

turn out that the conditional distributions have some advantages, they could be derived from the determinantal joint probability distributions. However, they would be rather more complicated than the expected value formulas of this paper and, because of this, I believe that the expected value formulas might well be tried first.

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X-ray Diffraction Studies on the Arrangement of Atoms in Carbon Blacks.

I. Results of Radial Distribution Analysis

BY S. K. SANYAL, B. K. SAMANTARAY AND G. B. MITRA

Indian Institute of Technology, Kharagpur – 721302, India

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Abstract

Radial distribution analysis studies by X-ray diffraction of carbon blacks obtained by pyrolysis of benzene C_6H_6 , toluene, C_7H_8 , and sucrose, $C_{12}H_{22}O_{11}$, and samples of ultracarbon of the medicinal variety have been carried out. Bonding distances, coordination numbers and the layer dimensions have been determined. It has been observed that the carbon blacks have turbostratic structures. The C–C distances in the carbon layers lie in the range of that for aromatic rings and double bonds. Ultracarbon has the C–C bonding distance corresponding to graphite.

1. Introduction

Because of their increasing uses, various allotropic modifications of carbon are being investigated more

and more regarding their structure–property relations. Atomic arrangements in carbon in its various forms – especially the amorphous forms – are becoming more and more fascinating to study.

X-ray diffraction patterns of all types of amorphous carbons have one feature in common: they all have two broad peaks in the approximate neighbourhood of diffraction angles corresponding to 002 and 100 peaks of graphite. This led early workers like Asahara (1922), Mahadevan (1929), Blayden, Gibson & Riley (1944), Siever (1952), Mitra (1953), Nelson (1954) and Hirsch (1954) to assume that amorphous carbon consisted of very small particles of graphite so disordered that only the 002 and 100 reflections remained intact while other peaks cancelled out. Some additional peaks were observed by some of these workers, but the model essentially remained the same.

The concept of the defective graphite crystallite as the basic model of amorphous carbon – though implicit in many previous works – was first explicitly and quantitatively stated by Biscoe & Warren (1942) and Houska & Warren (1954). According to this concept amorphous carbon is not truly amorphous but is turbostratic in which the graphite-like crystallite consists of perfectly crystalline lattice planes stacked parallel to each other but oriented in all directions perpendicular to the stacking direction. Wilson (1949), Franklin (1950), Hirsch (1954), Diamond (1957), Méring & Maire (1960), Ruland (1965), Warren & Bodenstern (1966), Pauling (1966) and Ergun & Gifford (1968) considered various aspects of the problem and put forward new theoretical ideas supported by experimental data in this direction.

However, Nelson (1954) was the first to apply the technique of radial distribution analysis developed by Warren & Gingrich (1934) to the analysis of the structure of amorphous carbon. This method has the advantage of not being based on any specific model. Warren & Mozzi (1966) and Warren (1969) improved this method and Nicholas, Marjoram & Whittaker (1972) included crystallite size effects on the radial distribution analysis of carbon films. One important result of such an analysis is the determination of the number of atoms surrounding any given atom or the 'coordination number' at a given radial distance from the given atom. This coordination number can be compared with the given model and the best possible match can be interpreted as the most probable arrangement of atoms in the sample under study. The purpose of the present paper is to determine by using this technique the arrangements of atoms in amorphous carbons prepared by pyrolysis of different organic substances and to investigate to what extent they differ from one another.

2. Experimental

2.1. Preparation of the samples

Benzene and toluene of the AR type were placed separately in a Pyrex phial with a Pyrex lid and an asbestos wick. The asbestos wick was carefully cleaned with acid and alcohol. The phial was placed in a water-cooled container inside an enclosure whose air supply could be controlled. The wick was lighted and the carbon black was collected on Pyrex plates. Similarly, analytically pure sucrose was carbonized in excess of air. A sample of ultracarbon of the 'Merck' variety, tested to be of very high purity, was also studied. The samples were finely powdered for diffractometric investigation.

2.2. Recording of intensities and calculation of the radial distribution function

The distribution of the X-ray diffraction intensities in reciprocal space was obtained with the help of a Norelco X-ray diffractometer using Cu $K\alpha$ radiation monochromatized by a balanced filter. The unit was operated at 38 kV and 15 mA. Intensities were recorded at $0.1^\circ 2\theta$ intervals in the region 2 to $151^\circ 2\theta$ by a constant-time point counting technique. The GM-counter output was fed to a decade scaler unit by EIT tubes. The number of counts recorded was chosen such that the statistical error was always less than 1.0%. The experimental intensities were corrected for polarization and absorption following the procedure described by Klug & Alexander (1974).

Tabulated values of the atomic scattering factor (Cromer & Waber, 1965) and incoherent scattering factors (Hajdu, 1971) were used for obtaining the independent scattering curves. The corrected intensities I_{corr} were scaled to electron units ($I_{\text{e.u.}}$) first by a high-angle method and then by the integral method (Krogh-Moe, 1956) and the contribution of the multiple scattering to the intensities was deducted following the method described by Warren & Mozzi (1966).

For a flat diffractometer sample the diffracted intensity is given by (Warren, 1969)

$$I_{\text{e.u.}} = Nf^2 + Nf^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho(0)] \frac{\sin sr}{sr} dr + \frac{\rho(0)^2 f^2 \lambda^2 D^2}{4(\mu^2 + s^2 \sin^2 \theta)} \quad (1)$$

with

$$N = \frac{A_0 \rho(0)}{2\mu},$$

where A_0 is the cross-sectional area of the X-ray beam, $\rho(0)$ is the atoms per unit volume, D is the radius of the focusing circle, μ is the absorption coefficient, and

$$s = \frac{4\pi \sin \theta}{\lambda}.$$

By subtracting the contribution of the third term for the low-angle region and using the inversion relations of the Fourier integral, the radial distribution function can be expressed as

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho(0) + \frac{2r}{\pi} \int_0^\infty s i(s) \sin sr ds, \quad (2)$$

with

$$i(s) = \frac{I_{\text{e.u.}}(s) - Nf^2}{Nf^2}.$$

The radial distribution function $4\pi r^2 \rho(r)$ gives the number of atoms lying between shells of radius r and r

+ dr with respect to a representative atom at the origin. An artificial temperature factor e^{-bs^2} was introduced for suppressing spurious ripples due to truncation of the integration at finite value of s_{\max} , so that (2) can be modified and written as

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho(0) + \frac{2r}{\pi} \int_0^\infty s i(s) \sin sr e^{-bs^2} ds. \quad (2a)$$

The value of b was adjusted till the ripples in the low region were considerably reduced. $b = 0.01 \text{ \AA}^2$ was the optimum value for all the samples used in the present investigation.

2.3. Determination of layer dimensions

The dimensions of the crystallites parallel and perpendicular to the layers (L_a and L_c , respectively) have been determined from the line-width measurements of the 11 band and the 002 reflection, respectively, by following the procedure described by Warren (1941) and Warren & Bodenstein (1966).

3. Results and discussions

3.1. Peak position

The intensity distribution ($I_{e.u.}$ vs s) curves for the samples under study are shown in Fig. 1. It is seen that all the substances give peaks corresponding to 0.025, 0.033, 0.070, 0.112, 0.147, 0.236, 0.278, 0.320 and 0.420 \AA^{-1} . However, in the case of sucrose black the peak corresponding to 0.025 \AA^{-1} is absent and those

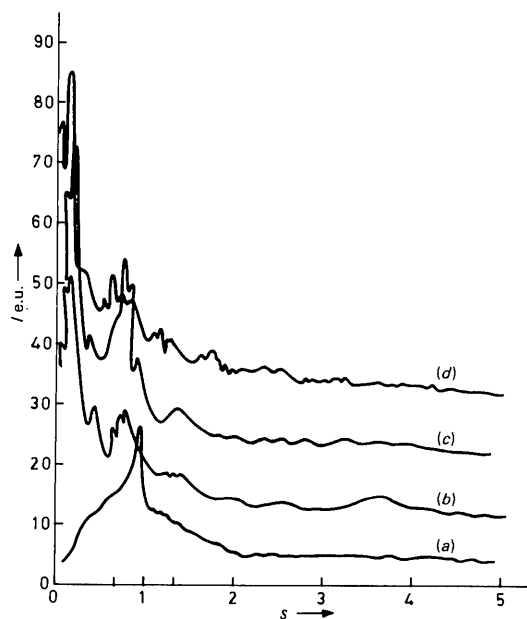


Fig. 1. Plots of I (electron units) vs $s = 4\pi \sin \theta/\lambda$ for (a) sucrose, (b) toluene, (c) benzene carbon blacks and (d) ultracarbon. For the sake of clarity the origins of the successive curves along the ordinates have been shifted by ten units.

corresponding to 0.033, 0.070 and 0.112 \AA^{-1} are very weak. This is in agreement with the observations of Mitra & Chatterjee (1958) who reported that sucrose black did not give the 0.070 \AA^{-1} peak, unlike the other substances. Existence of the 0.025 \AA^{-1} band has been reported by many workers, such as Siever (1952), Hirsch (1954), Nelson (1954), *etc.* The origin of the 0.025 and 0.033 \AA^{-1} bands can be explained as being due to the interparticle scattering, the crystallite size, especially the crystallite thickness, being of the same order, which is in agreement with the views of other workers. However, there is uncertainty about the origin of the 0.07 \AA^{-1} band. Siever (1952) and Mitra (1953) observed it while studying coals. Later Mitra & Chatterjee (1958) observed the same band in the case of carbon blacks of benzene, toluene and xylene, though it was absent in the case of sucrose black; they explained it as being due to the presence of periodic defects in the interplanar distances of the graphite-like lattice. Recent advancement of high-resolution electron microscopy has led to a direct observation of imperfections and has been applied extensively for the study of carbons (Ban, 1972). It has been reported from laser optical diffraction of electron micrograph studies that interlayer spacings associated with the distorted layers of carbon blacks are not confined in the narrow range of 3.3–3.8 \AA as was believed from X-ray studies but are found to be in a very wide range from 3.1 to 8.2 \AA . The histograms of the layer spacings show that a considerable number of layers have spacings around 6.9–7.2 \AA . Hence the 7.1 \AA band ($\sin \theta/\lambda = 0.07 \text{ \AA}^{-1}$) can be explained as being due to these sets of distorted layers, the X-ray intensity depending upon the proportion of the layers. A similar explanation is also valid for the 0.112 \AA^{-1} band. The rest of the bands correspond to those of the graphite structure.

3.2. Radial distribution function

The radial distribution functions (r.d.f.) for the four samples are shown in Fig. 2. The position of the peaks in the r.d.f. curves (Table 1) give the interatomic vectors and the areas under them give the respective coordination numbers (Table 2). From an examination of the r.d.f. curves and Table 1, it is seen that the shortest bond distance in the ultracarbon sample is 1.45 \AA compared with 1.42 \AA for graphite. The coordination number is slightly larger than three, which is the accepted value for graphite. Sucrose, benzene and toluene blacks show bonding distances of 1.35, 1.40 and 1.30 \AA , respectively. These values are comparable with the C–C bond distance of 1.396 \AA in the aromatic rings and the double-bond distance of 1.33 \AA . The coordination numbers obtained for the three carbon blacks and the ultracarbon have values slightly greater or less than three for the first-nearest neighbours and have values between five to seven for the second-nearest neighbours. From the observation

that the bond distances of the carbon blacks in the present investigations lie between the values of those for the aromatic rings and the double-bond distance we may infer that the structure of the mother substance plays a vital role in the formation and structure of the carbon black. That the coordination numbers in carbon blacks will be substantially different from those of perfect graphite planes is only to be expected. Firstly, the graphite-like planes in amorphous carbons are not likely to be perfect. Secondly, the arrangement of atoms need not always be hexagonal or rhombohedral as in graphite. Full discussions on the interpretation of the coordination numbers will be taken up in a following paper in the series.

3.3. Crystallite size

It is seen in Table 3 that the thickness (L_c) of the crystallites varies between 24 and 33 Å and that L_a varies between 34 and 63 Å. This is in agreement with the findings of early workers. The apparently small values of the crystallite size in the case of the carbon blacks signify a low degree of graphitization and the presence of a large concentration of distortions.

Table 1. Peak positions from the r.d.f. curves

Sample	Peak positions (Å)							
Sucrose carbon black	1.35	2.48	3.15	3.80	4.75	5.75	6.60	7.50
Benzene carbon black	1.40	2.35	3.20	4.00	4.80	5.60	6.45	7.30
Toluene carbon black	1.30	2.25	3.10	4.05	4.95	5.85	6.75	7.80
Ultracarbon	1.45	2.30	3.10	3.95	4.70	5.55	6.40	7.20

Table 2. Coordination numbers for the first four nearest neighbours

Sample	Coordination number			
Sucrose carbon black	2.4	4.8	4.4	13.0
Benzene carbon black	4.2	6.8	10.4	14.0
Toluene carbon black	2.7	5.6	11.2	16.6
Ultracarbon	4.3	5.8	11.0	15.0

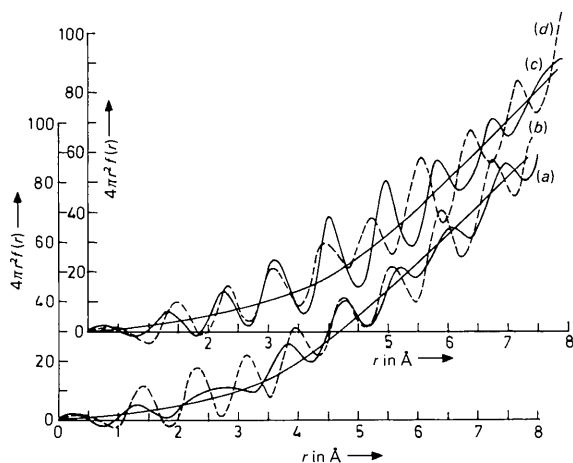


Fig. 2. Atomic radial distribution function curves for (a) sucrose, (b) benzene, (c) toluene carbon blacks and (d) ultracarbon.

Table 3. Layer dimensions of the samples

Sample	L_a (Å)	L_c (Å)
Sucrose carbon black	55	25
Benzene carbon black	34	28
Toluene carbon black	—	24
Ultracarbon	63	33

The computations were carried out with the help of a R1030 computer.

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