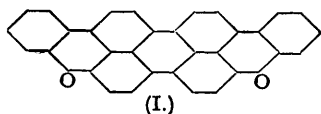# 87. *Amorphous Carbon.*

By J. Gibson, M. Holohan, and H. L. Riley.

X-Ray diffraction photographs of the so-called "amorphous" carbons have hitherto been interpreted as indicating that they consist of exceedingly minute turbostratic graphite crystallites: this view requires modification in the case of cokes and chars prepared at temperatures below 1200°. The nature of the organic substance, from which such carbons are prepared, is an important factor in determining their crystallographic character. It has been found possible to prepare carbons which are completely amorphous, *i.e.*, that give no coherent diffraction of *X*-rays, and indications have been obtained of three-dimensional, covalent cross-linking in such carbons. The bearing of these results on the crystallographic character of cokes and chars is discussed.

The term " amorphous carbon " is usually employed to describe more or less impure forms of carbon which are devoid of any obvious crystalline characteristics. Debye and Scherrer (*Physikal. Z.*, 1917, **18**, 291) found that such carbons, prepared by a variety of methods, all gave essentially the same type of *X*-ray powder photograph with the maxima of the diffuse diffractions in the same positions : " Amorphe Kohle ist also Graphit in einer so feinen Verteilung, wie dieselbe durch mechanische Mittel niemals erreicht werden kann ". From the diffraction broadening they estimated that the individual " molecule " often contains only about 30 atoms. Detailed *X*-ray examination of a large number of related series of " amorphous " carbons (see Blayden, Gibson, and Riley, " The Ultra-Fine Structure of Coals and Cokes," B.C.U.R.A., London, 1944, 176—231 : *J. Inst. Fuel*, 1945, War Time Bulletin, 117) indicates that the above view requires modification, and further work has shown that truly amorphous carbon does exist. By measuring the half-peak widths of the diffraction bands in *X*-ray powder photographs it is possible to follow the growth of the carbon crystallites with increasing temperature of carbonisation. The inner (002) diffraction halo gives the average height (c dimension) of the minute carbon crystallites, conceived as small cylinders, and the less intense (10) halo gives the average diameter (a dimension). The corrected half-peak width (β) of the 002 diffraction is related to the c dimension (L) by Jones's formula $\beta = 1.0\lambda/L\cos\theta$, where λ is the *X*-ray wave-length, and θ the Bragg angle : the half-peak width of the 10 diffraction, which is a cross-lattice diffraction, is related to the a dimension by Warren's formula, $\beta = 1.84\lambda/L\cos\theta$ (*Physical Rev.*, 1942, **49**, 693). Fig. 1 summarises the results of these crystallite growth studies already obtained. Fig. 1*a* shows the average c and a dimensions of the crystallites present in chars obtained by carbonising pure cellulose at 5° per min. up to various temperatures. The increase in the a dimension (*i.e.*, experimentally, the sharpening of the 10 diffraction band) is probably due to the progressive lamellar growth of the hexagon layer-planes of carbon atoms, brought about by a process of aromatic condensation which commences at about 200°. The constancy of the c dimension is, however, somewhat surprising and suggests that the layer-planes of the individual crystallites are rigidly cross-linked in some way or other. It should be remembered that these chars do not consist of pure carbon but contain appreciable quantities of

oxygen and hydrogen, and that it is only when the carbonisation temperature has been well above 1000° that the product obtained approximates to pure carbon. There is evidence that it is these foreign oxygen and possibly also nitrogen and sulphur atoms which play a crucial rôle in the structure of these rigid turbostratic crystallites. The word " turbostratic " was coined by Biscoe and Warren (*J. Appl. Physics*, 1942, **13**, 364) to describe those mesomorphous crystallites in which the layer-planes are stacked parallel to each other and equally spaced along the *c* axis, but are otherwise disordered along the *a* and *b* axes : such crystallites show only 00*l* and *hk* diffractions. There is much evidence in support of this hypothesis of the crucial rôle of oxygen atoms in carbon crystallites, *e.g.*, the carbohydrates cellulose, starch, sucrose (see also Hofmann and Sinkel, *Z. anorg. Chem.*, 1940, **245**, 85), and glucose; lignin and wood, *i.e.*, compounds containing a relatively high proportion of oxygen, all give chars on carbonisation which contain crystallites with an average *c* dimension between 9 and 10 A. The carbonising conditions can be varied between wide limits, with respect to both temperature (up to 1200°) and speed, without any consequential change in the half-peak width of the 002 diffraction of the resulting char. If, however, glycine is used as the parent organic substance, or if cellulose is carbonised in an atmosphere of ammonia (Blayden, Gibson, Riley, and Taylor, *Fuel*, 1940, **19**, 24) a similar phenomenon is observed but the constant *c* dimension is now between 12 and 13 A., instead of 9—10 A. The essential chemical difference between the carbohydrate chars and those from nitrogenous organic compounds is that whereas the former contain residual oxygen, in the latter, it is more or less completely replaced by nitrogen (Hook, *Carnegie Schol. Mem. Iron and Steel Inst.*, 1936, **25**, 81), which suggests that these foreign atoms have similar functions in the carbon lattice and that the nitrogen atom is preferentially retained.

Perhaps the most convincing evidence in support of this hypothesis is that, if the proportion of oxygen in the parent organic compound falls below a certain value (probably critical), then an entirely different type of *c* dimension curve results. Fig. 1*b* shows the *c* dimension curve obtained on carbonising that part of a bituminous coal pitch which is soluble in carbon tetrachloride. This type of curve is also given by pitches, certain bitumens, bituminous coals, the γ-solvent extracts of coals and certain pure organic compounds. It appears to be characteristic of the presence in the parent carbonaceous substance, of large, stable, lamellar aromatic molecules which contain a small proportion of oxygen : it has been interpreted as follows. The ascending part of the curve, between room temperature and about 500°, suggests the occurrence of a unidimensional crystallisation, brought about by the packing together of stable lamellar molecules. The maximum at about 500° reflects the conversion of a system which consists essentially of independent stable organic molecules, held together by weak dispersion forces (molecular lattice), into one which consists of rigid (cross-linked) carbon crystallites. This fundamental change in the crystallographic character of the system occurs over a relatively narrow range of temperature, the magnitude of which appears to be a function of the proportion of

FIG. 1.

oxygen in the carbonaceous material. If the proportion is large then, as in the case of cellulose, the rigid cross-linked crystallites are formed at a temperature as low as 200° : at the other extreme, certain coal bitumens give *c*-dimension curves showing maxima in the neighbourhood of 550°. If the proportion of oxygen present in the carbonaceous substance is less than the critical proportion, then even with large, relatively complex, highly condensed molecules, the carbon yield obtained on carbonisation is less and there is an increasing tendency for the substance to volatilise. Support for the above interpretation of the variation of the half-peak width has been obtained by a study of the carbonisation of pure organic compounds; *e.g.*, if dibenzanthrone (I) is precipitated quickly, in the cold, from a soluble vat, the product gives a diffuse diffraction pattern (See Plate I*a*). Annealing the compound at temperatures up to 475° brings about a progressive sharpening of the diffractions and the appearance of new diffractions. This phenomenon is analogous to the sharpening of the 002 diffraction with increasing temperature, in the
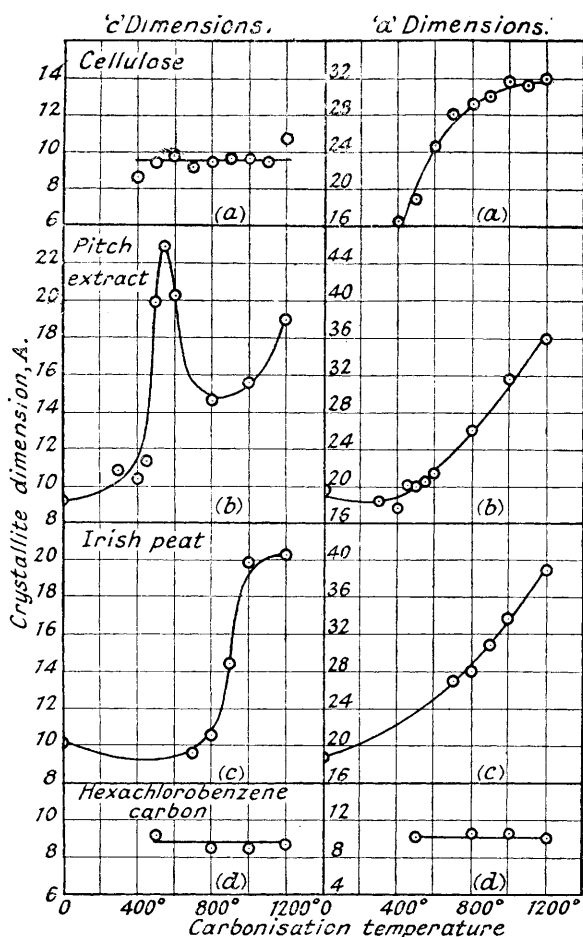
case of the pitches and bitumens which are, of course, mixtures of complex molecules of a similar type and consequently do not give line patterns. Between 475° and 500° the diffraction pattern of dibenzanthrone changes completely to that of " amorphous " carbon (see Plate I*b* and *c*).

The interpretation of the descending portion of the *c*-dimension curve between 550° and 900° (Fig. 1*b*) is not quite so clear. The following experimental facts are, however, significant. The phenomenon, as far as our experiments have gone, is of general occurrence. Whenever a carbonaceous substance on heating to some temperature below 550°, gives a product which contains crystallites having an average *c* dimension greater than about 12 A., then a further increase of temperature causes a decrease in the *c* dimension (experimentally, a broadening of the 002 diffraction). Carbonaceous substances with as different histories as South Wales anthracites, chars prepared at 500° from dibenzanthrone and similar compounds, carbonised bitumens, and pitches all show this phenomenon. In the case of bitumens and pitches it is possible partly to prevent the initial increase in the *c* dimension by preliminary oxidation, or extreme dispersion on an inert inorganic colloid, before carbonisation : if this is done then the subsequent decrease in the *c* dimension is much less pronounced. Those organic compounds which contain a high proportion of oxygen and carbonise at relatively low temperatures presumably do so because the cross-linking of the crystallites occurs at low temperatures; it is this that prevents any appreciable growth of the crystallites along the *c* axis in the temperature range 200—500°. When a smaller proportion of oxygen is present the cross linkages are only formed at higher temperatures and consequently, as aromatisation progresses, *c*-dimension growth becomes possible. Further increase in temperature (*i.e.*, above the maximum in the curve; Fig. 1*b*) is accompanied by the evolution of oxygen, in the form of oxides of carbon, presumably with the reduction in the number of the cross-linkages and a consequent possibility of some disruption in the rigid lamellar arrangement of the lattice. The subsequent increase in *c* dimension which occurs above 900° is perhaps facilitated by the remnants of the ordered structure which the system possessed at 550°. In the case of cellulose and similar chars, crystallite growth along the *c* axis shows little tendency to occur at temperatures below 2000°.

A still further type of *c*-dimension curve is shown in Fig. 1*c* : it is characterised by an abrupt increase in the average *c* dimension of the crystallites in the temperature range 800—1000°. This type of crystallite growth is shown by peats and to a less extent by brown coals and lignites. So far we have only succeeded in reproducing this crystallographic behaviour with laboratory-prepared substances in the case of " bituminised " cellulose and lignin, *i.e.*, cellulose or lignin which has been heated in an autoclave to about 300° with excess of aqueous alkali : these dark products on carbonisation behave crystallographically remarkably similarly to peat. If the peat (but not the bituminised cellulose) is boiled with 2% hydrochloric acid and then carbonised, the chars do not show this pronounced increase in *c* dimension, but, like cellulose chars, have a constant *c* dimension up to 1200°. This result indicates that the anomalous crystallographic behaviour of the peat chars is a consequence of some structural property in the original peat. The pronounced increase in *c* dimension between 800° and 1000° further suggests that the crystallographic nature of low-temperature peat chars is fundamentally different from that of either cellulose chars or bitumen cokes prepared at similar temperatures. Although the 800° peat chars are not pure carbon they contain more than 92% of the element, the balance being largely oxygen and hydrogen : there is little doubt also that they contain some turbostratic crystallites, since the *X*-ray diffraction pattern is not greatly different from that of the corresponding cellulose char. In the case of the peat char, however, the crystallite growth between 800° and 1000° is so great as to suggest the occurrence of some profound atomic rearrangement in this temperature range, perhaps a kind of polymorphic change. Neglecting the finer points in the lattice structure of microcrystalline carbons, such as the variation of the *c* spacing and the parallel stacking of the layer-planes, only two lattice structures of carbon atoms are known, *viz.*, the three-dimensional, covalent diamond lattice and the aromatic, semi-metallic, layer-lattice of graphite; nevertheless, there is a third possible spatial arrangement of carbon atoms. The relationship of this third lattice to that of graphite is shown in Plate II*a*. It can be constructed from the graphite lattice by tilting alternate hexagon rings of the layer-planes and attaching the valencies so freed to those of similarly tilted hexagons in the adjacent planes above and below; Plate II*b* shows the rhombohedral unit cell of such a lattice. The disappearance in this lattice of the flat layer-planes suggests that the resonance energy of such a structure would be much less than that of a corresponding graphite lattice and its existence, therefore, less probable. The lattice contains, however, an orderly network of conjugated double linkages running through the whole structure, and its resonance energy would, therefore, be of an appreciable magnitude. The possible existence of such an arrangement of carbon atoms is suggested by the results of the electron diffraction studies by Karle and Brockway (*J. Amer. Chem. Soc.*, 1944, **66**, 1974), who have established the non-co-planarity of *o*-tetraphenylene. The suggested lattice is a three-dimensional repetition of *o*-tetraphenylene residues (see Plate II *c*). Theilacker and Ewald (*Naturwiss.*, 1943, **31**, 302) have given experimental evidence which they suggest throws doubt on the view that the stability of the triphenylmethyl radical depends upon the co-planar arrangement of the phenyl groups : the chemical similarity of graphite and the triarylmethyls has been pointed out (Riley, *J. Inst. Fuel*, 1937, **10**, 149). Wheland (" The Theory of Resonance," J. Wiley & Sons, New York, 1944, 192 ff.) has discussed the respective parts played by resonance and steric factors in determining the stability of aryl-substituted ethanes and similar compounds. These considerations indicated that an attempt to synthesise a carbon possessing this aromatic cross-linked structure would perhaps give interesting results.

Conditions of interaction which would inhibit the formation of flat, honeycomb net-works of carbon atoms
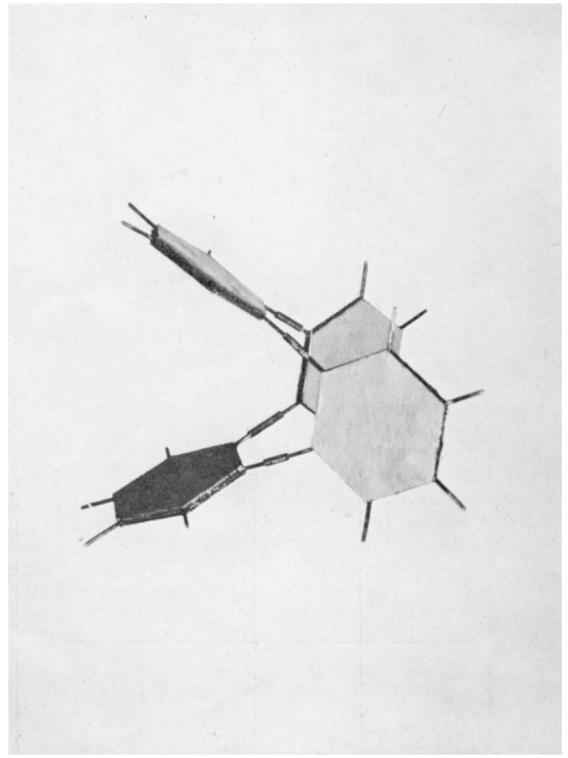
PLATE I.
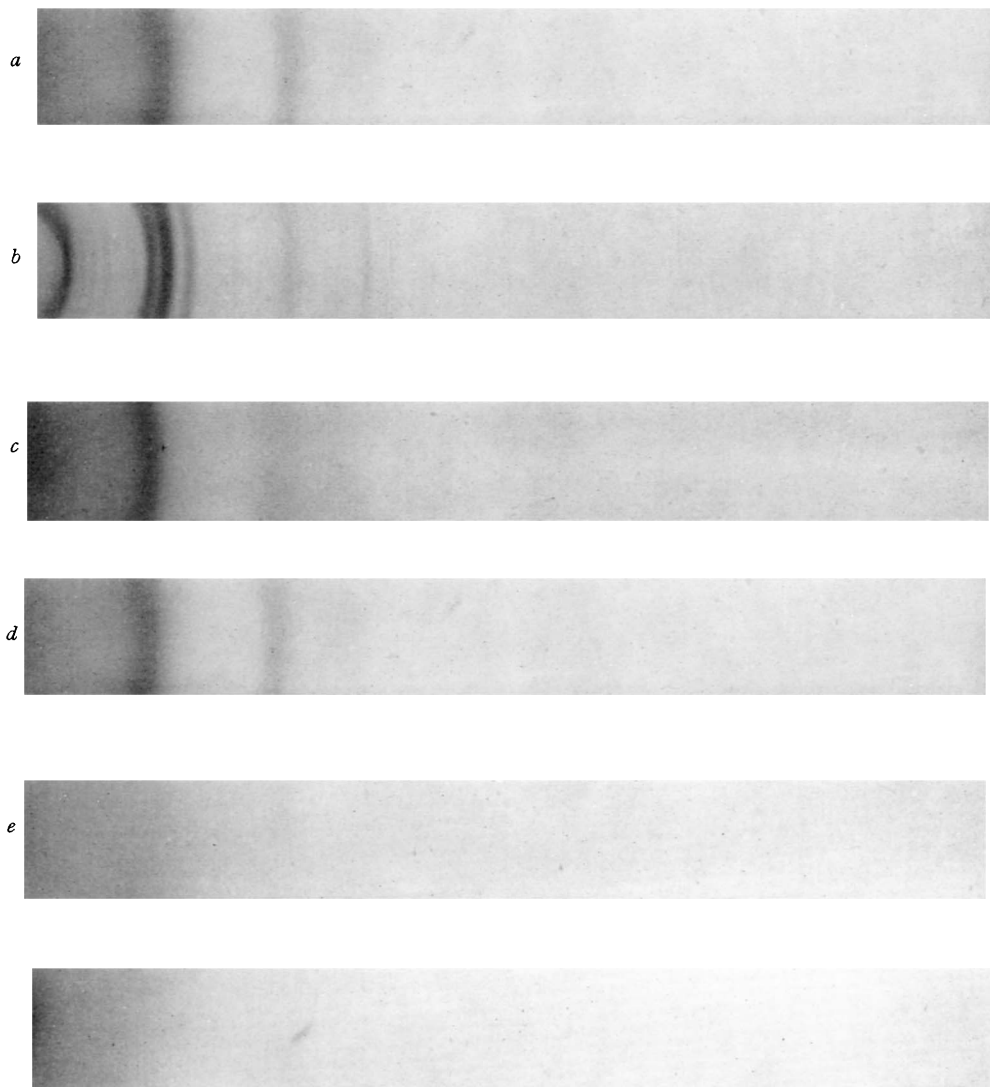
(a) *Dibenzanthrone precipitated cold.*
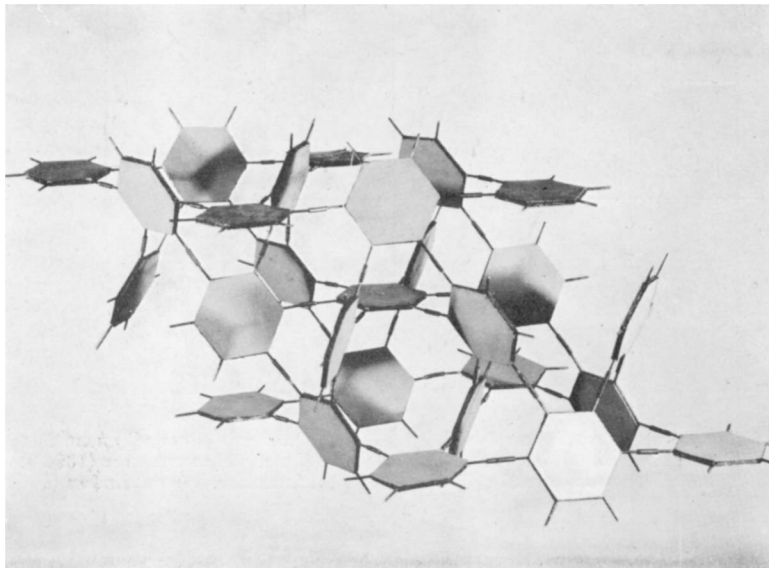(b) *Dibenzanthrone heated to 475°.*
(c) *Dibenzanthrone carbonised at 500°.*
(d) *Dibenzanthrone coke heated to 1000°.*
(e) *Hexaiodobenzene char (1000°).*
(f) *Hexachlorobenzene carbon (1000°).*

PLATE II.
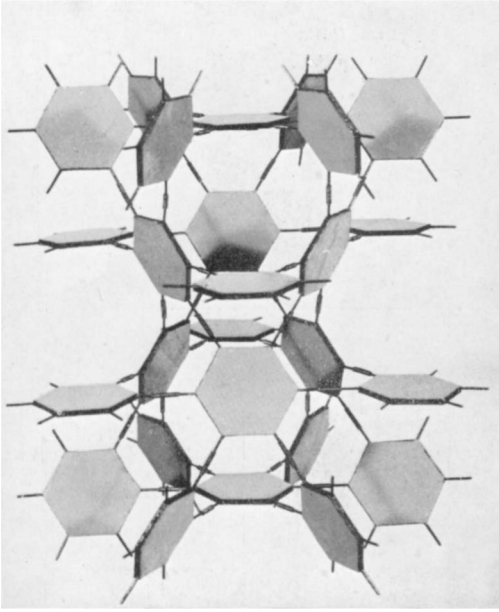
a

c

b

appeared to offer the best possibilities of building up this structure, and the carbonisation of hexaiodobenzene suggested itself as a possible method. Fig. 2 shows a scale drawing of two molecules of hexaiodobenzene, each less one iodine atom : the linking of two such residues with the C_6 rings co-planar is impossible. The C–C bond could only be formed by tilting one ring at a considerable angle with respect to the other. Hexa-iodobenzene was accordingly prepared and carbonised in a porcelain boat in a silica tube at 5°/min. up to 1000° in an atmosphere of nitrogen. The carbon residue in the porcelain boat consisted of pseudomorphs of the original crystals of hexaiodobenzene; there was a transluscent carbon mirror on the walls of the silica tube and also a fluffy deposit of carbon. The product was, however, contaminated with silica, probably because of the formation of volatile silicon–iodine compounds, together with the high adsorptive properties of the carbon

formed. After extraction of it with hydro-fluoric and hydrochloric acids, an *X*-ray powder photograph of the product was made. A reproduction of this is shown in Plate I *e* contrasted with that (*d*) of a carbon prepared by carbonising dibenzanthrone up to 1000°. Small-scale reproductions of microphotometer traces of these two photo-graphs are shown in Fig. 3, *a* and *c*. The powder photographs were made, as far as
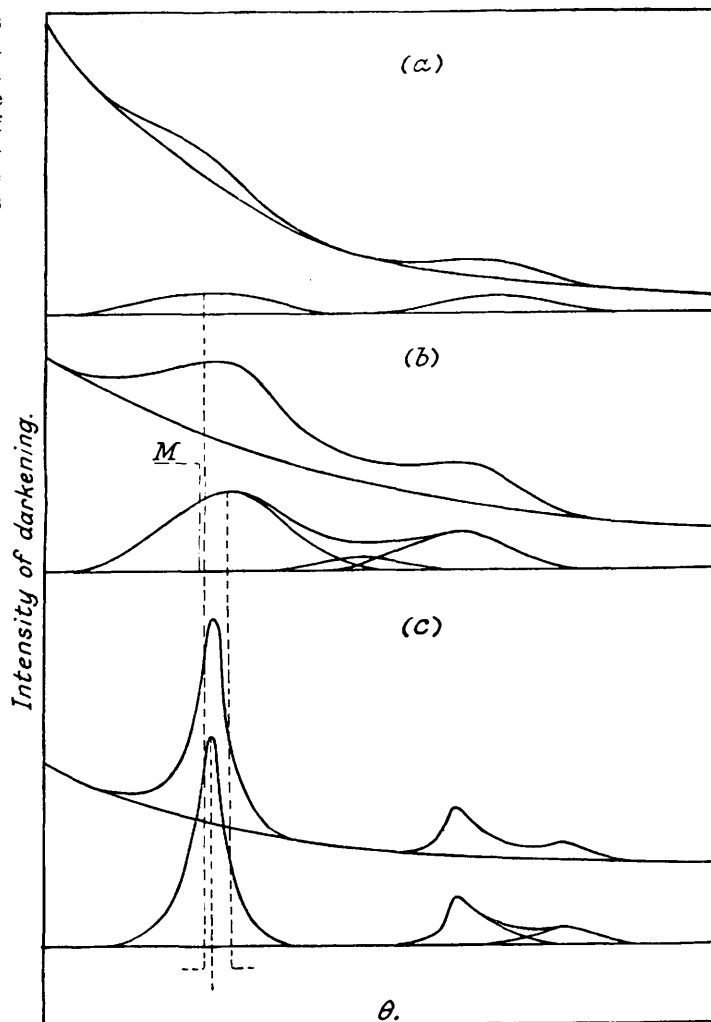
Fig. 2.
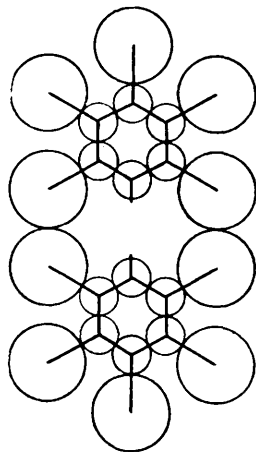
possible, under identical conditions. The hexaiodobenzene carbon gives practically no coherent scattering of the *X*-rays and indicates that the carbon is almost com-pletely devoid of any ordered structure. If " amorphous " carbon merely consists of extremely minute graphite crystallites, it is difficult to understand how such a dis-ordered structure as hexaiodobenzene-carbon could exist, for the shape of the lamellar hexagon layer-planes alone would cause them to pack together with a fairly high degree of order. A cross-linked struc-

Fig. 3.

(*a*) *Cf. Plate* I*e*.   (*b*) *Cf. Plate* I*f*.   (*c*) *High temperature coke.*

ture similar to that shown in Plate II, but highly disordered because of the presence of foreign oxygen and hydrogen atoms, appears to offer a more reasonable explanation of the existence of such a form of carbon (cf. Zachariasen, *J. Amer. Chem. Soc.*, 1932, **54**, 3841, on the structure of silica glasses).

The nature of hexaiodobenzene-carbon was sufficiently interesting to warrant further experimental work. It was thought possible that the rapidity of the decomposition of the hexaiodobenzene was in some way con-nected with the formation of the amorphous product. The method was not ideal owing to the difficulty of preparing hexaiodobenzene, the small yield of carbon obtained from it on carbonisation, and the corrosive action of the liberated iodine on the silica tube. Another method was therefore tried, *viz.*, by adding sodium amalgam, in small quantities at a time, to molten hexachlorobenzene kept at a temperature just below its b. p. (320°). The product was purified by water, dilute hydrochloric acid, and finally by heating to various tem-peratures in a stream of nitrogen to remove unchanged hexachlorobenzene and in vacuum to remove adsorbed

hydrogen chloride. Thus prepared, the carbons were voluminous, highly dispersed, black powders. Powder photographs were made of specimens which had been reheated to 500°, 800°, 1000° and 1200° in nitrogen; as far as could be judged the four photographs obtained were identical (see Plate I*f*). A typical small-scale micro-photometer trace is shown in Fig. 3*b*; it indicates a somewhat less disordered structure than that obtaining in the hexaiodobenzene-carbon, but it is different from the photometer traces of chars, cokes, etc. (see Fig. 3*c*). It differs in four important respects : (1) The maximum of the inner diffraction band is not in the position corresponding to its half-peak width, as judged from the photographs of chars and cokes : this is marked by *M* in Fig. 3*b*. (2) There are indications of the presence of an additional diffraction band between the 002 and the 100 diffraction. (3) The 100 diffraction gives a symmetrical trace, indicating that it is a three-dimensional and not a two-dimensional cross-lattice diffraction. (4) There is no sign of the 004 diffraction band.

The table below gives typical analyses, lattice parameters, and crystallite dimensions of carbons prepared by the above method and subsequently heated to various temperatures (see also Fig. 1*d*). The *a* dimensions

Carbonisation temp.	Percentage.				Lattice parameter, A.		Half-peak width, mm.		Crystallite dimension, A.	
	C.	H.	O (diff.).	Cl.	*a.*	*c*/2.	100'.	002.	*a.*	*c.*
400°	81·7	1·2	13·3	2·8	—	—	—	—	—	—
500	—	—	—	—	2·45	3·30	8·9	9·2	10·2	9·2
800	94·8	0·7	4·5	0·0	2·43	3·33	8·6	10·0	10·5	8·5
1000	96·2	0·5	3·3	0·0	2·42	3·34	8·5	10·0	10·6	8·5
1200	—	—	—	—	2·41	3·33	9·0	9·8	10·0	8·7

and the *a* spacings have been calculated by using Jones's formula and not Warren's, *i.e.*, it has been assumed that the 100 band is a three-dimensional and not a two-dimensional diffraction. The highly adsorptive character of the carbons made the interpretation of the analytical results difficult : the oxygen present is probably irreversibly adsorbed as water or atmospheric oxygen. The analytical results were, to some extent, dependent upon the thoroughness of the washing and thermal treatment in vacuum, but it was not possible to bring about further reductions in the percentage of oxygen. The constancy of both the *a* and the *c* dimensions is interesting and provides additional evidence of a rigid, cross-linked lattice structure. When heated to temperatures a little above 1200°, the carbons, as judged from their *X*-ray powder photographs, assumed a character more like that of cellulose chars.

It was thought possible that here, too, the velocity of reaction had an important effect in the formation of this type of carbon. Local overheating, involving perhaps large rises in temperature at the instant when the sodium amalgam was added to the molten hexachlorobenzene, probably occurred. There was definite evidence of momentary rapid reaction, which was occasionally accompanied by a flash of light if pure sodium instead of sodium amalgam was used. The reaction was made smoother and more controllable in the following manner. Freshly cut sodium was melted under medicinal paraffin in a bolt-head flask; small quantities of solid hexachlorobenzene were added from time to time, the temperature being kept at about 150—160°. Under these conditions the temperature may rise as high as 300° if the solid is added too quickly. The carbon and sodium chloride formed a crust on the surface of the molten sodium : it was broken periodically, and the sodium squeezed out by means of a glass rod.

The energetics of the reaction $C_6Cl_6 + 6Na = 6NaCl + 6C_{(solid)}$ suggest that it might be explosive. No explosions occurred either in these experiments or in those with sodium amalgam. When certain aliphatic halides were heated with molten sodium, however, even on a very small scale, violent explosions occurred : such mixtures should be considered highly dangerous. The smoothness of the reaction between hexachlorobenzene and sodium suggests that it does not involve the rupture of the aromatic ring system.

The carbons prepared by this method were thoroughly extracted and heated as described above. The *X*-ray powder photographs indicated that the *c* dimension was not altered by heating the product in nitrogen or in a vacuum to temperatures as high as 1000° : the *a* dimension, however, showed a distinct increase, reaching, in one experiment, a value of 16 A. after heating to 1000° : this growth was probably due to the presence of absorbed paraffin. Evidence in favour of this view was obtained by subjecting a sample in a high vacuum to a very slow rise of temperature : an appreciable amount of paraffin was collected in a liquid-air trap.

The above experiments indicate that the idea that black carbons, usually termed amorphous, are merely graphite in a very fine state of sub-division needs modification, although it is probably substantially correct in the case of certain carbons deposited from the gas phase (from either carbon monoxide or hydrocarbons). The nature of carbon prepared by carbonisation, *i.e.*, in the condensed phase, however, is influenced by the chemical and structural characterisitcs of the parent carbonaceous matter : cross-linking of the lamellar planes appears to be present, possibly brought about through the agency of oxygen atoms and also through the tilting of the aromatic hexagons. Although unequivocal evidence has not been obtained of the existence of the idealised structure shown in Plate II, yet there are indications that small disordered chunks of this type of structure may play a greater or a less part in building up chars and cokes. In this connection it is interesting to record that a specimen of a highly purified artificial graphite was recently found to give an *X*-ray powder photograph containing at least 16 faint sharp lines which cannot be indexed on the basis of either the Bernal or the Lipson structure : these lines also appear on the powder photographs of certain highly purified natural graphites. This concept of the two types of aromatic structure, *viz.*, the turbostratic lamellar and the disordered cross-linked, which build up the structure of chars and cokes, appears to offer a reasonable basis for explaining

the great range of properties shown by various carbons, *e.g.*, the highly specific nature and range of magnitude of adsorptive properties, the great variation of chemical reactivity, the subtle differences, quite apart from particle size, which determine the rubber-filling properties of carbon blacks; the differences in the tendency to graphitise at high temperatures; the differences in mechanical properties; the different degrees of atomic disorder which obtain in various carbons. The carbons prepared at low temperatures from hexachlorobenzene and sodium do not conduct electricity; they become electronic conductors after being heated to temperatures over 600°, in a similar manner to that shown by chars and cokes. The curves shown in Fig. 1 probably represent extreme types of crystallographic behaviour : intermediate behaviours are shown by other materials. The rapid increase in the c dimension between 800° and 1000° in the peat curve is perhaps an indication of a transition from the disordered cross-linked to the turbostratic lamellar type of structure.

EXPERIMENTAL.

Hexaiodobenzene was prepared by the method described by Rupp (*Ber.*, 1896, **29**, 1631). Benzoic acid (3 g.) was dissolved in fuming sulphuric acid (30 g.), heated to 120°, and iodine (20 g.) added in small quantities with continuous stirring, during ½ hour. After a further 6 hrs.' heating at 180°, the product was cooled and poured into cold water, and the solid formed was filtered off and heated on the water-bath to remove excess of iodine. Iodinated benzoic acid was extracted from the product by means of aqueous alkali, and the residue recrystallised from nitrobenzene. It formed reddish-brown needles, m. p. 340—360° (decomp.) (Found : I, 92·1. Calc. for C_6I_6 : I, 91·36%). The product was carbonised in an atmosphere of oxygen-free nitrogen in an electrically-heated Vitreosil tube furnace.

Hexachlorobenzene crystals were melted in a 1 l. round-bottomed flask and then heated to about 320°; liquid sodium amalgam, prepared by grinding small pieces of freshly cut sodium with mercury, was added carefully, in small quantities at a time, the heating being continued throughout. The carbon liberated, mixed with the mercury and sodium chloride, formed in the middle of the flask a conglomerate, which was broken up from time to time. In order to avoid over-heating the carbon, the addition of sodium amalgam was discontinued whilst a considerable excess of hexachlorobenzene still remained : some of this was removed by decantation. Most of the mercury liberated was also poured out of the flask. Water was then carefully added, followed by sufficient hydrochloric acid to neutralise the sodium hydroxide formed and leave the liquid faintly acid. The remainder of the mercury separated and was decanted. The carbon was washed thoroughly with hot water to remove the sodium chloride and the excess of hydrochloric acid, and then dried. The product still contained a large amount of unchanged hexachlorobenzene, which was removed by heating in a stream of nitrogen for an hour at 500°. The final vacuum heating was done in a fused quartz tube connected to a pumping system consisting of two stages of oil diffusion backed by a high-capacity rotary oil pump.

Carbon was also prepared from hexachlorobenzene as follows. To medicinal paraffin (B.P.) (100 c.c.) contained in a wide-necked bolt-head flask in an oil-bath, freshly cut sodium (about 7 g.) was added, and the whole heated to 150°. The sodium melted and formed a mercury-like layer. Hexachlorobenzene crystals, which are readily soluble in the paraffin, were added in small batches, about 90 mins. being taken to added 8 g. The mixture was stirred from time to time. The reaction, which proceeded slowly and quietly at about 150—160°, started with the tarnishing of the bright sodium surface and the gradual and progressive discoloration of the paraffin near the sodium surface. A jet-black deposit was quickly formed at the interface, which gradually formed a coherent incrustation, presumably consisting of a conglomerate of carbon and sodium chloride. This was periodically broken and squeezed by means of a glass rod, in order to expose a fresh sodium surface. Too rapid addition of the hexachlorobenzene led to a considerable rise in temperature. After being cooled, the reaction mixture was treated with rectified spirit followed by water, to remove the greater part of the excess sodium and the sodium ethoxide, hydroxide and chloride which had been formed. The product was then placed in a Soxhlet apparatus and thoroughly extracted with (*a*) dioxan (to remove paraffin and hexachlorobenzene), (*b*) water, and (*c*) alcohol : it was finally dried at 130°. Analysis of the product indicated that it still contained adsorbed impurities, and various modifications of the above treatment were tried, *e.g.*, a stage of prolonged steam-distillation, the exclusion of all organic solvents, a final treatment with a volatile solvent like ether, etc., but the results described above suggested that some paraffin remained in the product. For this reason the sodium amalgam method of preparing this type of carbon is preferable. The subsequent purification should be carried out with water (organic solvents should not be used), followed by thermal treatment in a high vacuum.

The *X*-ray powder photographs were made by using a cylindrical camera (radius 45·43 mm.) and cobalt-$K\alpha$ radiation. The electrical conductivity of the carbon samples was measured in a semimicro-apparatus consisting of a glass capillary tube carrying two closely fitting metal plungers. The conductivity measurements were made with the sample under high compression.