503. *Hydrogen Resonance Spectra at Low Temperatures of Pure Hydrocarbons and of Selected Coal Samples.*

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Measurements of the hydrogen magnetic resonance line widths and of the second moments of many solid hydrocarbons and of selected samples of coal have been used to obtain an indication of the types of hydrogen atom present and hence of the types of ring and of the positions of methyl groups.

The proportions of the main chemical elements in different types of coal lie within the ranges C, 65—95%; O, 3—30%; H, 2—6%. Microscopic examination discloses a number of components (termed macerals), differing in optical properties and chemical composition. Vitrinite, exinite, and micrinite are the most important. The most homogeneous is vitrinite, which constitutes the major portion of the bright coals. Exinite and micrinite both occur in high proportions in the dull coals; they have no general dominant constituent (contrast vitrinite in bright coal) and therefore have a more variable composition than the bright coals. Vitrinite can be isolated in an almost pure state, *e.g.*, by hand-picking. Exinite and micrinite, which are richer and poorer respectively than vitrinite in hydrogen, differ in density and can be fractionated, though with difficulty, by means of liquids differing in specific gravity.

The elucidation of coal structure has been attempted by many methods. In the present state of knowledge the simplest likely model consists of central aromatic nuclei with flat conjugated benzenoid ring systems or lamellæ to which are attached alicyclic rings and also aliphatic groups linking one cluster to another. This model has mainly been built up from physical evidence.

Recent *X*-ray measurements by Hirsch,[1] on a range of vitrains, suggest that the aromatic layers in coals containing up to about 90% of carbon are small in that they contain only a few condensed rings and that these layers are cross-linked to form larger units.

Infrared absorption spectra [2] of coals show that methyl and methylene groups are present, as well as hydrogen-bonded hydroxyl (probably phenolic), diaryl ethers, and aromatic carbon–hydrogen linkages.

Preliminary measurements [3] have shown that the hydrogen magnetic resonance line widths of different samples of coals at low temperatures vary markedly with the carbon content, and it was suggested that this is associated with variations of the ratio of aromatic to aliphatic hydrogen atoms in the coals. Measurements have therefore been made of the second moments of many solid hydrocarbons and of carefully selected samples of coal.

Experimental

Nuclear magnetic resonance measurements were performed with the spectrometer described previously,[4] at 90° K (liquid oxygen as refrigerant unless otherwise specified). Care was taken to ensure that the radio-frequency level used was low enough to avoid saturation.

Commercial decalin was purified in the usual manner. From refractive-index measurements it was estimated that 79% was in the *cis*-form. 9,10-Dihydroanthracene was obtained from Messrs. Light. The remaining hydrocarbons were kindly provided by Dr. J. C. Smith.

The National Coal Board kindly supplied samples of a range of vitrain coals which, from petrographic analysis, contained at least 96% of vitrinite (by vol.) except for the Coegnant, Gellideg Seam coal (this contained 89% of vitrinite and 11% of micrinite). The analytical figures for the Blaenhirwaun coal are estimated values from other similar coals. The National Coal Board also supplied two samples of durain, dense, spore-rich, dull coal from the " branch

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[1] Hirsch, Institute of Fuel Conference, April, 1958.

[2] Cannon, *Nature*, 1953, **171**, 308.

[3] Newman, Pratt, and Richards, *Nature*, 1955, **175**, 645.

[4] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261.

band " of the Aldwarke Main, Silkstone Seam. European Research Associates kindly lent three macerals separated from an American bright coal (83·3% of carbon; dry, mineral-matter-free) and dull coal (84·2% of carbon; d.m.m.f.) of the same rank. The resultant vitrinite has C, 84·5; H, 5·4%; O, 8·5%. A series of coals derived by solvent-extraction were also received from European Research Associates. Step-wise extraction from a vitrinite (84·0% of carbon; d.m.m.f.) was made, starting with pyridine. The pyridine-soluble part was then extracted with trichlorobenzene, the trichlorobenzene-soluble part with benzene, and the benzene-soluble part with carbon tetrachloride. The coal samples studied by Newman, Pratt, and Richards were prepared from hand-selected lumps of bright coals containing more than 50% of vitrain.

Results

Hydrocarbons.—The results of the magnetic resonance measurements on the hydrocarbons and other model compounds are shown in Table 1.

Coal Samples.—The nuclear-resonance measurements for the range of vitrain coals from the National Coal Board are shown in Table 2. The results are average values of six recordings for each sample.

The results obtained from the macerals supplied by European Research Associates and for the solvent-extracted materials are shown in Tables 3 and 4 respectively.

Measurements of second moments of six samples of vitrains have been mentioned by Smidt,

TABLE 1. *Second moments at* 90° K.

Compound	No. of traces	Mean second moment (gauss^2)	Line width (gauss)
Decalin	8	15·9 ± 0·7	9·3 ± 0·3
Tetralin	8	21·8 ± 0·5	12·9 ± 0·3
9,10-Dihydroanthracene	6	15·5 ± 0·6	8·7 ± 0·7
Acenaphthene	8	15·9 ± 0·7	9·3 ± 0·3
1,6-Di-2′-naphthylhexane	8	17·5 ± 0·6	9·1 ± 0·3
6-Methyltetralin	8	20·2 ± 0·5	9·4 ± 0·5
6-n-Propyltetralin	8	21·4 ± 0·8	11·6 ± 0·3
1-n-Nonylnaphthalene	8	20·6 ± 0·7	11·4 ± 0·3
1-Ethylnaphthalene *	8	12·8 ± 0·5	8·6 ± 0·5
1-n-Propylnaphthalene *	8	14·9 ± 0·6	8·5 ± 0·1
2,3-Dimethylnaphthalene *	8	9·2 ± 0·3	7·8 ± 0·2
1,8-Dimethylnaphthalene	8	17·5 ± 0·9	8·6 ± 0·3
Equimolar mixture of benzene and decalin	8	21·6 ± 0·6	12·3 ± 0·4
Mixture of benzene and decalin (3 : 1)	8	17·7 ± 0·5	9·9 ± 0·2
1,4,5-Trimethylnaphthalene *	8	15·2 ± 0·6	8·0 ± 0·3
5-Acetamido-6-nitrotetralin	8	16·2 ± 1·1	7·7 ± 0·2
2,3-Dihydro-6-nitrobenzo-1,4-dioxin	8	13·7 ± 0·8	5·3 ± 0·1

* Measured by C. L. M. Bell.

TABLE 2.*

Coal	C (%)	H (%)	N (%)	S (%)	O, etc. (%)	Line width (gauss)	Second moment (gauss^2)
Nailstone Yard seam	79·2	5·3	1·4	1·0	13·1	8·4 ± 0·3	21·2 ± 0·3
Markham Main Barnsley Seam	82·0	5·5	1·8	1·0	9·7	7·6 ± 0·1	18·9 ± 0·8
Dinnington Main Barnsley Seam	84·9	5·4	1·9	1·0	6·8	7·5 ± 0·2	17·8 ± 0·3
Houghton Main Parkgate Seam	86·7	5·3	1·8	1·0	5·2	7·1 ± 0·1	16·2 ± 0·3
Coegnant Gellideg Seam	91·4	4·6	1·6	0·5	1·9	7·2 ± 0·2	14·1 ± 0·5
Blaenhirwaun Pumpquart Seam	94·0	2·2	1·0	0·8	2·0	6·6 ± 0·2	12·5 ± 0·4
Aldemark Main Silkstone Seam	87·9	6·3	1·2	0·6	4·0	7·7 ± 0·2	17·1 ± 1·1
						8·5 ± 0·1	17·8 ± 0·6

* Compositions (%) are given on a dry, mineral-matter-free basis.

TABLE 3.

Maceral	Line width (gauss)	Second moment (gauss^2)
Micrinite (*d* 1·40—1·43)	6·7 ± 0·1	12·7 ± 0·9
Vitrinite (*d* 1·27—1·33)	7·6 ± 0·2	14·5 ± 0·6
Exinite (*d* <1·25)	8·5 ± 0·7	20·0 ± 0·5

TABLE 4.

Coal	Line width (gauss)	Second moment (gauss^2)
Vitrinite	7·4 ± 0·3	15·1 ± 0·7
Pyridine-soluble	7·5 ± 0·2	14·5 ± 0·6
Trichlorobenzene-soluble	6·6 ± 0·2	13·1 ± 0·3
Benzene-soluble	6·8 ± 0·3	15·1 ± 0·7
CCl_4-Soluble	7·1 ± 0·3	15·9 ± 0·4

van Raayen, and van Krevelen.[5] The results are in approximate agreement with those described here, except that a sample of carbon content 80·2% gives a second moment of 19 gauss^2, compared with 21·2 gauss^2 obtained in this work for a sample of 79·2% carbon content. These authors also found a difference of about 3·8 gauss ^{2} between samples measured after 4 hours' drying at 80° at 0·2 mm. compared with the same sample treated at a pressure of 10^{-5} mm. at 165° until no further change in second moment occurred. It is presumed that coals of low carbon content contain significant amounts of water which is only removed with great difficulty, so that the results obtained in this work for the carbon of content 79·2% may be too high.

DISCUSSION

Comparison between Theoretical Second Moments and Experimental Values.—The crystal structure of tetralin has not been determined. From a scale model, with standard interatomic distances and angles, the intramolecular contribution to the second moment was found to be 13·7 gauss^2. The intermolecular broadening can be estimated to be between the intermolecular broadening for cyclohexane (9·6 gauss^2) and naphthalene (6·9 gauss^2); [6] if the intermolecular broadening is taken to be 8·2 gauss^2, the total rigid theoretical second moment is found to be 21·9 gauss^2, in close agreement with the experimental value of 21·8 gauss^2, from which it is concluded that any molecular motion in tetralin at 90° K is too slow to affect the nuclear resonance spectrum.

The crystal structure of acenaphthene has been determined by Banerjee and Sinha.[7] However, according to Wyckoff,[8] certain molecular separations in the crystal are so large that a reconsideration of the structure seems needed. Only the intramolecular second moment was therefore calculated from the published data and by this means a value of 7·2 gauss^2 was obtained. It seems likely that the intermolecular broadening will be similar to that in tetralin (8·2 gauss^2). In this case the total theoretical second moment would be 15·4 gauss^2, very close to the observed value. So there is no molecular motion in any part of the acenaphthene molecule at 90° K.

The same model was used for the ring system of 6-methyltetralin as for tetralin, and the methyl group was arranged so that one hydrogen atom was in the plane of the benzene ring and the other two were symmetrically above and below. The rigid intramolecular second moment is 16·7 gauss^2. If the intermolecular broadening is estimated to be about 8 gauss^2, the total rigid second moment would be 24·7 gauss^2. This value is larger than the experimental value of 20·2 gauss^2, and indicates some molecular motion. The most likely form of motion is reorientation of the methyl group about the $C_{(Me)}$–C axis.[6b] If the second moment of this compound is then recalculated by assuming this motion of the methyl group only, the intramolecular broadening becomes 13·2 gauss^2. If the intermolecular broadening is assumed to be about 7 gauss^2 the total theoretical value of 20·2 gauss^2 is obtained, in exact agreement with the observed value. The assumption of rotation of the methyl group is therefore supported.

From a scale model of 6-n-propyltetralin, with various arrangements of the n-propyl group, second moments from 17 to 20 gauss^2 were obtained. If an intermolecular broadening of about 7 gauss^2 is assumed, the total rigid second moment would then be 24—27 gauss^2. The experimental value of 21·4 gauss^2 lies well below this range and so once again it is assumed that some molecular motion is present. If the rotation is assumed to be restricted to the terminal methyl group, a value of 15 gauss^2 is obtained for the intramolecular second moment, and an intermolecular contribution of 7 gauss^2 being assumed, a value of 22 gauss^2 is obtained. This is reasonably consistent with the experimental value. Further motion involving the whole propyl group would very significantly reduce the second moment, well below the experimental value.

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[5] Smidt, van Raayen, and van Krevelen, *Fuel*, 1959, **38**, 539.

[6] (*a*) (Cyclohexane) Andrew and Eades, *Proc. Roy. Soc.*, 1953, *A*, **216**, 398; (*b*) (naphthalene) Andrew, *J. Chem. Phys.*, 1950, **18**, 607.

[7] Banerjee and Sinha, *Indian J. Phys.*, 1937, **11**, 21.

[8] Wyckoff, " Crystal Structures," Interscience, New York, 1953, Vol. 3, p. 88.

For the scale model of 1,8-dimethylnaphthalene the structure of the naphthalene nucleus determined by Ahmed and Cruickshank[9] was used. The *peri*-methyl groups are very close together and the arrangement which gave the greatest possible separation of hydrogen atoms was chosen. The rigid intramolecular second moment was found to be 16·1 gauss^2, of which 13·9 gauss^2 is contributed by the methyl groups. The total second moment is 23·0 gauss^2 if the intermolecular second moment is assumed to have the same value as that calculated by Andrew[6b] for naphthalene (6·9 gauss^2). The observed value of 17·5 gauss^2 indicates that the methyl groups are probably in motion. In view of the large interaction between the methyl groups a more exact calculation was carried out, by assuming that they are in three-fold rotation in opposite directions like meshed gear-wheels. On this basis a total second moment of 17·2 gauss^2 is obtained in good agreement with the observed value.

These results and those of other authors (see below) indicate that (*a*) the contributions of the hydrogen atoms in normal aliphatic and in aromatic groupings to the second moment of a compound at low temperatures are very similar in all hydrocarbons, (*b*) at 90° K terminal methyl groups are always undergoing molecular motion about the $C_{(chain)}$–C axis at a sufficient rate to reduce their contribution to the second moment, and (*c*) when the *peri*-methyl groups in condensed aromatic systems give second moments greater than normal on account of their close proximity. It may therefore be possible to estimate the second moments of the hydrocarbons by considering the proportions in the molecule of (i) aromatic hydrogen atoms, (ii) hydrogen atoms in methyl groups not in adjacent *peri*-positions, (iii) hydrogen atoms in methyl groups in adjacent *peri*-positions, and (iv) aliphatic hydrogen atoms excluding the hydrogen atoms in methyl groups, in conjunction with definite values for the contribution of these different types of hydrogen atoms to the total second moment. The values will include both intramolecular and intermolecular interactions and their use assumes that the intermolecular interactions on the specific type of hydrogen atom considered does not vary much from one hydrocarbon to another. This assumption is partly justified because the broadening depends on the inverse sixth power of the H–H distances and therefore only the nearest atom in other molecules will produce a marked effect.

The value of the contribution of aromatic hydrogen atoms to the total width was chosen by considering the observed and the theoretical second moments of benzene[10] and naphthalene[6b] obtained by Andrew. The observed and theoretical second moment of benzene of 9·7 gauss^2 at 80°K is about half-way between the observed value of 9·1 gauss^2 of naphthalene at 96° K and the theoretical value of 10·1 gauss^2, so 9·7 gauss^2 was chosen for the contribution of aromatic hydrogen atoms.

The second moment of decalin was determined (see above) in order to obtain the contribution of the aliphatic hydrogen atoms (S_{al}). The fact that it is a mixture of *cis*- and *trans*-forms is not important. This molecule contains eighteen hydrogen atoms, of which sixteen are aliphatic and the other two can be regarded as aromatic. The observed second moment of 25·5 gauss^2 may therefore be treated as follows:

$$25{\cdot}5 = \tfrac{16}{18} \times S_{al} + \tfrac{2}{18} \times 9{\cdot}7$$

The value of S_{al} which is obtained is 27·5 gauss.

The contribution of the hydrogen atoms in methyl groups not in adjacent *peri*-positions (S_x) was chosen by taking Andrew's value[6b] of 9·9 gauss^2 at 95° K for the second moment of *p*-xylene, which contains ten hydrogen atoms and two methyl groups undergoing rotation about their $C_{(Me)}$–C axes:

$$9{\cdot}9 = \tfrac{6}{10} \times S_x + \tfrac{4}{10} \times 9{\cdot}7$$

The value of 10·0 gauss^2 is obtained for S_x.

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[9] Ahmed and Cruickshank, *Acta Cryst.*, 1952, **5**, 852.

[10] Andrew and Eades, *Proc. Roy. Soc.*, 1953, *A*, **218**, 537.

The contribution of hydrogen atoms in methyl groups in adjacent *peri*-positions (S_y) was calculated from the observed second moment of 17·5 gauss^2 of 1,8-dimethylnaphthalene. This molecule contains twelve hydrogen atoms, of which six are aromatic and six are in methyl groups in adjacent *peri*-positions:

$$17{\cdot}5 = \tfrac{6}{12} \times S_y + \tfrac{6}{12} \times 9{\cdot}7$$

A value of 25·3 gauss^2 is obtained for S_y.

The use of these values can be illustrated by reference to 6-n-propyltetralin. This molecule contains eighteen hydrogen atoms, of which twelve are aliphatic, three are aromatic, and three are in the terminal methyl group. The second moment would therefore be expected to be

$$\tfrac{12}{18} \times 27{\cdot}5 + \tfrac{3}{18} \times 9{\cdot}7 + \tfrac{3}{18} \times 10{\cdot}0 = 21{\cdot}6 \text{ gauss}^2$$

The observed value is 21·4 gauss^2.

Second moments calculated in this way are given in col. 4 of Table 5. The agreement between cols. 3 and 4 is surprisingly good. The greatest discrepancies are found with acenaphthene and 1,4,5-trimethylnaphthalene. The difference between the observed value of 15·9 gauss^2 for acenaphthene and calculated value of 16·8 gauss^2 is accounted for by the fact that this compound has methylene groups with an abnormally large carbon–carbon distance of 2·01 Å. With 1,4,5-trimethylnaphthalene the difference between the observed value of 15·2 gauss^2 and calculated value of 16·4 gauss^2 is accounted for by the close proximity of the two *peri*-methyl groups. The broadening due to these two groups will therefore be very sensitive to the distances between their carbon atoms. Comparison of cols. 3 and 4 confirms that for the tetralin, acenaphthene, and 9,10-dihydroanthracene there is no rotation of the aliphatic ring or chains. Similarly in 1,6-di-(2′-naphthylhexane there is evidently no rotation of the chain linking the two naphthalene nuclei. This type of structure must be considered because the coals probably contain aliphatic bridges between adjacent graphitic layers as well as rings attached to one graphitic layer. The agreement for 1-n-nonylnaphthalene indicates that only the terminal methyl group is rotating, as found for all the other compounds studied.

TABLE 5.

		Second moment (gauss^2),		$\dfrac{H_{ar} + H_{Me}}{H_{CH_2} + H_{peri\text{-}Me}}$	
Compound	T, °K	obs.	calc. (see text)	True	Calc. from second moment
Decalin	90	25·5	25·5	0·13	0·13
Tetralin	90	21·8	21·6	0·50	0·47
Acenaphthene	90	15·9	16·8	1·50	1·87
9,10-Dihydroanthracene	90	15·5	15·7	2·00	2·07
1,6-Di-2′-naphthylhexane	90	17·5	17·9	1·17	1·28
6-Methyltetralin	90	20·2	20·0	0·75	0·70
6-n-Propyltetralin	90	21·4	21·6	0·50	0·52
1-n-Nonylnaphthalene	90	20·6	20·7	0·63	0·63
1-Ethylnaphthalene	90	12·8	12·7	5·00	4·74
1-Propylnaphthalene	90	14·9	14·9	2·50	2·42
1,8-Dimethylnaphthalene	90	17·5	17·5	1·00	1·28
1,4,5-Trimethylnaphthalene	90	15·2	16·4	1·33	2·24
2,3-Dimethylnaphthalene	90	9·2	9·8	—	—
p-Xylene [6b]	95	9·9	9·9	—	—
o-Xylene [6b]	95	9·8	9·9	—	—
m-Xylene [6b]	95	9·8	9·9	—	—
Mesitylene [6b]	95	9·8	9·9	—	—
Benzene–Decalin (1 : 1)	90	21·6	21·6	0·50	0·50
Benzene–Decalin (3 : 1)	90	17·7	17·6	1·25	1·23

The values derived for the specific types of hydrogen atoms in the hydrocarbons were applied to the mixtures of benzene and decalin studied, by adding together the different types of hydrogen atoms for the two molecules according to the molar proportions of the mixtures. As seen in Table 5, agreement between the observed and the calculated values of the second moments is good.

The compounds with the large polar groups were studied to see how much effect these have upon the calculations. 5-Acetamido-6-nitrotetralin gave a calculated second moment of 21·2 gauss^2, and this is in serious disagreement with the experimental value of 16·2 gauss^2. Clearly, the two large polar groups seriously upset the intermolecular broadening between the molecules and invalidate the calculations.

A similar situation occurs with 6-nitrobenzo-1,4-dioxin which has a calculated second moment of 19·9 gauss^2 and an experimental value of 13·7 gauss^2.

A number of measurements have been made in this Laboratory [11] on some polymethylene terephthalate polymers, $(\cdot C_6H_4\cdot CO\cdot O\cdot [CH_2]_n\cdot O\cdot CO)_m$. When $n = 4$, 5, or 6, the experimental second moments were 15·1, 19·3, 22·3, and 23·1 gauss^2, the values calculated as above being 18·6, 21·6, 22·4, and 23·0 gauss^2 respectively. These clearly show that when there is a large proportion of polar groupings as when $n = 2$, the calculations are not accurate, but as the proportion of polar groupings to hydrocarbon material becomes smaller, the calculations are more successful.

From these measurements it may therefore be concluded that the above semi-empirical calculations can be expected to apply reasonably well to materials which are largely of a hydrocarbon nature. If the molecule contains substantial proportions of strongly polar groupings or large atoms, then the method breaks down. It seems that the calculations might be expected to apply reasonably well to materials of coal-like structure.

The conclusions reached above show, however, that it is not possible to make the calculations backwards so as to obtain the ratio of aromatic to aliphatic hydrogen content. Nevertheless, the contribution of the methyl groups not in adjacent *peri*-positions is nearly the same as the contribution of the aromatic hydrogen atoms. Also the contribution of adjacent *peri*-methyl groups is not far from the contribution of aliphatic components. Further, any other relatively isolated hydrogen atoms in groups such as OH, CH, CHO, would make a small contribution to the second monent similar to that of an aromatic hydrogen. The calculated proportion of aromatic hydrogen would therefore include hydrogen atoms in these groups. It is therefore possible to calculate from the observed second moment the ratio of aromatic hydrogen atoms and hydrogen atoms in methyl groups not in adjacent *peri*-positions to hydrogen atoms in the CH_2 and adjacent *peri*-methyl groups. Thus, let this ratio be a/b, then the second moment is

$$\langle(\Delta H_2)^2\rangle_{Av} = \frac{a}{a+b} \times 9\cdot 7 + \frac{b}{a+b} \times 27\cdot 5 \text{ gauss}^2$$

and

$$\frac{a}{b} = \frac{27\cdot 5 - \langle(\Delta H_2)\rangle_{Av}}{\langle(\Delta H_2)^2\rangle_{Av} - 9\cdot 7}$$

In the case of tetralin, $\langle(\Delta H_2)^2\rangle_{Av} = 21\cdot 8$ gauss^2, whence $a/b = 0\cdot 47$. The correct ratio is 0·50. The calculated ratios for the compounds are compared with the correct ones in the last two columns of Table 5.

The above equation was applied to the range of vitrain coals and the results are given in Table 6. The resultant ratio (P_0) given in col. 2 of Table 6 must be corrected for the hydroxyl content of the coal (H_{OH}) as suggested by Dryden,[12] since hydrogen attached to oxygen probably behaves like aromatic hydrogen. This being assumed, if H is the total hydrogen content of coal, then the corrected ratio (P) is given by $P = P_0 - (1 + P_0)(H_{OH})/H$. The corrected values are given in col. 3 of Table 6. The value of H_{OH} has been calculated by assuming that the hydroxyl-oxygen amounts to 60% [12] of the total oxygen in a bright coal.

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[11] Land, Richards, and Ward, *Trans. Faraday Soc.*, 1959, **55**, 225.

[12] Dryden, *Fuel*, 1958, **37**, 444.

There is also the complication of the hydrogen in methyl groups in adjacent *peri*-positions. Infrared studies[13] indicate that there are not many methyl groups present. Support is obtained from the study of the kinetics of coal carbonisation[14] covering a range of vitrinites from 80·2 to 93·7% of carbon. This indicates that there is only one methyl group per lamella and that higher hydrocarbon radicals are rare, only about one in five lamellæ having one containing between two and three carbon atoms. This suggests the presence of "side groups" and alicyclic rings rather than "side chains." Recent *X*-ray studies[15] also indicate the presence of alicyclic structures in appreciable amounts. A reasonable assumption from the infrared measurements is that the ratio of non-aromatic hydrogen in methyl to that in CH_2 is of the order of 1·10.[12] In this case upper and lower limits of the ratio $H_{ar}/(H_{CH_2} + H_{Me})$ can be calculated in which respectively all or none of the methyl groups are in the *peri*-position:

TABLE 6.

C (%) in coal	$\dfrac{H_{ar} + H_{Me}}{H_{CH_2} + H_{peri\text{-}Me}}$	Corr. for OH	$\dfrac{H_{ar}}{H_{CH_2} + H_{Me}}$ Upper limit	Lower limit	f_a * Upper limit	Lower limit
79·2	0·5	0·4	0·4	0·3	0·75	0·75
82·0	0·9	0·8	0·8	0·6	0·80	0·78
84·9	1·2	1·1	1·1	0·9	0·84	0·82
86·7	1·7	1·6	1·6	1·4	0·87	0·86
91·4	3·0	2·9	2·9	2·5	0·93	0·92
94·0	5·4	5·2	5·2	4·6	0·98	0·98

* f_a = Fraction of aromatic carbon.

$$\text{Upper limit} = r. \qquad \text{Lower limit} = (10r - 1)/11.$$

These upper and lower limits are included in cols. 4 and 5 of Table 6. It must be emphasised that the "aromatic" hydrogen in Table 6 still includes any tertiary CH hydrogen which may be present. Estimates of the proportion of these tertiary CH groups vary and so at present this cannot be disentangled from the aromatic content. The conclusions drawn in this paper are based on the estimates given by Dryden.[12]

The fraction of aromatic carbon (f_a) was calculated from these figures, it being assumed[12] that the proportion of tertiary CH groups is small. This was done by first calculating the percentage of hydrogen in CH_2 and methyl groups in the coal from the total hydrogen less that in the form of hydroxyl. Then the percentage of carbon in this form was calculated by using a weight factor of 12/2·1, in order to allow for a small number of methyl groups.[12] The carbon in aromatic form was calculated by difference from the total carbon content, and finally the fraction of aromatic carbon (f_a).

It seems from the evidence quoted above that the proportion of *peri*-methyl groups in the coals is likely to be very small and that therefore the lower limit of f_a is likely to be more accurate.

The above procedure may be carried out on the second moments of the coals studied by Newman, Pratt, and Richards.[3] The results are shown in Table 7. It is assumed that the carbon content of the coals were on a dry, mineral-matter-free basis (d.m.m.f) (for low-ash coals this is roughly equivalent to the air-dried coal basis). The correlation between the values of f_a for the two sets of coals is very good.

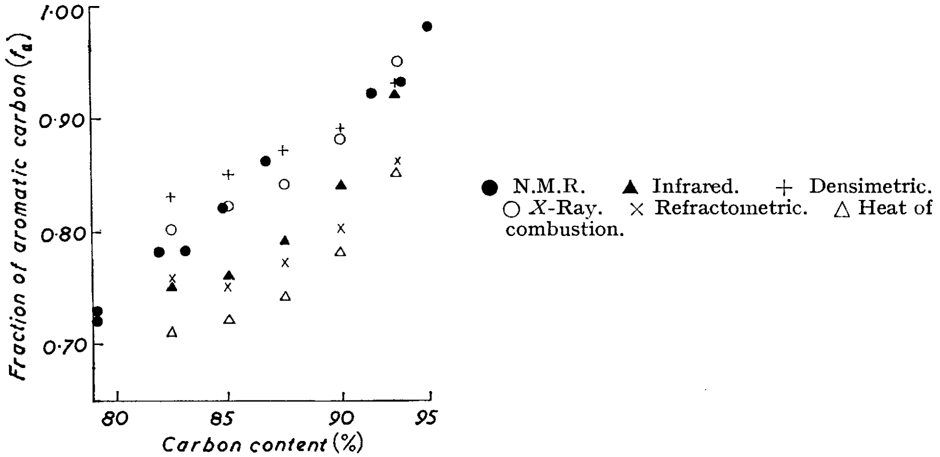
These values may be compared with similar results obtained from other methods. The other physical methods which have been reported can be classified broadly into those that yield (directly or after preliminary calculations) values of the fraction of carbon in

[13] Brown, *J.*, 1955, 744.
[14] Fitzgerald and Van Krevelen, *Fuel*, 1959, **38**, 17.
[15] Ergun and Tiensuu, *Nature*, 1959, **183**, 1669.

aromatic form (*e.g.*, infrared spectroscopy and density in relation to elementary composition) and those that yield parameters related to the size of the aromatic nuclei (*e.g.*, *X*-ray diffraction, molecular refraction in relation to elementary composition, and calorific value in relation to composition). Values of f_a have, however, been calculated by Dryden [12] from the results of the last three methods. Thus in the *X*-ray method the experimental average diameters of the lamellæ were correlated with the number of carbon atoms in them and values of f_a were obtained by successive approximations of estimated values. Similar methods were used with the molecular refraction and calorific value results.

TABLE 7.

				$\frac{H_{ar}}{H_{CH_2} + H_{Me}}$			
C (%) in coal	Second moment (gauss^2)	$\frac{H_{ar} + H_{Me}}{H_{CH_2} + H_{peri\text{-}Me}}$	Corr. for OH	Upper limit	Lower limit	Upper limit	Lower limit
79·2	21·5	0·5	0·4	0·4	0·3	0·74	0·72
83·1	19·5	0·8	0·7	0·7	0·5	0·80	0·78
92·6	16·0	1·8	1·7	1·7	1·5	0·94	0·93



The values of f_a from these physical methods have been plotted against carbon content in the Fig., together with the values obtained above from the second moments of the two series of coals studied. Infrared results for a hydrogen/optical density factor of 3 and the lower limit of the nuclear resonance results have been plotted. It is seen that the nuclear resonance values of f_a are somewhat greater than those of the infrared, refractometric, and heat of combustion methods at all values of carbon content. They are generally in good agreement, however, with the results from the densimetric and *X*-ray methods within the limits of experimental error.

The calculations were also applied to the two samples of dull coal studied. The second moment of 17·1 and 17·8 gauss^2 led to values of f_a of 0·81 and 0·79 respectively for the lower limit. Unfortunately, the petrographic analysis of these coals was not available. However, the values of f_a are somewhat smaller than obtained above for a vitrinite of the same carbon percentage, and it follows that there is probably a large proportion of exinite present, as would be expected in a dull coal.

The measurements on the range of coals obtained by solvent-extraction showed that there was little difference in second moment between the extracted samples and the original vitrinite. Thus the extracts obtained closely resemble the parent coal and there is no appreciable separation of the aromatic from the aliphatic material. This confirms the fact that the aromatic and the aliphatic portion of coal form parts of the same molecules rather than separate molecular species. Similar results have been obtained in the attempted separation of coal in solution by chromatography.[16] The value of the second moment for the benzene extract is rather greater than that for the trichlorobenzene extract, indicating a slight enhancement of the proportion of aliphatic hydrogen atoms. It is interesting that an infrared investigation by Hertog and Berkowitz [17] of the benzene extract of a coal showed a similar increase of the aliphatic hydrogen atoms over that of the parent coal.

The calculations above were also carried out on the three macerals studied. The results are shown in Table 8. There is a remarkable difference in the fraction of carbon in aromatic form between the three macerals. The exinite is considerably less aromatic than vitrinite of the same carbon content and with micrinite the converse is the case. Dormans, Huntjens, and van Krevelen,[18] using the densimetric method, have determined values of f_a for a range of similar macerals, and found that when the vitrinite had a carbon percentage of 85·0%, the values of f_a for the micrinite, vitrinite, and exinite were 0·92, 0·84, and 0·75 respectively. These values are in reasonable agreement with the lower limit of nuclear-resonance values determined above. In line with this general trend of aromatic proportions, it has been found that more volatile matter can be obtained from exinite, and less from micrinite, than from the corresponding vitrinite, and also that the yield of coke falls into the sequence micrinite, vitrinite, exinite. Thus it would be expected that the volatile matter arises mainly from the aliphatic carbon in the coal. Actually, not quite all the aromatic carbon is left in the coke residue, some of the smaller aromatic clusters being set free as volatile matter, but this is not enough to upset the general conclusions.

TABLE 8.

Coal	$\frac{H_{ar} + H_{Me}}{H_{CH_2} + H_{pert\text{-}Me}}$	Corr. for OH	$\frac{H_{ar}}{H_{CH_2} + H_{Me}}$ Upper limit	Lower limit	f_a Upper limit	Lower limit
Micrinite	4·9	4·6	4·6	4·1	0·94	0·93
Vitrinite	2·7	2·5	2·5	2·2	0·90	0·89
Exinite	0·7	0·6	0·6	0·5	0·79	0·77

Measurements by Smidt, van Raayen, and van Krevelen [5] show that a sample of coal containing 96·5% of carbon gave a second moment of 8·6 gauss^2. This would suggest that the intermolecular broadening is smaller in coal than in the hydrocarbons studied so far. On the other hand, the difference is small in any case, in relation to the assumptions which must be made about the coal structure, and this has only a small influence on the derived value of f_a.

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[16] Dryden, Institute of Fuel Conference, April, 1958.

[17] Hertog and Berkowitz, *Fuel*, 1958, **37**, 253.

[18] Dormans, Huntjens, and van Krevelen, *Fuel*, 1957, **36**, 321.