¹H and ¹³C Nuclear Magnetic Resonance Studies of Ethenyl-Substituted Benzenoid Aromatic Compounds

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¹H and ¹³C NMR studies were carried out on 1-ethenylnaphthalene, 2-ethenylnaphthalene, 9-ethenylanthracene, 9-ethenylphenanthrene, 1-ethenylpyrene and 1-ethenylperylene. Assignments of proton and carbon resonances were made with the aid of 2D COSY, 2D HETCOR, 2D COLOC, 2D COLOCS, ³J(H,C) INAPT, and NOE difference spectral techniques.

KEY WORDS ¹H NMR ¹³C NMR Ethenyl-substituted benzenoid aromatics

INTRODUCTION

The unequivocal assignment of resonances in the ¹H and ¹³C NMR spectra of polycyclic aromatic hydrocarbons is not without problems. The typically congested nature of the ¹H NMR spectra of such compounds makes unambiguous assignments, based on the observation of coupling constants or of recognizable splitting patterns (e.g. AB, ABX, ABMX), exceedingly difficult.¹⁻⁵ Until recently, the assignment of ¹³C resonances generally relied on the availability of specifically labelled substrates, the use of reported chemical shift substitution constants or the prior identification of coupled protons. The advent of high-field NMR spectrometers and of two-dimensional NMR techniques has greatly facilitated the assignment of both ¹H and ¹³C resonances. In general, however, the task is still a challenging one.

We have recently prepared a number of deuterio- and ¹³C-labelled ethenyl-substituted polycyclic aromatic compounds for studies relating to their polymerization. Considering the industrial interest in such monomers, we were surprised to find little in the literature regarding the NMR analysis of the parent alkenes.^{6–8} Therefore, we have recorded the NMR spectra of a series of six such compounds and, in all but one of these, we have unambiguously assigned each of the proton and carbon resonances using two-dimensional and other pulse sequence NMR techniques.

Five NMR techniques were used to accomplish the assignments, illustrating the way in which a combination of relatively straightforward NMR experiments can solve difficult structural problems.

For less complex aromatic polycyclics, proton resonance assignments can usually be made by the determination of H-H coupling relationships apparent with two-dimensional correlation spectroscopy (COSY).⁹ Once the protons have been assigned, identifying the

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proton-bearing carbon atom resonances is straightforward by two-dimensional heteronuclear chemical shift correlation (HETCOR) spectroscopy.¹⁰ Quaternary carbon atom resonances of such compounds may be assigned by the observation of long-range heteronuclear coupling.¹¹ The one-dimensional INAPT¹² (selective INEPT¹³) and the two-dimensional COLOC/ COLOCS^{11,14,15} experiments allow the optimized observation of ³J(H,C) coupling.

As the size of a condensed aromatic system increases, the problem of overlap renders the assignment of proton resonances more difficult. Although general trends which relate to the expected chemical shifts of ortho/para versus meta disposed protons and the recognition of isolated spin systems assist, unambiguous assignments frequently cannot be achieved. Without the assignment of proton resonances, HETCOR and INAPT techniques are of limited value. In such cases, the COLOC/COLOCS technique is often the NMR experiment of choice. The use of two-dimensional spectroscopy^{16,17} INADEQUATE to determine carbon-carbon connectivity is often impractical owing to the long acquisition times required for such experiments.

The six compounds (1-6) studied in this work (1- and 2-ethenylnaphthalene, 9-ethenylanthracene, 9-ethenylphenanthrene, 1-ethenylpyrene and 1-ethenylperylene) have all been assigned essentially using COSY, HETCOR, INAPT and COLOC/COLOCS techniques. The ethenyl substituent also allowed additional information to be obtained from NOE effects observed on irradiation of the alkenyl protons.¹⁸

RESULTS

For all the compounds other than 1-ethenylnaphthalene (1) and 9-ethenylanthracene (3), the alkenic hydrogen resonances were directly assigned by observation of ${}^{3}J(H,H)$ coupling constants.^{8,18-20} The H-1' resonances

















in 1 and 3 were partially obscured by the overlapping resonances of aromatic hydrogens. In both cases, however, the chemical shift of H-1' could be established by decoupling H-2'. The chemical shifts and coupling constants for the alkenic hydrogen resonances are reported in Table 1 and the chemical shifts of the aromatic hydrogen resonances are reported in Table 2.

When hydrogen assignments could be made to unique chemical shifts, assignment of carbon resonances follow from APT and HETCOR experiments. Chemical shifts of carbon resonances are reported in Table 3. ¹H and 13 C chemical shift increments on ethenyl substitution of the parent hydrocarbon^{4,21,22} are reported in Tables 2 and 3, respectively.

Table 1. ¹H NMR chemical shifts (ppm), multiplicity, and coupling constants for the alkenic hydrogen resonances of compounds 1-6

Compound	H-1'	H-2', cis	H-2', trans	
1	7.42 (dd, 17.3 Hz, 11.0 Hz)	5.41 (dd, 11.0 Hz, 1.7 Hz)	5.74 (dd, 17.3 Hz, 1.7 Hz)	
2	6.80 (dd, 17.6 Hz, 10.9 Hz)	5.27 (d, 10.9 Hz)	5.80 (d, 17.6 Hz)	
3	7.35 (dd, 17.9 Hz, 11.5 Hz)	5.88 (dd, 11.5 Hz, 2.0 Hz)	5.51 (dd, 17.9 Hz, 2.0 Hz)	
4	7.44 (dd, 17.2 Hz, 10.9 Hz)	5.50 (dd, 10.9 Hz, 1.7 Hz)	5.84 (dd, 17.2 Hz, 1.7 Hz)	
5	7.59 (dd, 17.3 Hz, 11.0 Hz)	5.46 (dd, 11.0 Hz, 1.4 Hz)	5.85 (dd, 17.3 Hz, 1.4 Hz)	
6	7.38 (dd, 17.3 Hz, 11.0 Hz)	5.46 (dd, 11.0 Hz, 1.5 Hz)	5.80 (dd, 17.3 Hz, 1.5 Hz)	

Proton	1	2	3	4	5	6
1	_	7.65	8.22	7.86		_
		(-0.2)	(0.3)	(0.1)		
2	7.57		7.34	7.56	8.00	7.59
	(0.1)		(0.0)	(0.0)	(0.1)	(0.2)
3	7.39	7.55	7.34	7.58	7.90	8.11
	(-0.1)	(0.1)	(0.0)	(0.0)	(~0.2)	(0.0)
4	7.72	7.70	7.86	8.62	7.80	8.13
	(-0.1)	(-0.1)	(0.0)	(0.0)	(-0.2)	(0.0)
5	7.78	7.71	—	8.69	7.80	7.45
	(0.0)	(-0.1)		(0.1)	(-0.2)	(0.1)
6	7.43	7.36		7.60	7.96	7.65
	(-0.1)	(-0.1)		(0.0)	(-0.1)	(0.1)
7	7.44	7.38	—	7.62	7.80	7.65
	(-0.1)	(-0.1)		(0.1)	(-0.1)	(0.1)
8	8.05	7.71		8.12	7.96	7.45
	(0.3)	(-0.1)		(0.3)	(-0.1)	(0.1)
9					7.84	8.13
					(-0.2)	(0.0)
10	—	—	8.25	7.82	8.13	8.16
			(-0.1)	(0.2)	(0.1)	(0.0)
11		_				7.64
						(0.1)
12		_	—	—		7.92
						(0.4)

1-Ethenylnaphthalene (1)

The aromatic region of the ¹H NMR spectrum consists of two one-proton deshielded multiplets, two oneproton broad doublets and an unresolved three-proton multiplet.

Irradiation of the H-2' protons resulted in observation of a 3.1% NOE effect at the doublet at 7.57 ppm (7.2 Hz).⁸ This resonance is assigned to H-2 on the basis of the simplicity of its coupling and the results of INAPT experiments. No substantial NOE effect was observed between H-2' and H-8, and this may reflect a conformational preference avoiding 'fjord' type interactions of these hydrogens.⁵ Weak *meta* coupling (*ca.* 1 Hz) between the doublets at 7.57 and 7.72 ppm (8.1 Hz) was observed in the COSY spectrum of the compound. The latter resonance may be assigned to H-4. Further, both H-2 and H-4 are coupled to a proton in the unresolved multiplet which centres at 7.39 ppm, allowing assignment of H-3.

The most deshielded multiplet (8.05 ppm) displayed fine structure consistent with the terminal proton of an XAA'Y system and can be assigned to H-8. Coupling of H-8 to a proton centred at 7.44 ppm in the unresolved multiplet allows this to be assigned to H-7. The deshielding of H-8 may be explained by the familiar anisotropy of the *peri* ethenyl substituent.⁵ Such

Table 3. ¹³C NMR chemical shifts of compounds 1-6 (ppm) with substituent chemical shift constants in parentheses

Carbon	1	2	3	4	5	6
1	135.51 (7.5)	126.35 (-1.7)	125.95 (-2.2)	128.66 (0.4)	132.12 (7.5)	135.07
2	123.55 (-2.5)	134.92 (8.9)	125.30 (0.0)	126.71 (0.4)	123.46 (-2.0)	124.38
3	125.55 (-0.5)	123.07 (-2.9)	125.05 (-0.2)	126.49 (0.2)	124.85 (0.3)	а
3a		_	/		130.79 (-0.1)	b
3b	—		_			ь
4	128.04 (0.0)	128.09 (0.1)	128.55 (0.5)	122.48 (0.1)	127.26 (0.3)	а
4a	133.51 (-0.2)	133.09 (-0.6)	131.35 (-0.5)	130.23 (-1.7)		_
4b	_		_ /	130.29 (-1.6)	_	
5	128.45 (0.5)	127.60 (-0.4)		123.03 (0.6)	127.09 (0.1)	с
5a					131.29 (0.4)	
6	125.67 (-0.3)	125.83 (-0.2)		126.44 (0.3)	124.85 (0.3)	d
6a	_	_	-	_ ,	_	ь
6b		_	_			ь
7	125.98 (0.0)	126.15 (0.2)	_	126.60 (0.1)	125.74 (0.2)	d
8	123.68 (-4.3)	127.99 (0.0)	_	124.59 (-3.7)	125.08 (0.5)	c
8a	131.05 (-2.7)	133.49 (-0.21)	129.17 (-2.6)	130.50 (0.4)	130.71 (-0.2)	_
9		_	133.58 (7.4)	134.63 (8.0)	127.36 (0.4)	а
9a	_	_		'		b
9b					_	b
10	_		126.29 (0.1)	124.59 (-2.0)	122.79 (-4.2)	120.33
10a	_	_		131.76 (1.7)	127.92 (-3.0)	
10b		_	_		124.68 (0.1)	_
10c					124.73 (0.1)	_
11		_	_			c
12	—		<u> </u>	—		123.59
12a			—		_	ь
12b		_	_		_	128.83
1′	134.29	136.86	133.47	135.03	134.08	134.22
2′	116.99	114.07	112.85	117.51	116.95	116.87
Inombi		not mode .				

Unambiguous assignments not made:

^a 120.29, 120.16, 120.12.

^b134.65, 133.31, 132.35, 131.53, 131.35, 131.22, 131.00.

° 126.56 (two carbon resonances), 126.52.

^d 127.79, 127.72.

deshielding of *peri* hydrogens was repeatedly observed in the spectra of all the compounds under investigation. Weak *para* coupling was observed in the COSY spectrum between H-8 and the multiplet at 7.78 ppm, and irradiation of the multiplet at 8.05 ppm results in the loss of one coupling from the multiplet at 7.78 ppm. This latter resonance is coupled to a proton centred at 7.43 ppm. These resonances are therefore assignable to H-5 and H-6, respectively. Interestingly, the nature of the couplings, and the difference in chemical shifts (*ca.* 0.25 ppm) of the resonances associated with H-5 and H-8 in this compound are very similar to those observed for H-1 and H-4 in 9-ethenylanthracene.

The quaternary carbon resonances of 1 were assigned by the use of the INAPT technique for the selective observation of ${}^{3}J(H,C)$ coupling. Irradiation of *trans*-H-2' results in an enhancement of the quaternary carbon resonance at 135.51 ppm (C-1). Irradiating H-2 enhances the methine at 128.04 (confirming our assignment of C/H-4), the C-1' resonance at 134.29 and the quaternary carbon at 131.05 (C-8a). Irradiation of H-8 also enhances C-1, the methine at 125.67 (C/H-6) and the quaternary carbon resonance at 133.51 ppm (C-4a).

2-Ethenylnaphthalene (2)

The aromatic region of the ¹H NMR spectrum consists of a singlet and a doublet of doublets, each integrating for a single hydrogen resonance. Two multiplets make up the remainder of the spectrum, the more shielded resulting from three overlapping resonances, the less shielded from the remaining two protons.

On irradiation of *trans*-H-2' a 1.8% NOE effect on the singlet at 7.65 ppm and a 4.4% effect on the doubledoublet at 7.55 ppm (8.6 Hz, 1.7 Hz) were observed. These resonances can be attributed to H-1 and H-3, respectively. Coupling was noted in the 2D COSY spectrum between H-3 and a resonance centred at 7.70 ppm in the more shielded multiplet, which was therefore assigned to H-4.

The pair of resonances associated with H-5 and H-8 overlap and comprise the remainder of the three-proton multiplet (7.71 ppm). Similarly, the H-6 and H-7 signals are superimposed and form the less shielded multiplet. The centres of the resonances, however, could be assigned in the COLOCS spectrum of this compound at 7.36 and 7.38 ppm, respectively.

The extensive superimposition of hydrogen resonances allows only C-1, -3, -1' and -2' to be identified by the use of APT and HETCOR spectra alone. Use of the INAPT sequence permitted the identification of C-1 and C-4a $[^{3}J(H,C)$ enhanced on irradiation of H-2' and H-3, respectively]. By elimination, the remaining quaternary carbon is therefore C-8a. Further use of the INAPT technique could not be made, owing to the necessity for selective proton irradiation. The remaining carbon resonances were assigned using a combination of COLOCS and HETCOR techniques. ³J(H,C) coupling was observed in the COLOCS spectrum between H-1 and C-8 and between C-8 and H-6, identifying the C-6 and -8 carbon resonances. The resonance of C-7 can be assigned by its ${}^{1}J$ coupling to H-7 (HETCOR), and ${}^{3}J$ coupling between H-7 and C-5 allows the remaining resonances of C-5 and C-4 to be identified.

9-Ethenylanthracene (3)

The aromatic region of the ¹H NMR spectrum consists of three multiplets and a singlet. The singlet integrates for a single proton, the two deshielded multiplets from two protons each and the shielded multiplet from the remaining four protons. Owing to the plane of symmetry in the molecule, assignments need only be made for H-1, -2, -3, -4 and -10.

The singlet is assignable to H-10. The two deshielded multiplets can be assigned to the pairs of protons H-1 and -8 and H-4 and -5. The most deshielded multiplet appears as a superimposition of a singlet and two doublets with fine structure, similar to those observed in the four-spin system of 1-ethenylnaphthalene. Irradiation at H-2' of the ethenyl substituent results in a 9.4% NOE effect at the more deshielded of these two multiplets (8.22 ppm), and this was therefore assignable to H-1. The more shielded of these multiplets (7.86 ppm) was assigned to H-4 and, as expected, is very similar to the observed chemical shift of H-1 in anthracene (7.9 ppm).

The four-proton multiplet consists of six main lines, and is produced by the overlapping resonances of the apparently isochronous pairs of protons H-2 and -7 and H-3 and -6.

The quaternary carbon atoms were assigned by the use of two INAPT experiments. Irradiation of the *trans*-H-2' results in enhancement of the quaternary carbon resonance at 133.58 ppm (C-9), whereas irradiation of H-4 enhances the quaternary carbon resonance at 129.17 ppm (C-8a) and the resonance of C-2 (125.30 ppm). The remaining carbon resonances were thereby established as C-4a and C-3.

9-Ethenylphenanthrene (4)

The ¹H NMR spectrum consists of four deshielded multiplets, a singlet and an unresolved multiplet at higher field. Each lower field multiplet and the singlet integrate for one proton. The remaining multiplet originates from the remaining four protons.

The singlet can be unambiguously assigned to H-10. Irradiation at trans-H-2' of the ethenyl substituent results in observation of a 7.6% NOE effect at H-10; no NOE effect was observed at H-8 (cf. ethenylnaphthalene). The four deshielded multiplets originate from the resonances of H-1, -4, -5 and -8 and appear at 7.86, 8.12, 8.62 and 8.69 ppm, respectively. The chemical shifts of H-1 and H-4 in phenanthrene are 7.80 and 8.62 ppm, respectively. Considering that the chemical shift substitution constants for the ethenyl substitution of benzene are small for all ring positions $(-0.10 \text{ to } 0.06 \text{ for } {}^{1}\text{H})$, the two less shielded multiplets are assignable to H-4 and -5 and the more shielded pair correspond to H-1 and -8 [this assumption was later confirmed by the observation of ${}^{3}J(H,C)$ coupling in INAPT and COLOCS experiments]. Weak para couplings (ca. 1.0 Hz), observed in the 2D COSY spectrum, between the signals at 8.69 and 8.12 ppm, and between those at 8.62 and 7.86 ppm, allow the assignment of these resonances to each pair of para related protons. Further, the resonance of the multiplet at 8.12 ppm is significantly deshielded when compared with the H-1

resonance of unsubstituted phenanthrene (7.80 ppm), and may therefore be assigned to H-8 (again this assumption was later confirmed by a COLOCS experiment). The remaining 'bay' hydrogen resonances⁵ follow automatically.

The unresolved multiplet originates from the overlapping resonances of H-2, -3, -6 and -7. Their assignments are straightforward via their couplings to H-1, -4, -5 and -8, clearly observed in the COSY spectrum. The assigned chemical shifts apply to the centre of resonance; individual couplings were not resolved.

The quaternary carbon resonances of the phenanthrene were established by a series of INAPT experiments. Thus, irradiation of H-2' results in ${}^{3}J(H,C)$ enhancement of the carbon resonance at 134.63 (C-9), irradiation of H-4 that of the resonances at 131.76 (C-10a) and 126.71 (C-2), irradiation of H-5 that of the resonances at 130.50 (C-8a) and 126.60 (C-7) and irradiation of H-8 that of the signals at 130.29 (C-4b) and 126.44 ppm (C-6). The remaining quaternary resonance is C-4a (130.23 ppm).

1-Ethenylpyrene (5)

The ¹H NMR spectrum of 5 consists, in order of increasing shielding, of an isolated doublet, an overlapping series of lines consisting of three doublets and a multiplet and an unresolved multiplet. The four doublets consist of one proton each, the multiplet in the overlapping series of lines integrates for two protons and the remaining three protons are superimposed in the unresolved multiplet.

The most deshielded resonance is the doublet at 8.13 ppm (9.3 Hz), and this can be assigned to the *peri* deshielded H-10 (an assumption later confirmed by the COLOC experiment). Irradiating this proton collapses the doublet at 7.84 ppm (9.3 Hz) and this resonance was established as H-9. Irradiation of *trans*-H-2' results in an 11.7% NOE effect on the doublet at 8.00 ppm (8.1 Hz, H-2). Analogously to 1-ethenylnaphthalene, no NOE effect was observed between H-2' and H-10. A strong cross-peak was observed in the COSY spectrum between H-2 and the doublet at 7.90 ppm (8.1 Hz), hence this resonance was assigned to H-3.

The remaining proton resonances can be assigned by comparison of the chemical shifts of the two multiplets [(two-proton) 7.96 and (three-proton) 7.80 ppm)], with the chemical shifts of the three hydrogen species in pyrene [8.10 H-1), 7.93 (H-2) and 8.00 ppm (H-4)].⁴ Since the hydrogens to be identified are remote from the ethenyl substituent, it is clear that the two multiplets may be partially assigned. Hence the deshielded multiplet originates from overlapping resonances of H-6 and -8 and the shielded multiplet from H-4, -5 and -7. Similar comparison of the ¹³C chemical shifts of C-1, -2 and -4 of pyrene (124.6, 125.5 and 127.0 ppm, respectively) with those observed for the α -carbons of H-4 to H-8 (C-6 and -8, 124.85, 125.08 ppm; C-4, -5 and -7, 127.26, 127.09 and 125.74 ppm) are also in good agreement with our partial assignment.

Many of the ¹³C resonances of 5 cannot be identified by the use of APT and HETCOR spectra, a consequence of the superimposition of their associated proton resonances. With partial assignment of the hydrogen resonances the use of the INAPT sequence permits further assignment of the carbon peaks. Irradiation of *trans*-H-2' results in enhancement of the lowest field quaternary carbon resonance at 132.12 ppm (C-1). The remaining resonances were identified by a COLOC experiment, the additional information provided by observation of both ${}^{1}J(H,C)$ and ${}^{3}J(H,C)$ [in comparison with the COLOCS experiment in which ${}^{1}J(H,C)$ is suppressed] proving useful in confirming our proton assignments. The greater sensitivity of the COLOC experiment was also found to be useful.

No ${}^{3}J(H,C)$ coupling was observed for the carbon resonance at 125.74 ppm. Thus, as expected from its chemical shift (c.f. C-2 of pyrene, 125.5 ppm), this can be assigned to C-7. The resonance at 127.26 ppm is ${}^{3}J(H,$ C) coupled to H-3, whereas that at 127.09 ppm is ${}^{3}J(H,$ C) coupled only to a proton in the deshielded multiplet. These resonances are thereby established as C-4 and C-5, respectively. Of the remaining two protonated carbons, the resonance at 124.85 ppm (superimposed with the signal of C-3) is ${}^{3}J(H,C)$ coupled to a proton in the deshielded multiplet and is assigned to H-6. By elimination the remaining protonated carbon resonance [weakly ${}^{3}J(H,C)$ coupled to H-9] is therefore H-8.

The quaternary carbon resonances appear at two chemical shift ranges. Thus the resonances of the quaternary carbon atoms on the perimeter of the pyrene appear at 132.12, 131.29, 130.79, 130.71 and 127.92 ppm (c.f. C-3a of pyrene, 130.9 ppm), whereas the internal quaternary carbons appear at 124.73 and 124.68 ppm (c.f. C-3b of pyrene, 124.6 ppm).

From the COLOC experiment the resonance at 124.73 ppm is ${}^{3}J(H,C)$ is coupled to hydrogens in the shielded multiplet, whereas that at 124.68 ppm is coupled to H-3 and to H-10. These resonances are assigned to C-10c and C-10b, respectively. Considering the remaining four quaternary carbons, the resonance at 131.29 ppm (C-5a) is ${}^{3}J(H,C)$ coupled only to protons in the shielded multiplet, the resonance at 130.79 ppm (C-3a) is ${}^{3}J(H,C)$ coupled to H-2 and to a proton in the shielded multiplet and the resonance at 130.71 ppm (C-8a) is coupled to H-10. Finally, by elimination, the resonance at 127.92 ppm must be assigned to C-10a and is ${}^{3}J(H,C)$ coupled to H-2 and H-9.

1-Ethenylperylene (6)

1-Ethenylperylene exhibits remarkably different physical properties to the other aromatic alkenes of this series. Its melting point is high (162–164 °C; c.f. 1ethenylpyrene, 88–89 °C), and its solubility is very low in most organic solvents (including those most commonly employed in NMR spectroscopy). NMR analysis of this compound is therefore difficult and, to our knowledge, no data have yet appeared in the literature.

The low solubility of 1-ethenylperylene has prevented us from completely assigning its carbon spectrum (although this may be achieved by the techniques used in this work with sufficient acquisition time). However, we have assigned the ¹H NMR spectrum of this compound, and report our partial assignment of the ¹³C NMR spectrum. Further investigations into the application of two-dimensional double-quantum-filtered-coherence NMR^{23,24} to the assignment of the spectra of this molecule are continuing.

The aromatic region of the ¹H NMR spectrum consists of three superimposed multiplets and an isolated doublet. The most deshielded multiplet integrates for four protons, the isolated doublet for a single proton and the two most shielded multiplets for two and four protons, respectively.

Irradiation of the *trans*-H-2' proton results in observation of a 4.7% NOE at a doublet located at 7.59 ppm (7.8 Hz), on the higher field edge of the multiplet centred at 7.65 ppm. The simplicity of the coupling confirms the assignment as H-2. Coupling of this hydrogen to a resonance at 8.11 (COSY) allows the identification of H-3. The isolated doublet is assigned to H-12 (7.92 ppm, 8.3 Hz; later confirmed by INAPT experiments). Use of the COSY spectrum allows the observation of the coupling of this hydrogen to a resonance centred at 7.46 ppm (H-11), and this latter hydrogen is further coupled to a proton at 8.16 (H-10).

The remaining six hydrogen resonances were not resolved. However, they could be assigned in pairs to each of the three multiplets; H-4 and -9 (coupled only to hydrogens in the region 7.38-7.53 ppm) comprised the remainder of the lowest field multiplet 8.09-8.17 ppm, H-6 and -7 (coupled only to hydrogens in the 7.38-7.53 ppm region) comprised the multiplet at 7.61-7.71 ppm and H-5 and -8 (coupled to protons in both regions 7.61-7.71 and 8.09-8.17 ppm) comprised the multiplet at 7.38-7.53 ppm.

Only a small number of resonances in the ¹³C NMR spectrum of this compound have been assigned, owing to the inconveniently long times necessary to obtain spectra from the less sensitive NMR techniques. C-2, -10 and -12 were assigned via HETCOR spectroscopy, whereas the INAPT sequence allowed assignment of C-1 (H-2' irradiation) and C-12b (H-12 irradiation). The remaining resonances in the spectrum are partially assigned to the appropriate 'types' of proton as indicated in Table 3.

EXPERIMENTAL

2-Ethenylnaphthalene was purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. All other alkenes were prepared by the Wittig reaction under the following conditions.

The reaction was maintained under an atmosphere of dry nitrogen. Methyltriphenylphosphonium iodide $(4.85 \times 10^{-3} \text{ mol}, 1.96 \text{ g})$ was dissolved in dry tetrahydrofuran (THF) (20 ml, refluxed over sodium) and cooled to -78 °C. With stirring, lithium diisopropylamide mono(tetrahydrofuran) complex (4.85 \times 10⁻³ ' mol. 3.23 ml of a 1.5 mol dm^{-3} solution in cyclohexane; Aldrich Chemical) was added and the mixture allowed to warm to room temperature overnight (16 h). The mixture was recooled to -78 °C and a solution of the appropriate aldehyde (4.85 \times 10⁻³ mol) in THF (10 ml) was added. The reaction was warmed to room temperature and stirred for 6 h. The solvent was then removed under reduced pressure. The crude product was taken up in a minimum volume of dichloromethane and the alkene was separated and purified by repeated flash column chromatography (E. M. Science, silica gel 60, 230-400 mesh) using hexane as eluent. Immediately after purification, 200 ppm of dihydroquinone were added to inhibit polymerization. The yields were 85-97%. The purity of the samples was established by TLC, ¹H NMR and by comparison of physical data with reported literature values (1-ethenylnaphthalene,²⁵ 9-ethenylanthracene,^{7,26} 9-ethenylphenanthrene,⁶ 1ethenylpyrene,²⁷ 1-ethenylperylene²⁸). All samples were stored at -20° C prior to analysis.

Spectra were recorded on a Varian VXR 300 NMR spectrometer (¹H, 300 MHz; ¹³C, 75 MHz) at room temperature (22 °C) using a 5-mm probe. All samples were freshly prepared (*ca.* 150 mg) dissolved in CDCl₃ (1 ml). The deuterium resonance of the solvent was used as an internal lock, and tetramethylsilane (0.1% w/v) was used as an internal reference for all spectra. Degassing of samples prior to recording NOE difference spectra was found to be unnecessary. Full details of all NMR pulse sequences may be found in the original literature, and these were used without alteration.

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