The Infrared Spectra of Coals.

By J. K. Brown.

The infrared spectra from 650 to 4000 cm.⁻¹ for twelve vitrains are presented and their variations with carbon content are discussed. A similar basic skeleton for coals over a wide range of carbon content is indicated by the general similarity of the spectra, but two well-defined changes in the absorption bands assigned to substituent groups have been observed. One indicates a decrease in the number of hydrogen-bonded OH groups with increase in carbon content; this is virtually complete in the region of 89% of carbon, and is accompanied by an increase in aromatic hydrogen. The other is a reduction in the aliphatic material with increase in carbon content which is most marked between 90 and 94% of carbon. This is accompanied by an increase of structureless absorption in the spectra which is tentatively interpreted as due to an electronic absorption of condensed aromatic rings. A semiquantitative measure of the ratio of CH (aliphatic)/CH (aromatic) links is made. The possibility of aromatic ether or quinone structures is discussed with particular reference to the 1600-cm.⁻¹ absorption band. The region between 900 and 700 cm.⁻¹ is analysed in terms of the pattern of aromatic hydrogen atoms.

Few infrared spectra of coals have been published, but several papers deal with the spectra of thin sections of coal (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279; Friedel and Pelipetz, *J. Opt. Soc. Amer.*, 1953, **43**, 11), of coal as powder suspensions in Nujol (Cannon and Sutherland, *Nature*, 1945, **156**, 240; Gordon, Adams, and Jenkins, *ibid.*, 1952, **170**, 317; Cannon, *ibid.*, 1953, **171**, 308), and of various solvent extracts and reaction products (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279). This paper describes the spectra of a series of coals covering a wide range of carbon content; comparison of these spectra allows an analysis to be made in terms of chemical structure,

so that the relation between structures present in different coals can be established, and information about the chemical changes accompanying coalification can be derived. Some work on these lines has already been carried out by Cannon (*loc. cit.*). Although the spectrum of a thin section of coal shows all the absorption bands without interference, the Nujol mull method is more convenient for the study of a wide range of coals and coal products, and this technique has been used in the present work.

EXPERIMENTAL

All coals consist of a number of components which are distinguished mainly by their appearance under the microscope though partly by their chemical composition. Of these constituents vitrain is the most abundant and homogeneous; the materials used in the present investigation were all vitrains picked out by hand from the seams listed in Table 1 (where the analyses given are those of the vitrains, not of the whole coal).

The coals were examined as mulls in the spectral region 650—2000 cm.$^{-1}$ in Nujol and in the region 2000—4000 cm.$^{-1}$ in hexachlorobutadiene. The lump coals were powdered and dried in a vacuum-desiccator for 24 hr. They were transferred to the mulling agent in an agate mortar and ground for 8 hr.; longer periods of grinding did not reduce the scattering of the radiation significantly. About equal weights of powdered coal and mulling agent were used for each coal, though for the hexachlorobutadiene mulls the liquid tended to evaporate slowly during grinding and more had to be added from time to time to maintain a smooth paste. Finally, the paste was spread in the usual manner between rock-salt plates separated by a fixed spacer.

TABLE 1. *Analyses of vitrains.*

						Per cent. by wt. of coal analysed		Loss in wt. on heating to 925° : % of dry ash-free coal †
	Per cent. by wt. of dry, mineral-matter-free coal							
Source	C	H	N	S	O (by diff.)	Mois-ture *	Ash	
Leicestershire, Eureka Seam	78·3	5·2	1·6	0·7	14·2	12·4	1·0	42·2
Staffordshire, Cannock Wood Shallow Seam	80·4	5·3	1·7	0·9	12·0	13·0	0·7	43·1
Northumberland, Ellington High Main ...	81·8	5·3	1·8	—	11·1	9·6	0·9	37·4
N.E. Division, Steetley Unit Clowne Seam	83·2	5·6	2·0	0·7	8·5	8·0	1·2	—
Orgreave Colliery (Yorks), Flockton Brights (coking coal ‡)	85·4	5·3	1·6	1·0	6·6	2·7	0·9	35·2
N.E. Division, Grimethorpe Unit, Parkgate Seam (coking coal ‡)	87·3	5·4	1·8	0·9	4·6	1·8	0·7	—
S.W. Division, Coedley, Pentre Seam (coking coal ‡)	88·7	5·1	1·4	0·6	4·2	1·0	1·7	30·2
Durham Division, Langley Park, Victoria Seam (coking coal ‡)	89·3	5·1	1·8	0·9	2·9	1·1	0·2	26·4
S.W. Division, Coegnant, Gellideg Seam (steam coal ‡)	91·4	4·4	1·4	0·8	2·0	0·7	1·1	15·9
S.W. Division, Fforchaman, Gellideg Seam (steam coal ‡)	92·8	3·9	—	—	—	1·0	1·2	9·8
S.W. Division, Llandebie Middle Seam (anthracite ‡)	94·1	3·1	—	—	—	2·4	0·7	5·3
S.W. Division, Pontyberem, Lower Pump-quart Seam (anthracite ‡)	94·1	3·0	0·9	—	1·4	1·4	1·2	5·3

* Loss in wt. at 105—110° in 1½ hr. *in vacuo.*

† Under conditions specified for " Volatile Matter " test in B.S.S. No. 1016; results corrected for CO_2 (data included as additional means of identifying the material used).

‡ These descriptions of the vitrains are used in the Discussion and are included here for reference. For the relation of these to coal classification, see Moffatt, Hicks, and Matthews, *Combustion Engineering*, 1950, 150.

A Hilger D209 double-beam spectrometer was used, with a 30° rock-salt prism for the region 650—2000 cm.$^{-1}$ and a 30° fluorite prism for the region 2000—4000 cm.$^{-1}$. No allowance was made for any change in the level of background absorption with wave-length in the region 650—2000 cm.$^{-1}$; the signal in the blank beam of the spectrometer was adjusted so that at the beginning of the run (near 700 cm.$^{-1}$) the trace was close to the 100% transmission line. The only alteration made after this adjustment was in the slit width, which was periodically reduced throughout the region. For the region 2000—4000 cm.$^{-1}$ the instrument was again set so that at the beginning of the run (near 2000 cm.$^{-1}$) transmission was near the 100% line, and the

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spectrum was examined as before without any scattering material in the blank beam. In measuring the spectra obtained for this region, a background curve was drawn in; this coincided with the recorder trace outside the region of discrete absorption bands. In this way a quantitative estimate of each of the absorption bands was possible. The spectra of the range of vitrains are shown in Fig. 1.

Fig. 1. *Infrared spectra of a range of vitrains between* 650 *and* 4000 *cm.*$^{-1}$.

Wave-number (cm.$^{-1}$)

— — — — *Nujol absorption bands.*   . . . . *Uncertain intensity.*
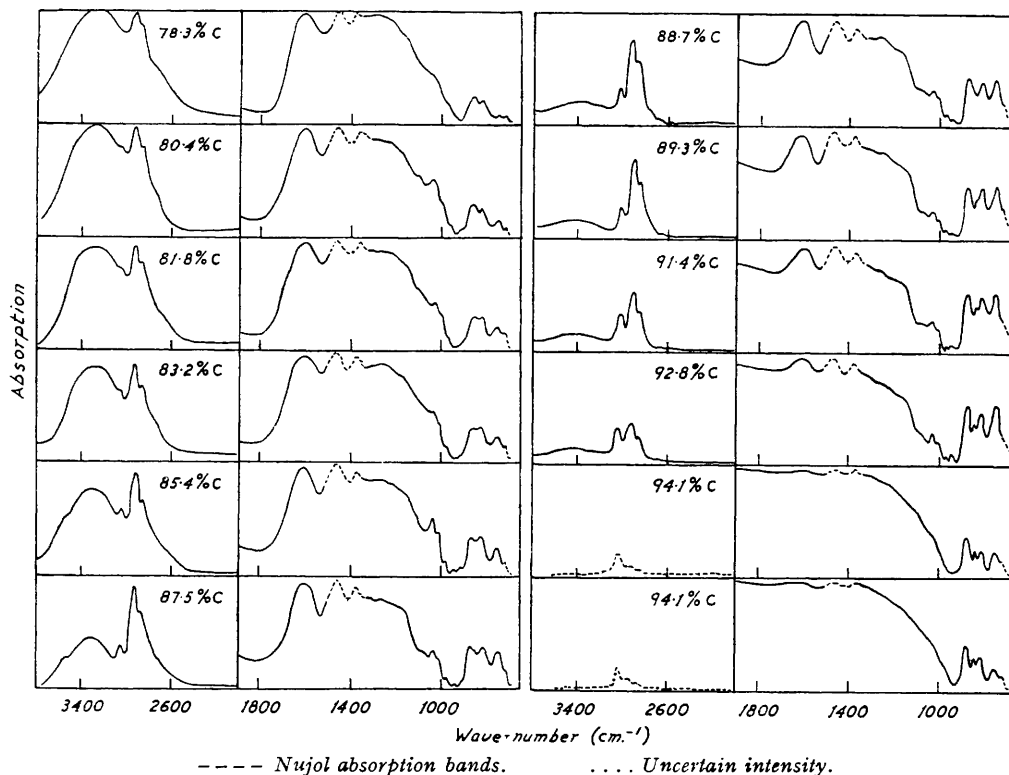
DISCUSSION

Assignment of Vibration Frequencies to Substituent Groups.—The spectrum of the Flockton coal (85·4% of carbon) can be taken as representative of the series, as it shows most of the frequencies observed in coal spectra; these are listed in Table 2 together with the assignments proposed. Since it is difficult to distinguish between the vibration frequencies of aliphatic chains and alicyclic or hydroaromatic systems in complex structures, the term aliphatic group will be used to include all these types.

The small amount (<2%) of nitrogen present in the coals makes it certain that the broad absorption band near 3300 cm.$^{-1}$ arises principally from hydrogen-bonded OH groups; the strong absorption near 1250 cm.$^{-1}$ suggests that these are mainly phenolic (cf. Cannon, *loc. cit.*). Adsorbed water can also give rise to a band near 3300 cm.$^{-1}$, but since heating a coal to 105° for one day under a high vacuum did not significantly reduce the intensity of the OH absorption band, this explanation seems unlikely. The frequencies near 3000 cm.$^{-1}$ indicate the presence of aromatic CH and aliphatic groups; the latter should give rise to the well-known frequencies at 1460 and 1380 cm.$^{-1}$, but in the spectra shown in Fig. 1 they are masked by the strong absorption bands of Nujol. These absorption bands have been detected in thin sections of coal and in coal extracts (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279; Friedel and Pelipetz, *loc. cit.*; Hadzi, *Acad. Sci. and Art, Sloven.*, Class III, Ser. A, 1951, **3**, 99; Brown, unpublished work). Absorption bands near 1460 cm.$^{-1}$ may also be assigned to aromatic ring frequencies.

The above conclusions are similar to those given by Cannon (*loc. cit.*) except that he observed absorption bands at 1730 and 1690 cm.$^{-1}$ (assigned to ester groups and aldehyde or keto-groups, respectively) which have not been detected in the vitrain spectra. They have, however, been found in a spore-rich durain (Brown, unpublished work), so it is possible

TABLE 2. *Assignment of frequencies observed in coal spectra.*

Frequency (cm.$^{-1}$)	Assignment
ca. 3500 (w)	Hydrogen-bonded OH/NH
ca. 3300 (s)	Hydrogen-bonded OH/NH
3030 (w)	Aromatic C-H stretching
2920, 2850 (s)	Aliphatic CH$_2$ and CH$_3$ stretching
ca. 1605 (s)	Aromatic ring frequency *
1160—1300 (s)	C-O stretching of phenols, aromatic ethers. OH deformation. Quinones
1060—1160 (m)	C-O stretching of alcohols, linear and cyclic ethers
ca. 1030 (m)	C-O stretching of aromatic ethers of the type Ph·O·CH$_2$R
860, 820, 750 (w)	Aromatic C-H out-of-plane vibration frequencies observed in a number of single and condensed ring structures

* See discussion (p. 751). (s) = strong; (m) = medium; (w) = weak.

that the absorption bands arose from spore material in the bright coals investigated by Cannon.

Changes in Spectra with Carbon Content.—(a) *The background.* The general background level of absorption in the infra-red spectra of coals has been shown to vary with carbon content (Cannon, *loc. cit.*). In the spectra studied in this work the level between 78 and 88% of carbon remains roughly constant. For higher carbon contents there is a marked increase which becomes very pronounced in the steam coals and anthracites. The background level increases with decrease in wave-length and is most clearly seen at the short wave-length end of the Nujol mull spectra (*i.e.*, 2000 cm.$^{-1}$). The effect is not illustrated in the region 2000—4000 cm.$^{-1}$, as here the background trace was taken as coincident with the 100% transmission line.

The effect could be explained as an apparent absorption, which arises from the scattering of radiation by the powdered coal. This explanation seems unlikely, since microscopic examination showed that the average particle size in the mulls of coals with carbon contents between 89 and 94% did not differ significantly from those of coals with lower percentages of carbon. Further, although the refractive index of vitrains increases with carbon content (Cannon and George, Proc. Conf. Ultrafine Structure of Coals and Cokes, B.C.U.R.A., London, 1944, 290; van Krevelen, *Brennstoff-Chem.*, 1953, **34**, 167) the change cannot be closely correlated with the variation in background absorption. The change does, however, follow the development of marked optical anisotropy (Cannon and George, *loc. cit.*) and the growth of graphitic crystallites established by *X*-ray studies (Riley *et al.*, Proc. Conf. etc., 176). The reflectance and absorption coefficient of vitrains in the visible region also increase markedly in the range 89—94% of carbon (Seyler, *ibid.*, p. 270; Cannon and George, *ibid.*, p. 290; van Krevelen, *loc. cit.*). The structureless absorption in the infra-red region can be explained, following Cannon (*loc. cit.*), as arising from the transition of an aromatic structure to a graphite-type lattice. The observation that a dispersion of graphite in Nujol of 2-μ thickness shows a continuous structureless absorption of 70—80% over the whole range 5000—650 cm.$^{-1}$ (Cannon, *loc. cit.*) supports this view. Further, Kmetko (*Phys. Review*, 1951, **82**, 456) has found that in the infra-red spectra of Cellophane chars an " absorption " edge moves across the region 5000—650 cm.$^{-1}$ from the visible with increasing temperature of carbonisation. He attributes this effect to the motion of electrons in a graphite-type lattice and discusses it in terms of semi-conductor properties. Work on the electrical conductivity of polycyclic aromatic compounds (Inokuchi, *Bull. Chem. Soc. Japan*, 1951, **24**, 222) has been interpreted in a similar manner; the energy difference between the empty and the occupied levels in these semiconductors decreases with increasing number of π-electrons in the molecule. This number is directly related to the number of condensed rings. Ultimately the energy difference is sufficiently small for electronic transitions to lie in the infra-red region. It is therefore reasonable to attribute the absorption edge observed in the coal spectra to the presence of condensed-ring structures which

increase markedly in size at carbon contents higher than approximately 89%. Even in the anthracite spectra the absorption edge lies well within the range 4000—650 cm.$^{-1}$, which suggests that the structures in these coals are somewhere between an assembly of large polynuclear hydrocarbons and graphite.

The spectrum of an anthracite published by Gordon, Adams, and Jenkins (*loc. cit.*) differs from those shown in Fig. 1 in that the increase in background absorption with decreasing wave-length is not shown. Presumably these authors have considered the effect to arise from the scattering of radiation and have consequently measured their curves from standard backgrounds obtained by suspensions of spectroscopic carbon in Nujol.

(b) *Variation of oxygen groupings with carbon content.* Fig. 1 shows that, as expected, the intensity of absorption bands assigned to oxygen-containing groups decreases with the oxygen content of the vitrain. The hydrogen-bonded OH absorption band near 3300 cm.$^{-1}$ shows the most marked effect. For the carbon content range 78—84% this band is strong and overlaps the C–H stretching absorption bands near 3000 cm.$^{-1}$; as the carbon content increases it becomes progressively less prominent, and in vitrains with more than 89% of carbon it is very weak. This change can be correlated with a change in the pattern of absorption between 900 and 700 cm.$^{-1}$. The decrease in intensity of the OH band also correlates well with the extractability of coals by solvents such as ethylenediamine (Dryden, *Fuel,* 1951, **30**, 217).

The broad region of absorption between 1300 and 1160 cm.$^{-1}$ also decreases in intensity with carbon content in accordance with the assignment given in Table 1. However, marked absorption remains in this region even when the hydrogen-bonded OH band at 3300 cm.$^{-1}$ is weak; this residual absorption may arise from aromatic ether linkages.

(c) *The aliphatic and aromatic hydrogen.* The variation in the proportions of aliphatic and aromatic CH groups in the structure with increase in carbon content can readily be followed from the intensities of the absorption bands that arise from their stretching vibrations at 2850, 2920, and 3030 cm.$^{-1}$. Fig. 1 shows that the aliphatic C–H stretching absorption bands are strong over a considerable range of carbon content; there is a decrease in intensity with increase in the percentage of carbon which is particularly marked in the range 90—94% of carbon. The aromatic C–H stretching absorption band increases in intensity as far as the beginning of the anthracite region (93% carbon); at 94% of carbon, qualitative estimates indicate that there is a decrease in intensity.

In order to compare quantitatively the relative intensities of the aromatic and aliphatic C–H stretching absorption bands for coals of different carbon contents, the optical densities for the 3030 cm.$^{-1}$ absorption band, $D_{ar.}$ and for the 2920 cm.$^{-1}$ absorption band, $D_{al.}$, were measured; D, the optical density, is defined by $D = \log_{10} I_0/I$, where I_0 is the intensity of the incident radiation and I that transmitted by the sample. To estimate the optical densities, a background was drawn in as accurately as possible and allowance was made for the overlapping wings of the two absorption bands. No attempt was made to correct for the presence of the 2850-cm.$^{-1}$ absorption band, as the method was only used empirically. The strength of the hydrogen-bonded OH band in the coals with carbon contents between 78 and 84% prevented quantitative estimate of $D_{ar.}/D_{al.}$. A rough measure was possible for coals with carbon contents near 84%; at higher percentages of carbon the accuracy was improved since the OH absorption band intensity was much reduced. At 94% of carbon, measurement was again difficult owing to the high background absorption. A large number of runs were made for each coal and the average of the results taken. The values of $D_{ar.}/D_{al.}$ are plotted against the percentage of carbon in Fig. 2. Several coals not listed in Table 1 are included; these fit on to the curve very satisfactorily. It is clear that there is a marked increase in the ratio of $D_{ar.}/D_{al.}$ with increase in carbon content; this is most pronounced in the region 90—94% of carbon.

The optical densities, $D_{ar.}$ and $D_{al.}$, are related to the extinction coefficients per C–H bond, $\varepsilon_{ar.}$ and $\varepsilon_{al.}$, and to the number of bonds of each type, $n_{ar.}$ and $n_{al.}$, by $D_{ar.}/D_{al.} = (\varepsilon_{ar.}/\varepsilon_{al.})(n_{ar.}/n_{al.})$.

The exact nature of the chemical structures present in coal is unknown, so that values of $\varepsilon_{ar.}/\varepsilon_{al.}$ must be obtained indirectly in order to estimate $n_{ar.}/n_{al.}$. Aromatic molecules certainly occur which, it will be assumed, have aliphatic chains attached to them or contain

alicyclic rings. A number of reference compounds of this type (with 3—5 condensed rings) were examined as mulls in hexachlorobutadiene. From the measurements of $D_{ar.}/D_{al.}$ and the known values of $n_{ar.}/n_{al.}$ in these compounds the values of $\varepsilon_{ar.}/\varepsilon_{al.}$ were found to vary between 0·3 and 1·0. A value of 0·5 has been taken for the coals, so that an order of magnitude of $n_{ar.}/n_{al.}$ can be deduced from Fig. 2. At 92% of carbon, where $D_{ar.}/D_{al.}$ is approximately 0·5, there is roughly one aromatic C–H bond for each aliphatic C–H bond in the structure; at 84% of carbon the ratio of $n_{ar.}/n_{al.}$ is approximately 0·25.

(d) *Variation in aromatic substitution with carbon content.* The pattern of absorption bands between 900 and 700 cm.$^{-1}$ (which arises from the out-of-plane vibration of aromatic CH bonds) can be used to follow the changes in aromatic substitution with carbon content. Fig. 1 shows that, as the carbon content of the vitrain increases, the absorption bands in the above region also increase in intensity. Three main absorption peaks are observed in the spectra; at the beginning of the range they lie at approximately 860, 825, and 750 cm.$^{-1}$. The 750-cm.$^{-1}$ absorption band is markedly weaker than the others. With increase in carbon content there is a gradual shift in the position of the 860 and 825 cm.$^{-1}$ absorption bands; in coals with carbon contents above 90% they reach positions near 874 and 814 cm.$^{-1}$, respectively. The 750-cm.$^{-1}$ absorption band increases in intensity relative to the others as the percentage of carbon increases until, in coals with carbon contents near 89%,

Fig. 2. *Ratio of the optical density of the 3030-cm.$^{-1}$ and 2920-cm.$^{-1}$ absorption bands, plotted against carbon content for a range of vitrains.*
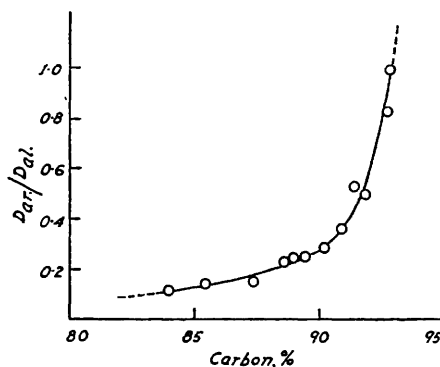
it has a strength approximately equal to that of the two higher-frequency absorption bands. In the spectra of coals with percentages of carbon between 90 and 93% the pattern remains almost unchanged although there is an overall increase in intensity; a weaker, but nevertheless clearly defined, absorption band appears in this range at 840 cm.$^{-1}$. In the anthracites (94% of carbon) there is a change in the pattern; the 750-cm.$^{-1}$ and 814-cm.$^{-1}$ absorption bands decrease in intensity and the 874-cm.$^{-1}$ absorption band becomes the strongest in the region 700—900 cm.$^{-1}$. The pattern observed for the anthracites is different from that shown in the spectrum published by Gordon, Adams, and Jenkins (*loc. cit.*), where only one absorption band, near 720 cm.$^{-1}$, has been recorded.

Strong absorption bands in the region 700—900 cm.$^{-1}$ are present in the spectra of many single- and condensed-ring aromatic structures. These bands have mainly been assigned to out-of-plane C–H vibrations. Correlations between the type of substitution and the aromatic C–H out-of-plane vibration frequencies have been derived for a number of substituted benzenes and are now well established (*e.g.*, see McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318; Gourlay, *Research*, 1950, **3**, 342). A discussion of these in terms of the number of adjacent hydrogen atoms on the ring (Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 64) shows that, as this number is reduced by substitution, the frequency of out-of-plane motion increases from a value near 750 cm.$^{-1}$ when five C–H bonds are present to approximately 870 cm.$^{-1}$ when one remains. The trend is also observed in the spectra of condensed aromatic hydrocarbons. Several authors (Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, 373; Orr and Thompson, *J.*, 1950, 218; Dannenburg, Schiedt, and Steidle, *Z. Naturforsch.*, 1953, **8**, *b*, 269) have been able to

correlate regions of absorption in the range 900—700 cm.$^{-1}$ in the spectra of a number of linear and angular condensed aromatic systems by considering each ring in terms of its substituted benzene analogue; in such cases each condensed ring substitutes two positions on its neighbour. The correlations between number of neighbouring aromatic hydrogen atoms on each ring and the observed out-of-plane frequencies lead to similar conclusions but have the advantage that substitution in the coal structure can be discussed without detailed consideration of the ring configurations. If single aromatic nuclei are present in the coal structure the absence of strong absorption near 690 and 770 cm.$^{-1}$ means that the concentration of mono-, *meta-*, 1 : 2 : 3-, and 1 : 3 : 5-substituted rings must be small. The main conclusions concerning the degree of aromatic substitution are as follows :

(1) The presence of absorption near 860 cm.$^{-1}$ in coals at the lower end of the range of carbon contents, taken in conjunction with the fact that the 750-cm.$^{-1}$ absorption band is relatively weak, suggests that aromatic systems containing isolated C–H bonds are important, *i.e.*, the degree of substitution is high. This agrees with the observation that the aliphatic C–H and hydrogen-bonded OH absorption bands are strong in these coals.

(2) The marked increase in intensity of the absorption band at 750 cm.$^{-1}$ with increase in carbon content shows that the degree of substitution of part of the system is reduced. This change correlates well with the decrease in intensity of the OH absorption band, which appears only weakly in the spectra of coals with carbon contents of 89% and above. The analysis suggests that, if single ring systems are present, decrease in substitution produces *ortho*-disubstituted nuclei, whereas for condensed systems end rings (four neighbouring C–H bonds) or possibly certain corner rings (three neighbouring C–H bonds) are left unsubstituted as a result.

(3) The relative intensity of the absorption bands in the region 900—700 cm.$^{-1}$ does not change between 89 and 93% of carbon although there is an overall increase in intensity. Since there is a very pronounced loss of aliphatic groups in the above range, these groupings have been eliminated from the ring systems without affecting materially the overall balance of substitution in the system.

(4) At 94% of carbon (*i.e.*, in the anthracites) the overall degree of substitution again increases; the 874-cm.$^{-1}$ band is now the most prominent. This means that a large proportion of the aromatic systems contain isolated C–H bonds in spite of the further marked decrease in the aliphatic content which has taken place. Further, the intensity of some absorption bands in the anthracite spectra has decreased, which suggests that the amount of aromatic hydrogen on the rings in these coals is less than in those of 93% carbon content.

Further deductions can be made from the observations. The spectra show that a well-marked absorption band occurs near 870 cm.$^{-1}$ for all the coals; this implies that the degree of substitution of part of the system remains high throughout the range. In terms of isolated ring structures it indicates pentasubstitution which, in the anthracites, predominates over all other types. Such a high degree of substitution is not readily maintained because in the range 90—94% of carbon the aliphatic material is almost entirely eliminated. In a system containing condensed aromatic structures this difficulty does not arise, for a high degree of substitution can be maintained by neighbouring rings in the structure. The predominance of isolated C–H bonds in the anthracite structure is then readily explained in terms of large condensed aromatic systems, which would contain a considerable number of such bonds on their periphery. The process by which coking coals (89% of carbon) are converted into semi-anthracites (93% of carbon) is pictured as one in which the degree of condensation of the aromatic structures is increased by ring closure or by cross-linking with the elimination of aliphatic groups. The formation of the anthracites studied in the present work has entailed a loss not only of aliphatic but also of aromatic hydrogen; the interpretation given earlier suggests that some of this loss of aromatic hydrogen has taken place from end or corner rings of the condensed systems (correlated with the 750-cm.$^{-1}$ band). A possible mechanism would be one in which condensed ring structures, built up in the way already suggested, cluster together to form large polycyclic systems. The growth of the condensed units in coal structure in the range 90—94% of carbon is entirely consistent with the interpretation of the increase in background absorption observed in the above region.

(e) *The* 1600-*cm.*$^{-1}$ *absorption band.* Absorption bands near 1600 cm.$^{-1}$ occur in a wide range of single- and condensed-ring aromatic compounds; they arise from ring vibrations. The intensity of these bands is very variable but, with few exceptions, it is not great in the alkyl-substituted benzenes * and is generally weak in condensed aromatic hydrocarbons which contain more than three rings (Cannon and Sutherland, *Spectrochim. Acta, loc. cit.*). A very pronounced absorption band near 1600 cm.$^{-1}$ is present in the spectra of all the coals, except in the anthracites, where the high background absorption obliterates the spectra in this region. It is probable that the aromatic ring vibration bands are enhanced in intensity by a polar grouping attached to the aromatic systems, or the polar grouping itself may have a vibration frequency near to 1600 cm.$^{-1}$. Phenolic OH groups are not mainly responsible for the effect, as there is no marked diminution in intensity of the band with increase in carbon content. Aromatic ether linkages are one possibility. Very few reference compounds are available to test this hypothesis; diphenyl ether has a strong absorption band near 1600 cm.$^{-1}$ (Barnes, Gore, Liddel, and Williams, " Infra-red Spectroscopy," Reinhold Publ. Corp., New York, 1944, p. 70) and so also do lignins (*e.g.*, see Schubert and Nord, *J. Amer. Chem. Soc.*, 1950, **72**, 3835). Diphenylene oxide, which contains oxygen in a five-membered ring, does not show the effect (Barnes *et al., loc. cit.*). Another possibility is that the absorption band arises from a carbonyl group which forms part of the aromatic system. Polycyclic extended quinones which have hydroxyl groups in the *peri*-position to the carbonyl groups can have carbonyl frequencies close to 1600 cm.$^{-1}$; *e.g.*, hipericin, 1589 cm.$^{-1}$, and 4 : 4'-dihydroxyhelianthrone, 1607 cm.$^{-1}$. The strong internal hydrogen-bonding which, in part, is the cause of the very low carbonyl frequency also causes a marked shift and weakening of the hydroxyl absorption bands. Where such absorption bands have been detected in chelated six-membered ring systems they have been found to be centred in the region 2700—3000 cm.$^{-1}$. In the spectra of coals containing strong OH absorption bands these do indeed extend to the low-frequency side of the C—H stretching fundamentals. Other systems which give carbonyl frequencies close to 1600 cm.$^{-1}$ have been discussed by Hunsberger, Ketcham, and Gutowsky (*J. Amer. Chem. Soc.*, 1952, **74**, 4839).

It is not possible to distinguish further between the two types of structure which have been discussed above. A correct interpretation of the reasons for a pronounced 1600-cm.$^{-1}$ absorption band in coal spectra is important; the band has been observed in the spectra of coals carbonised at 500° (Brown, following paper, p. 756) and also in all the coal extracts which have so far been examined (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279; Hadzi, *loc. cit.*; Brown, unpublished work). A strong absorption band in the above position has also been found in the spectra of sugar and Cellophane chars (Friedel and Pelipetz, *loc. cit.*).

Conclusion.—The preceding discussion has shown that the infra-red spectra provide valuable information concerning the nature and variation with carbon content of the substituent groups in coal structure, as well as some indirect conclusions about the nature of the aromatic systems. Two well-defined changes have been detected; the first is the loss of hydrogen-bonded OH groups (probably mainly phenolic) which is near completion in coals containing 89% of carbon. In the range of carbon contents 78—89% there is a marked decrease in the oxygen to carbon ratios (78% C, O/C = 0·14; 89% C, O/C = 0·03) which, as expected, accompanies this change. It may be significant that coals near the upper limit of this range (89% of carbon) show the strongest coking properties, and further, that they have the lowest viscosity (van Krevelen, *loc. cit.*) and porosity (King and Wilkins, Proc. Conf. etc., *loc. cit.*, p. 46; Franklin, *Trans. Faraday Soc.*, 1949, **45**, 274). The second change, which is most marked between 89 and 94% of carbon, is a decrease in the amount of aliphatic material. There is a corresponding reduction in the H/C ratios (89% C, H/C = 0·7; 94% C, H/C = 0·4). The infra-red data for this range of carbon content suggest that condensed aromatic structures occur and the removal of aliphatic material promotes their growth.

Finally, the coals selected for study have, in a number of cases, been obtained from

* In these compounds the 1600-cm.$^{-1}$ absorption band is accompanied by a stronger one near 1500 cm.$^{-1}$; this is not evident in the coal spectra.

sources which are geographically widely separated. As the changes which have been followed occur continuously throughout the series, it appears that these aspects of the process of vitrinisation are of general applicability. Other modifications of coal spectra which are produced by carbonisation and solvent extraction will be discussed in further papers. Throughout the discussion in preceding sections it has been tacitly assumed that the aromatic and non-aromatic materials form part of a single system. It has not been possible, so far, to separate vitrains into widely different materials, and therefore the above assumption is reasonable.

Note added, January 31st, 1955.—Gordon *et al.* (*Nature*, 1954, **174** 1098) have shown recently that a large reduction of the background present in spectra of coals of high carbon content in Nujol mulls can be achieved by prolonged ball-mill grinding of the samples with potassium bromide and subsequent pressing to a disc. This strongly suggests that the effect arises from the scattering of radiation.