

## NMR Investigations on Pyrene

The  $^{13}\text{C}$ -H Satellite Spectrum. Calculation of Coupling Constants

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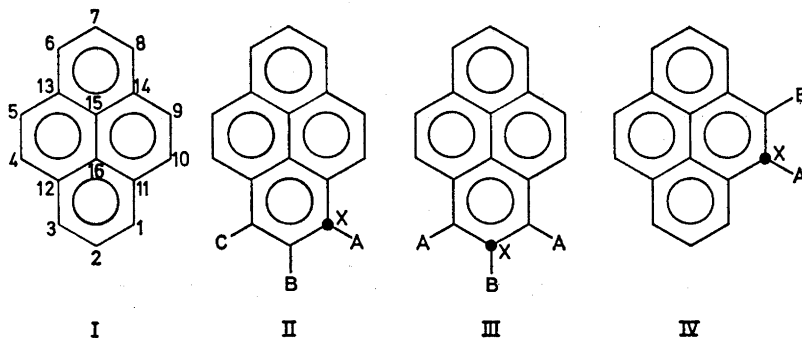
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NMR parameters for pyrene have been determined by analysis of the  $^{13}\text{C}$ -H satellite spectrum of pyrene. A CNDO calculation of a series of coupling constants in pyrene leads to values which parallel the experimental ones well.

From the  $^1\text{H}$  NMR spectrum of pyrene (I) it is only possible to determine  $\nu_{\text{H}(1)}$ ,  $\nu_{\text{H}(2)}$ ,  $\nu_{\text{H}(4)}$ , and  $J_{\text{H}(1)-(2)}$ , whereas the coupling constants  $J_{\text{H}(1)-\text{H}(3)}$  and  $J_{\text{H}(4)-\text{H}(5)}$ , which are without influence on the appearance of the spectrum, cannot be determined in this way.

The last two parameters besides the coupling constants  $J_{\text{C}(1)-\text{H}(1)}$ ,  $J_{\text{C}(2)-\text{H}(2)}$ ,  $J_{\text{C}(4)-\text{H}(4)}$ , the difference  $J_{\text{C}(1)-\text{H}(3)} - J_{\text{C}(1)-\text{H}(2)}$ , and the isotopic shift differences can be determined from the  $^{13}\text{C}$ -H satellite spectrum.\*

This spectrum originates from the three spin systems ABCX (II),  $\text{A}_2\text{BX}$  (III), and ABX (IV), where X denotes  $^{13}\text{C}$  in position 1, 2, and 4, respectively.



\* In the notation for coupling constants, for example  $J_{\text{C}(1)-\text{H}(1)}$ , C means  $^{13}\text{C}$ .

Recently the  $^{13}\text{C}$ -H satellite spectra of pyrene<sup>1\*</sup> and of 2,7-di-*tert*-butylpyrene and 1,3,6,8-tetraisopropylpyrene<sup>2</sup> have been utilized for directly estimating the H(4)-H(5) coupling constant. The latter work demonstrated that this coupling constant is subject to wide variations (8.9-9.8 Hz). In the present work all the parameters mentioned are determined (section A).

We have recorded the  $^{13}\text{C}$ -H satellite spectrum at both 60 MHz and 100 MHz in order to make the assignment of the signals more reliable. The  $^{13}\text{C}$ -H satellite spectrum of 1,3,6,8-tetradeuteriopyrene has also been recorded. From this simplified spectrum one of the parameters,  $J_{\text{H}(4)-\text{H}(5)}$ , can be more safely evaluated. The spectra have been analyzed by computer methods and the calculated parameters are presented.

The amount of information obtained by the analysis of the  $^{13}\text{C}$ -H satellite spectrum appears to be of value in the total analysis of the  $^{13}\text{C}$  resonance spectrum of pyrene, which we hope to carry out in a near future. Until now only the proton-decoupled spectrum has been published by Grant *et al.*<sup>3</sup>

Some of the H-H and  $^{13}\text{C}$ -H coupling constants in pyrene, including long-range couplings, have been calculated by a CNDO/2 procedure (section B).

#### A. $^{13}\text{C}$ -H SATELLITE SPECTRUM OF PYRENE

*Reagents.* Pyrene was purified by recrystallization from ethanol followed by column chromatography on silica gel mixed with 10 % caffeine.<sup>4</sup>

1,3,6,8-Tetradeuteriopyrene was prepared according to de Boer<sup>5</sup> except that phenyllithium was used instead of butyllithium.

*NMR-spectra* were recorded from degassed samples contained in sealed tubes. Satellite spectra were recorded in natural abundance. 125 mg (0.62 mmol) of pyrene were dissolved in 500  $\mu\text{l}$  of carbon disulfide containing 100  $\mu\text{l}$  TMS and a few  $\mu\text{l}$  of methylene bromide as a trigger substance. The tetradeuteriopyrene sample was prepared similarly.

The 60 MHz spectra were recorded on a Varian A-60 spectrometer. For accumulating the  $^{13}\text{C}$ -H satellite spectra a Varian C-1024 Time Averaging Computer was used. These spectra were calibrated by inserting audio-sidebands prior to spectrum accumulation.

The 100 MHz spectra were recorded on a Varian HA-100 (TMS as internal lock reference) in connection with a Varian Spectro System 100.

The theoretical calculation of spectra was carried out by aid of a LAOCOON II program<sup>6</sup> using an IBM 7094 computer. The calculation was based on a computer analysis of the PMR spectrum of pyrene. The reexamination of the PMR spectrum was made in order to obtain more accurate values of  $\nu_{\text{H}(1)}$ ,  $\nu_{\text{H}(2)}$ ,  $\nu_{\text{H}(4)}$ , and  $J_{\text{H}(1)-\text{H}(2)}$  by making use of the sharper lines in the spectrum, but also to arrive at parameters which apply to the actual sample used in recording the satellite spectrum. The chemical shifts, in particular, are very sensitive to variations in solvent and concentration.

In order to avert wrong solutions in the ABCX case first order calculations including second order perturbations have been made in advance of the iterative procedure.

Input parameters not obtainable by first order calculations were taken from the analysis of the  $^{13}\text{C}$  resonance spectrum of benzene.<sup>7</sup>

### Results

The 60 MHz and 100 MHz  $^{13}\text{C}$ -H satellite spectra of pyrene, both low and high field part, are shown in Figs. 1 a and b. The arbitrary line numbers indicated there are referred to in the sections *Analysis* and *Discussion* below.

\* The Patterson Ring Index numbering for pyrene is used in the present paper. In Ref. 1 a different numbering is adopted for indicating chemical shifts and coupling constants.

Table 1 presents the calculated NMR parameters for pyrene as well as the parameters for 1,3,6,8-tetradeuteriopyrene. The latter values can be taken from the  $^{13}\text{C}-\text{H}$  satellite spectrum (Fig. 1c) of the deuterio compound. This has been done because broadening of the lines in the ABX part (IV) of the satellite spectrum of pyrene makes the evaluation of these parameters uncertain.

The differences between the calculated and experimental line positions for the four most prominent lines (3, 4, 5, and 6 in the *usual* numbering of an  $\text{A}_2\text{B}$  system<sup>8</sup>) are not greater than 0.09 Hz.

The coupling constant  $J_{\text{H}(1)-\text{H}(2)}$  is in good agreement with the value (7.72 Hz) of Cooper and Manatt.<sup>1</sup>

The chemical shift data and the  $^{13}\text{C}-\text{H}$  coupling constants obtained from the 100 MHz spectra are only accurate within the range of 0.2 Hz, which means that the determination of the isotopic shift differences in this instance is without meaning and they are only tabulated in order to show that the values do not exceed 0.2–0.3 Hz (0.3 Hz is the upper limit for the isotopic shifts given by Goldstein<sup>9</sup>). The line positions in the 100 MHz spectra have been adjusted by resolution enhancement. The adjustments are of the order of 0.07–0.13 Hz.

By the *analysis* of the  $^{13}\text{C}-\text{H}$  satellite spectrum of pyrene the three spin systems (II, III, and IV) will be treated separately.

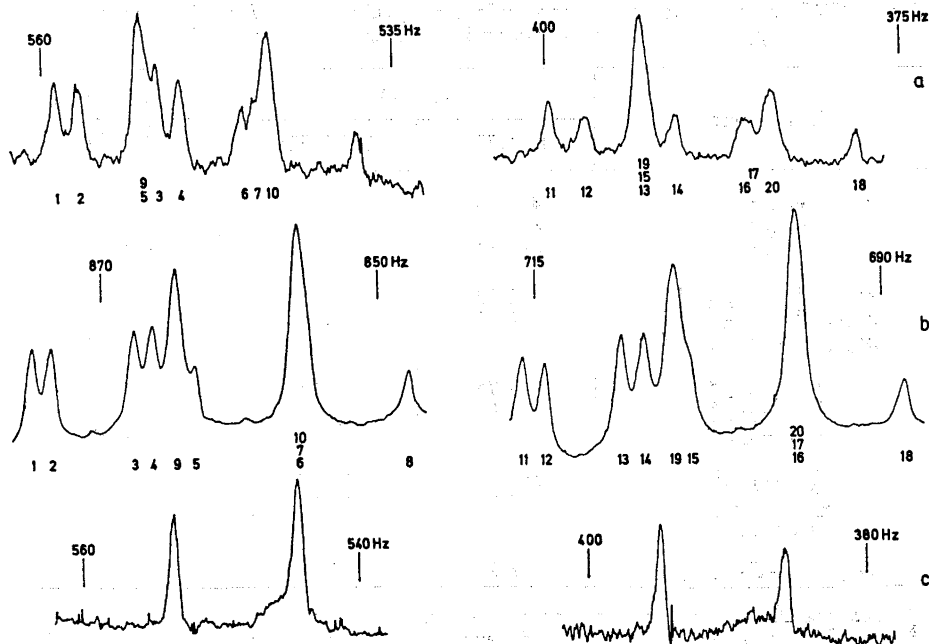


Fig. 1.  $^{13}\text{C}-\text{H}$  satellite spectra, low field (left) and high field (right). Line numbers are referred to in the text. a, pyrene, 60 MHz. b, pyrene, 100 MHz. c, 1,3,6,8-tetradeuteriopyrene, 60 MHz.

*The ABCX system (II).* The lines 1, 2, 3, 4 (low field), and 11, 12, 13, 14 (high field) (see Fig. 1) are assigned to this system. The asymmetry between the two satellites is due to the influence of the B–X and C–X couplings. Unfortunately, this type of spectrum gives only the difference between the two coupling constants.

The calculated intensities at 100 MHz as well as at 60 MHz are in good agreement with experimental values.

The RMS error in the calculation was 0.007 at 60 MHz (7 lines assigned) and 0.023 at 100 MHz (8 lines assigned).

The computer analysis shows that  $J_{AB} + J_{AC}$  is equal to the distance between the lines in each of the two pairs 1,4 and 11,14. This means that each part of the satellite spectrum can be analyzed as the X-part of an ABX spectrum, as could have been expected.

It follows also that in assuming  $J_{AB} = 7.75$  Hz the whole uncertainty in measuring the distance between the two lines is put into the small coupling constant,  $J_{AC} = 1.1$  Hz, which is probably accurate only to  $\pm 0.1$  Hz.

*The A<sub>2</sub>BX system (III).* The lines 5, 6, 7, 8 (low field), and 15, 16, 17, 18 (high field) (see Fig. 1) are assigned to this system. It is obvious that they form nearly the X-parts of two A<sub>2</sub>X systems. RMS errors were 0.038 at 60 MHz and 0.003 at 100 MHz.

Table 1. NMR parameters for pyrene (calculated values) and for 1,3,6,8-tetradeuteriopyrene. Chemical shifts and coupling constants in Hz.

Parameters	Pyrene		1,3,6,8-Tetra-deuteriopyrene 60 MHz
	60 MHz	100 MHz	
$\nu_{H(1)}^a$	475.09	791.47	
$\nu_{H(2)}^a$	465.75	776.04	
$\nu_{H(4)}^a$	468.49	780.67	470.00
$\Delta\nu_{H(1)}^{C(1)} - \Delta\nu_{H(2)}^{C(1) b, c}$	0.05	(0.29) <sup>e</sup>	
$\Delta\nu_{H(2)}^{C(2)} - \Delta\nu_{H(1)}^{C(2) c}$	0.19	(0.24) <sup>e</sup>	
$\Delta\nu_{H(4)}^{C(4)} - \Delta\nu_{H(3)}^{C(4) d}$			0.37
$J_{H(1)-H(2)}^a$	7.75	7.75	
$J_{H(1)-H(3)}^c$	1.09	1.00	
$J_{H(4)-H(5)}^d$			8.97
$J_{C(1)-H(1)}^c$	158.91	158.67	
$J_{C(2)-H(2)}^c$	158.75	158.71	
$J_{C(4)-H(4)}^d$			158.2
$J_{C(1)-H(3)} - J_{C(1)-H(2)}^c$	6.9	6.2	

<sup>a</sup> From the PMR spectrum of pyrene and tetradeuteriopyrene.

<sup>b</sup>  $\Delta\nu_{H(1)}^{C(1)} - \Delta\nu_{H(2)}^{C(1)}$  denotes the difference between the isotopic shifts of H(1) and H(2) due to <sup>13</sup>C(1). Similarly for the other two differences indicated.

<sup>c</sup> From the <sup>13</sup>C–H satellite spectrum of pyrene.

<sup>d</sup> From the <sup>13</sup>C–H satellite spectrum of 1,3,6,8-tetradeuteriopyrene.

<sup>e</sup> See text, p. 3379.

As the  $A_2BX$  spectrum depends on  $J_{C(2)-H(1)}$  it should be possible to determine this parameter. As the dependence is only a second order one and the uncertainty in measuring the distances 6–7 and 16–17 is great, it is not possible to determine this value with accuracy. In the theoretical calculations it has been set equal to 1 Hz, which is the value found for benzene.<sup>7</sup>

*The ABX system (IV).* The lines 9, 10 (low field), and 19, 20 (high field) (see Fig. 1) are assigned to this system. They can be seen as the X-parts of two AX systems.

Unfortunately overlapping with other signals makes the determination of  $J_{H(4)-H(5)}$  inaccurate.

Flammang<sup>10</sup> has shown that a deuterium atom at C(3) influences  $J_{H(1)-H(2)}$  in a negligible way. It seems reasonable that this also applies to  $J_{H(4)-H(5)}$ . This coupling constant can, therefore, be estimated from the  $^{13}C-H$  satellite spectrum of 1,3,6,8-tetradeuteriopyrene.

The first-order analysis of the ABX spectrum shows clearly that the quantities D+ and D– cannot in all cases be positive as defined by Pople *et al.*<sup>11</sup> as this definition would imply that the satellite lines would consist of two A and two B transitions.

### Discussion

*Chemical shifts.* The shift values reported here differ about 1 Hz from those reported by Cooper and Manatt,<sup>1</sup> but in their paper these authors give no attention to concentrations. The solvent used was the same ( $CS_2$ ) as in this work.

Recently it was shown<sup>9</sup> that the  $^{13}C-H$  satellite spectra of the symmetrical *p*-dihalobenzenes could be analyzed satisfactorily only by taking into account small but definite long-range isotope effects on the proton shifts due to  $^{13}C$ .

We have found such long-range isotope effects of importance for the analysis of the  $^{13}C-H$  satellite spectrum of pyrene. The isotope shift differences from the 60 MHz spectra given in Table 1 are within the range proposed for *p*-dihalobenzenes.<sup>9</sup> The somewhat greater values of the 100 MHz spectra are due to the recording technique.

*Coupling constants.* The value 8.97 Hz for  $J_{H(4)-H(5)} = J_{H(9)-H(10)}$  reported here (Table 1) agrees well with that predicted (9.03 Hz) by Cooper and Manatt<sup>1</sup> from the equation (eqn. (3) in Ref. 1) set up by them and including terms which depend on steric interactions. The authors have also extracted  $J_{H(4)-H(5)}$  directly from the  $^{13}C-H$  satellite spectrum of pyrene, but owing to rather broad peaks they could only give the uncertain value of  $8.8 \pm 0.2$  Hz.

This coupling constant has been found to be fairly invariable (9.0–9.1 Hz) in a series of 2-substituted pyrenes (F, Cl, Br, I, OH,  $NH_2$ ,  $NC_5H_{10}$ , COOH,  $COOCH_3$ , CN,  $CH_3$ , *t*- $C_4H_9$ ).<sup>12</sup> The less accurate value (8.9 Hz) formerly given for 2,7-di-*tert*-butylpyrene<sup>2</sup> was taken from the  $^{13}C-H$  satellite spectrum of this substance.

In contrast to this behaviour of 2-derivatives a great variation is observed of  $J_{H(9)-H(10)}$  in 1-substituted pyrenes. Especially large values are found when the substituents are spacefilling, 1-*tert*-butylpyrene<sup>12</sup> and 1,3,6,8-tetra-isopropylpyrene<sup>2</sup> both having  $J_{H(9)-H(10)} = 9.8$  Hz. For some other substituents Martin *et al.*<sup>13</sup> give the range 9.3–9.5 Hz.

Variations of this type which can be ascribed to steric grounds were noted recently by Cooper and Manatt<sup>1</sup> for 1,4-di-*tert*-butylnaphthalene. It may be noted that pyrene is a very well-suited molecule for investigating this *peri*-effect. Detailed results will be published later.

The other two coupling constants shown in Table 1,  $J_{\text{H}(1)-\text{H}(2)} = 7.75$  Hz (*ortho*) and  $J_{\text{H}(1)-\text{H}(3)} = 1.09$  Hz (*meta*) are both smaller than in pyrene derivatives. For the *ortho*-coupling constant Martin *et al.*<sup>13</sup> give the range 8.0–8.4 Hz as found for a series of 1-derivatives.

There are only few experimental data available for the *meta*-coupling constant. From the <sup>13</sup>C–H satellite spectrum of 2,7-di-*tert*-butylpyrene<sup>2</sup> and from the ordinary spectrum of 2,4,7,9-tetraisopropylpyrene<sup>12</sup> the values 1.7 Hz and 1.5 Hz, respectively, were found.

A comparison of the *ortho*-coupling constant  $J_{\text{H}(1)-\text{H}(2)}$  (7.75 Hz) and the *meta*-coupling constant  $J_{\text{H}(1)-\text{H}(3)}$  (1.09 Hz) for pyrene with the corresponding quantities for benzene shows a change which, according to Castellano and Sun,<sup>14</sup> should be expected if the two biphenyl rings in pyrene are regarded as benzene rings carrying electron attracting substituents.

The <sup>13</sup>C–H coupling constants in pyrene are near in magnitude to those for benzene,<sup>7,15</sup> although there seems to be a trend toward slightly greater values for the former.

In Table 2 are compared the <sup>13</sup>C–H coupling constants for pyrene and some polysubstituted pyrenes. It appears that introducing alkyl groups in one of the benzenoid rings decreases the magnitude of the <sup>13</sup>C–H couplings belonging to that ring and thus follows the general pattern found for benzene derivatives.<sup>9</sup>

Table 2. Comparison of <sup>13</sup>C–H coupling constants for pyrene and for some polyalkylated pyrenes.

Substituents Coupl. const.	None	2,7-di-t-Bu <sup>b</sup>	1,3,6,8-tetra-i-Pr <sup>b</sup>	1,3,5,7,9-penta-i-Pr <sup>c</sup>
	$J_{\text{C}(1)-\text{H}(1)}$	158.91	156	—
$J_{\text{C}(2)-\text{H}(2)}$	158.75	—	154	150.0
$J_{\text{C}(4)-\text{H}(4)}$	158.2	159	159	152.9
$J_{\text{C}(6)-\text{H}(6)}$	158.91 <sup>a</sup>	156 <sup>a</sup>	—	153.5

<sup>a</sup> Identical in this case with  $J_{13\text{C}(1)-\text{H}(1)}$ .

<sup>b</sup> See Ref. 2.

<sup>c</sup> The structure of this compound will be discussed in a forthcoming paper.<sup>12</sup>

## B. CNDO CALCULATIONS OF COUPLING CONSTANTS IN PYRENE

Although the rather broad lines in the NMR spectra of pyrene and other condensed aromatic hydrocarbons may be the result of relaxation mechanisms, the existence of long-range couplings must also be taken into account.<sup>16</sup> A

few such couplings have been observed,<sup>17</sup> but in most cases the generally small coupling constants are very difficult to obtain from the NMR spectra.

In order to get an idea of the magnitude of possible long-range couplings in pyrene we have undertaken a CNDO calculation of a series of coupling constants belonging to pyrene including those short-range couplings which are found by experiments.

The CNDO/2 programme was worked out by Voigt<sup>18</sup> on the basis of the theory of Santry and Segal<sup>19</sup> and the QCPE No. 91 by Segal. The atomic positions (Table 3) for the CNDO programme were based on averaged coordinates (corrected for thermal motion) from neutron diffraction measurements by Hazell.<sup>20</sup> The X- and Y-axes are in the directions of the short and the long axis of the pyrene molecule, respectively.

Table 3. Atomic positions (coordinates) in the pyrene molecule.<sup>20</sup>

Atom	Coordinates in Å		
	X	Y	Z
C(1)	1.2118	2.8325	-0.0033
C(2)	0.0081	3.5226	-0.0007
C(4)	2.4648	0.6835	-0.0004
C(11)	1.2343	1.4271	-0.0005
C(15)	-0.0045	0.7151	0.0090
H(1)	2.1524	3.3705	-0.0101
H(2)	-0.0044	4.5966	-0.0055
H(4)	3.3998	1.2271	0.0011

The small deviations from planarity are probably a result of crystal packing forces (Camerman and Trotter<sup>21</sup>). Assuming  $D_2$  symmetry will make all Z-coordinates zero, and also  $X_{C2} = X_{C7} = X_{H2} = X_{H7} = X_{C15} = X_{C16} = 0$ .

The coupling constants (Table 4) have been calculated with coulomb integrals included in the triplet excitation energies, but no semiempirical fit of the spin densities at the carbon atoms<sup>22</sup> has been used.

Nearly the same order, with respect to the magnitude of the coupling constants, is found for the theoretical and the experimental values. The calculated values for the one-bond coupling constants,  $^1J(\text{CH})$ ,\* are smaller than the experimental ones by a factor of about 0.37.

The precise magnitudes of the carbon to hydrogen couplings across two bonds in pyrene,  $^2J(\text{CH})$ , is not known, but as judged from the experimental value for benzene<sup>7</sup> they are probably smaller than 1.0 Hz. The calculated values for pyrene are all between 0.5 and 1.0 Hz.

\* In section B, when the number of bonds in a coupling is indicated, the notation shown is used for coupling constants.

Table 4. Coupling constants for pyrene. Comparison of calculated (CNDO) and experimental values.

Number of bonds	Coupling constants, calc.		$\pi$ -Contribution (McConnell <sup>24</sup> )	${}^{\sigma}J + {}^{\pi}J$	Coupling constants, exp. values <sup>b</sup>
	Notation	Coulomb int. included			
<sup>1</sup> J(CH)	J(C(1)–H(1))	60.918			158.91
	J(C(2)–H(2))	58.465			158.75
	J(C(4)–H(4))	60.346			158.2
<sup>2</sup> J(CH)	J(C(1)–H(2))	0.862			
	J(C(2)–H(1))	0.817			
	J(C(4)–H(5))	0.678			
<sup>3</sup> J(CH)	J(C(1)–H(3))	2.632			
<sup>3</sup> J(HH)	J(H(1)–H(2))	5.294	0.78	6.07	7.75
	J(H(4)–H(5))	5.702	1.05	6.75	8.97
<sup>4</sup> J(HH)	J(H(1)–H(3)) <sup>a</sup>	1.05	0	1.05	1.00–1.09
	J(H(1)–H(10))	0.319		0.32	
<sup>5</sup> J(HH)	J(H(1)–H(9))	0.134	0.072	0.21	
	J(H(2)–H(4))	–0.125	0.025	–0.100	
<sup>6</sup> J(HH)	J(H(1)–H(4))	0.018		0.018	
	J(H(2)–H(5)) <sup>a</sup>	–0.017		–0.017	
	J(H(4)–H(10)) <sup>a</sup>	–0.041	0	–0.041	
<sup>7</sup> J(HH)	J(H(1)–H(5))	0.084	0.058	0.142	
	J(H(1)–H(6)) <sup>a</sup>	0.058	0.035	0.093	
	J(H(1)–H(8))	0.093	0.046	0.139	
<sup>8</sup> J(HH)	J(H(1)–H(7))	–0.013	0	–0.013	

<sup>a</sup> Path of coupling is shaped like a w or an extended w.

<sup>b</sup> Cf. Table 1.

Govil <sup>23</sup> has observed that <sup>2</sup>J(CH) in ethylenes is very dependent on surroundings. This observation makes it reasonable to regard the variation found for the calculated values of the three <sup>2</sup>J(CH) in pyrene as significant.

From the difference <sup>3</sup>J(C(1)–H(3)) – <sup>2</sup>J(C(1)–H(2)) = 6.9 Hz, emerging from the analysis of the <sup>13</sup>C–H satellite spectrum of pyrene (see Table 1), and the reliable value <sup>2</sup>J(C(1)–H(2)) = 0.86 Hz (Table 4) a value of 7.76 Hz for <sup>3</sup>J(C(1)–H(3)) might be expected. The corresponding experimental value for benzene is 7.4 Hz.<sup>7</sup> The calculated value of <sup>3</sup>J(C(1)–H(3)) (Table 4) is smaller than the expected one by a factor of 0.34, or nearly the same that applied to the one-bond constants <sup>1</sup>J(CH).

H–H couplings across three to eight bonds have been calculated. Being at the moment without sufficient computer facilities for INDO calculations we have estimated the  $\pi$ -contribution to the coupling constants by means of the McConnell equation.<sup>24</sup> Assuming the McConnell  $\pi$ -contribution not to be greater than 1.05 Hz (the value obtained for <sup>3</sup>J(H(4)–H(5)) if  $\beta^2 Q_N Q_N' / \hbar \Delta E = 1.8$ , see Table 4) the two *ortho*-coupling constants, <sup>3</sup>J(HH), in pyrene appear somewhat smaller than the experimental ones.

Mainster and Memory <sup>25</sup> have calculated <sup>6</sup>J(H(1)–H(2)) for pyrene by the Fahey-Graham-Piccioni method. Their value, 5.52 Hz, which was based on



the bond lengths 1.40 Å and 1.10 Å for C–C and C–H, respectively, is only a little greater than the present one.

Only one *meta*-coupling constant,  ${}^4J(\text{H}(1) - \text{H}(3))$ , occurs in pyrene. The calculated and experimental values are nearly equal.

Another coupling, which goes across four bonds,  ${}^4J(\text{H}(1) - \text{H}(10))$ , is a *peri*-coupling. This type of coupling has been observed in a few condensed aromatic hydrocarbons and derivatives of them, most notably, as found by Brügel,<sup>26</sup> in 1,2-substituted naphthalenes. The *peri*-coupling constants,  ${}^4J(\text{H}(4) - \text{H}(5))$ , for these compounds are reported to be between 0.2–0.5 Hz. The value calculated for pyrene falls in this interval.

All the  $\sigma$ -contributions to H–H couplings across more than four bonds, which are shown in Table 4, are found not to exceed 0.134 Hz.

Regarding the trend of these long-range couplings an alternation of sign, although not entirely consistent, with the number of bonds separating the two protons can be observed, the sign being positive or negative for odd and even numbers, respectively. However, according to Voigt,<sup>18</sup> this behaviour may be expected from the programme used. The exceptions are  ${}^5J(\text{H}(2) - \text{H}(4))$  and  ${}^6J(\text{H}(1) - \text{H}(4))$ . It can be noted that  ${}^{\sigma}J(\text{H}(1) - \text{H}(8))$  and  ${}^{\pi}J(\text{H}(1) - \text{H}(8))$  are greater than  ${}^{\sigma}J(\text{H}(1) - \text{H}(6))$  and  ${}^{\pi}J(\text{H}(1) - \text{H}(6))$ , respectively, although the coupling between H(1) and H(6) is transmitted through an extended W-path. This may be connected with the fact that two equally long pathways between H(1) and H(8) exist.

For methyl substituted pyrenes the following couplings have been reported  ${}^8J(\text{CH}_3(1) - \text{H}(5)) = 1.2 \text{ Hz}$ <sup>27</sup> and  ${}^4J(\text{CH}_3(1) - \text{H}(2)) = {}^4J(\text{CH}_3(2) - \text{H}(1)) \sim 0.6 \text{ Hz}$ <sup>27,16</sup>.

The  $\sigma$ -contribution to the  $J(\text{CH}_3 - \text{H})$  has been estimated to be about 30 % of the total coupling.<sup>28</sup> Using this estimation a good agreement between the values from the McConnell equation and experiment is found.

The McConnell equation used on pyrene gives, among the long-range H–H couplings across more than four bonds, the greatest contribution to  ${}^5J(\text{H}(1) - \text{H}(9))$ . This equation always provides positive coupling constants or sets, in an alternant aromatic hydrocarbon, all couplings over an even number of bonds equal to zero. The calculated values (Table 4) for couplings between protons separated by an even number of bonds are negative but very small, so even if we assume as has been done by McConnell<sup>29</sup> that  ${}^{\pi}J$  in these cases is negative, we will not have any coupling of important magnitude.

We see that on the assumption of maximum  $\pi$ -contribution only two long-range couplings will exceed 0.2 Hz, namely  $J(\text{H}(1) - \text{H}(10))$  and  $J(\text{H}(1) - \text{H}(9))$ .

In order to try to verify the magnitudes of the calculated long-range coupling constants simulated PMR spectra of pyrene were calculated using experimentally known parameters (Table 1) as well as guess-values for long-range coupling constants. Spectrum plots were obtained using Lorentzian line shapes, and these plots were compared with the observed spectrum.

As it is impossible to break down the ten-spin system of pyrene into subsystems, the effects originating from long-range couplings were estimated by calculating two "pseudo" systems.

These systems, called I and II, consist of the following hydrogen nuclei: 1,2,3,4,5,9,10 and 1,2,3,6,7,8.

Long-range couplings between neighbouring rings can be included in system I and long-range couplings between equivalent positions in non-neighbouring rings in II.

The observed spectrum shows that the half-widths of lines 3 and 4<sup>8</sup> are of equal magnitude. But from calculations on system I it appeared that by inclusion of definite long-range couplings between H(2) and other hydrogens line 3 became broader than line 4. This probably indicates that all long-range couplings to hydrogens 2 and 7 are very small as is also indicated by the CNDO calculation.

We have, therefore, used the observed widths of lines 3 and 4 as natural line-widths in the plotting procedure.

Plots with and without inclusion of long-range couplings show that the former fits experiment better. This applies especially well to the reproduction of the very characteristic broadness of the lines 5, 6, and 7.

Because of the use of "pseudo" systems nothing can be said for sure about the best set of values to be used, but it seems as if the use of values greater than the calculated ones gives no further amelioration.

Besides by use of line-widths information about the long-range couplings in pyrene may be obtained by means of the fluorine substituted compounds.

In the <sup>1</sup>HNMR spectrum of 2-fluoropyrene a coupling constant of about 0.5 Hz clearly shows up, probably  $J(F(2)-H(4))$ . Further work on this subject is in progress.

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