-benzenes. [For correlation the ^{13}C chemical shifts in Ref. 2 (I-VII), supplemented by the measured data of the ultimate paragraph of the present Experimental section, are first normalized to CDCl_3 , $\delta = 77.00$ (TMS). The correlation coefficient for the compounds 1 always exceeded 0.98, and for compounds 2 and 3 they exceeded 0.94.] The ^{13}C NMR chemical shifts of 1,2-di-X'-benzenes, which have not been published earlier, i.e. for X' = CN, CHO and OCOCH_3 , are presented under Experimental.

EXPERIMENTAL

The synthesis of the 2,3-di-X'-dicarbomethoxydibenzobarrelenes (1) has been published elsewhere.⁶ The 2,3-di-

Table 1. ¹³C NMR chemical shifts (ppm) of dimethyl 2,3-di-X'-9,10-etheno-9,10-dihydroanthracene-11,12-dicarboxylates (1)

X	H	OH	OCH ₃	OCOCH ₃	F ^a	CH ₃	Cl	COOCH ₃	CN
C-1	124.38	112.05	108.98	118.90	113.35	125.21	125.64	124.19	127.69
C-2	125.52	144.19	147.54	141.93	147.31	133.14	129.01	129.69	114.91
C-5	124.38	123.48	123.43	123.86	123.81	123.54	124.03	124.08	124.29
C-6	125.52	125.32	125.21	125.59	125.70	125.21	125.88	125.97	126.13
C-9	52.36	51.92	52.30	51.87	51.65	52.14	51.41	52.19	51.44
C-11	146.43	144.54	146.40	146.78	146.89	147.21	146.50	147.16	145.49
C-13	143.67	140.69	144.35	139.02	143.01	144.14	142.62	142.41	142.00
C-15	143.67	136.43	136.70	143.44	140.15	141.44	143.77	146.29	149.69
C-17	165.73	166.46	165.98	165.44	165.44	165.93	165.39	165.28	164.31
C-19	52.36	52.46	52.30	52.25	52.36	52.14	52.56	52.41	52.09
C-2'			56.35	168.02		19.30		167.60	113.08
C-2''				20.38				52.50	

^a Coupling constants (1st order): C-2, F = 260, C-1, F = 9.8 Hz.

Table 2. ¹³C NMR chemical shifts (ppm) of 2,3-di-X'-9,10-anthraquinones (2)

X	H	OCH ₃	OCOCH ₃	F ^a	CH ₃	Cl	COOCH ₃	-(CH ₂) ₂ -
C-1	127.30	108.38	122.68	116.48	128.07	129.94	128.01	127.69
C-2	134.20	153.90	147.00	154.40	143.87	139.98	134.62	144.41
C-5	127.30	126.94	127.31	127.43	126.94	127.49	127.64	126.88
C-6	134.20	133.62	134.22	134.40	133.67	134.58	134.28	133.62
C-9	183.20	182.32	181.40	180.92	183.02	181.34	181.40	182.91
C-11	133.60	133.62	133.41	133.22	133.67	133.19	133.10	133.62
C-13	133.60	128.45	132.28	131.10	131.47	132.49	136.40	130.81
C-2'		56.45	167.20		20.00		166.40	29.17
C-2''			20.43				53.11	22.43

^a Coupling constants (1st order): C-2, F = 263, C-1, F = 17.1, C-13, F = 3 Hz.

Table 3. ¹³C NMR chemical shifts (ppm) of 2,3-di-X'-anthracenes (3)

X	H	OCH ₃	OCOCH ₃	F ^a	CH ₃	CHO	COOCH ₃	-(CH ₂) ₂ -
C-1	128.10	104.99	120.41	113.57	126.90	136.35	131.20	126.08
C-2	125.30	150.23	141.12	150.26	135.30	133.78	127.69	136.39
C-5	128.10	127.64	127.96	128.53	128.00	128.63	128.34	128.08
C-6	125.30	124.56	125.75	127.78	124.70	127.74	126.77	124.70
C-9	126.20	123.92	126.02	124.95	124.70	129.50	127.91	124.88
C-11	131.70	130.92	131.84	131.70	131.30	130.88	130.44	131.33
C-13	131.70	128.66	129.53	128.40	131.30	132.03	133.14	130.69
C-2'		55.81	168.41		20.40	192.36	168.03	30.03
C-2''			20.59				52.46	23.39

^a Coupling constants (1st order): C-2, F = 258, C-1, F = 7.7, C-13, F = 2 Hz.

X'-9,10-anthraquinones (2) and the 2,3-di-X'-anthracenes (3) were prepared by generally known methods.^{6,7}

Phthalonitrile and phthaldehyde were purchased from Aldrich Chemical and 1,2-diacetyloxybenzene was prepared by pyridine-catalysed condensation of catechol and acetic anhydride.

The ¹³C NMR spectra were recorded on (A) Bruker

WH 90 (22.64 MHz), (B) Bruker WH 250 (62.90 MHz) and (C) Bruker WM 400 (100.61 MHz) spectrometers. The pulse width was 6 μs for A, 8 μs for B and 4 μs for C and FIDs were collected in 8K data points for A, 16K for B and 16K for C with a sweep width of 1000 Hz for A, 15.625 kHz for B and 25.000 kHz for C. The flip angles were 30°, 30° and 50°, respectively. The number

of scans ranged from 250 to 20 000, depending on solubility. The samples were recorded in CDCl_3 at ambient temperature applying internal deuterium lock, and are referenced to the central peak ($\delta = 77.00$) corresponding to $\delta = 0.00$ for TMS; the chemical shifts are accurate to at least 0.05 ppm. ^{13}C NMR of 1,2-di-X'-benzenes: 1,2-dicyanobenzene, 115.30 C-1, 133.20 C-3, 133.50 C-4, 115.88 ppm CN; 1,2-diformylbenzene, 136.38 C-1, 133.73 C-3, 131.08 C-4, 192.33 ppm CHO; 1,2-

diacetyloxybenzene, 141.90 C-1, 123.10 C-3, 126.10 C-4, 167.60 CO, 20.10 ppm CH_3 .

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