ON THE STRUCTURE OF CARBON.

by ROSALIND E. FRANKLIN

An X-ray investigation of some « amorphous » carbons and graphites has revealed certain new features which it is the purpose of this note to describe.

As a preliminary to the wider problems of carbon structure and the dependence of structure on the origin and treatment of the material, a detailed quantitative study of a single carbon was made, in order to find out just how much information the diffuse X-ray diagram could be made to yield. The material was prepared by pyrolysis of polyvinylidene chloride at 1.000°, and is more than 99 % carbon. The following results were obtained.

65 % of the carbon is in the form of highly perfect graphite-like layers. The mean diameter of these layers is only 16 A. Of the graphite-like layers, about 45 %, show no mutual orientation and 55 % are grouped in parallel pairs with spacing 3,7 Å, the number of parallel-layer groups containing more than 2 layers per group being very small.

The remaining 35 % of the carbon is in a form so disordered as to give only a gaz-like contribution to the total X-ray scattering.

Application of the Fourier transform to the very extensive low angle scattering reveals a mean interparticulate distance of 25 Å.

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The details of this structure are, of course, peculiar to the carbon investigated, but the results suggested two properties which it might be of interest to investigate in other carbons. The first, a very fortunate result, was the sharp separation observed between the ordered and disordered parts of the structure. It might have been expected that in a carbon showing such a low degree of crystallinity there would be present all degrees of partial disorder, but this is not so. Apart from the small, perfect, graphite-like layers, only highly disordered material is present. It thus seems clear that the proportion of ordered and disordered material is an important feature of the structure of such carbons. The other point of interest is the spacing, 3,7 Å, observed between pairs of small parallel graphite-like layers, the spacing in true graphite being 3,35 Å.

Investigation of a number of other « amorphous » carbons showed that the sharp separation between the ordered and disordered parts is of general occurence. All the X-ray diagrams obtained can be satisfactorily interpreted by supposing the existence only of small, perfect, graphite-like layers together with some highly disordered material.

For carbons of widely different origin there is a general relationship between the diameter of the graphite-like layers and the proportion of amorphous material. This is shown in figure 1. For carbons which contain a measurable proportion of disordered material the layer diameter is less than 25 Å.

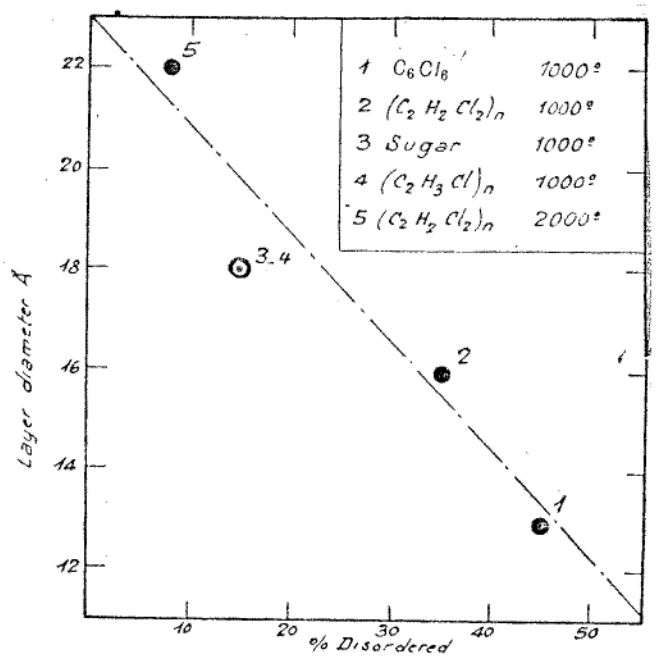

Fig. 1.

(The method of X-ray analysis used is directly applicable only to carbons which are nearly pure. This explains the absence, in figure 1, of carbons which are more than 50 % disordered or in which the layer diameter is less than 12 Å.).

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For the same carbons, the inter-layer spacing and the mean number of layers per parallel group (as indicated by the form of the (002) band) have been measured. It is found that for few (less than 5) layers per group the spacing decreases sharply as the number of layers increases. For 2 layers it is 3,7 Å, for a mean value of 2-3 layers it is 3,6 Å, and for carbons having 4 to 5 layers per group it is 3,44 to 3,445 Å. With further increase in the number of layers per group the change is small.

It will be noted that this value, 3,44 Å, is still markedly different from 3,35, the spacing in graphite. The carbons mentioned so far are all substances which show only 2-dimensional order. That is, the graphite-like layers are grouped parallel to one another and equidistant, but are not otherwise mutually orientated. The X-ray diagrams of such materials show only (0 0 *l*) crystalline reflections and 2-dimensional (*h k*) bands of the type described by Warren (*Phys. Rev.* **59**, 693, 1941). During further graphitisation — induced by thermal treatment — there is a gradual and continuous deformation of each (*h k*) band tending towards the transformation of the band into a series of (*h k l*) crystalline reflections, which are at first very diffuse but become more sharply defined as the process proceeds. *All carbons which show undeformed (h k) bands have an inter-layer spacing not less than 3,44* Å. When deformation of the (*h k*) bands sets in, showing the existence of some degree of 3-dimensional order, the inter-layer spacing again decreases. All carbons showing deformed (*h k*) bands or diffuse (*h k l*) reflections have apparent inter-layer spacings intermediate between 3,44 Å

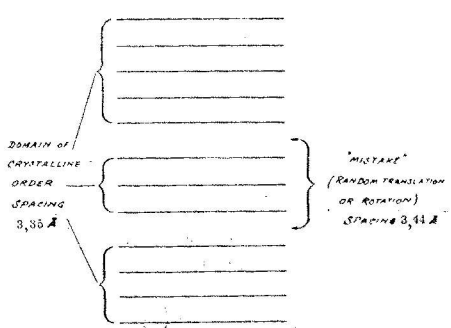

Fig. 2.

and 3,35 Å. In reality it appears that *the change in spacing from 3,44 to 3,35* Å *is discontinuous.* When neighbouring layers are mutually orientated as in a graphite crystal the spacing is 3,35 Å. When this orientation is destroyed by a random translation or rotation of a layer in its own plane, then the spacing is increased to 3,44 Å (see fig. 2). The apparent intermediate spacings observed are in reality average values. This is shown by the figure 3. From the

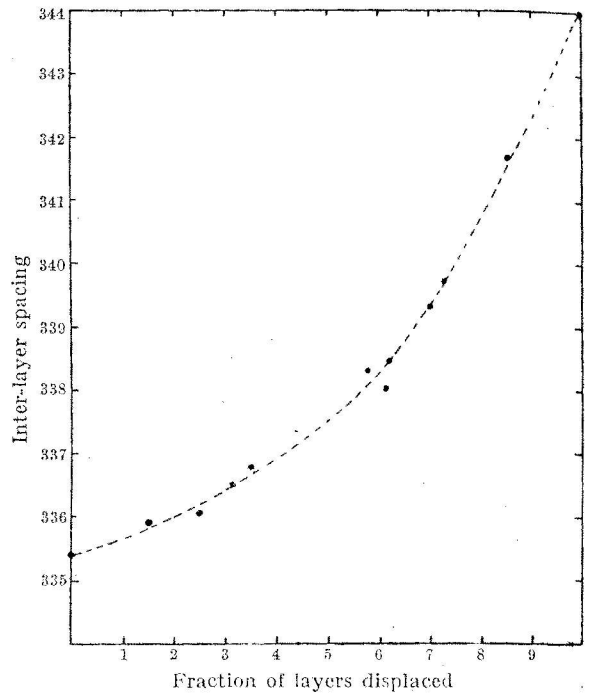

Fig. 3.

form of the deformed (*hk*) bands (or diffuse (*h k l*) reflections) it is possible to calculate the proportion of layers at which a translation or rotation, equivalent to a break in the crystalline order, or « mistake » occurs (fig. 2). This calculation has been carried out, and the apparent inter-layer spacing (given by the (002) line) measured for a number of carbons of different origin heated to temperatures between 2.300 and 3.000°C. In Figure 3 it is seen that the apparent inter-layer spacing is a function of the proportion of « mistakes » or displaced layers in the structure. For a mistake at each layer — that is, in the absence of any crystalline order — the spacing 3,44 Å is obtained. The spacing obtained by Nelson and Riley (*Proc. Phys. Soc.*, **57**, 477, 1945) for the best-crystallised natural graphite available to them is 3.354 Å, and this value has been confirmed during the course of the present work.

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Up to the present no attempt has been made to correlate the structural factors described above with

the chemical behaviour of the carbons, but there are certain obvious lines which it is hoped to follow in the near future. In the case of the « amorphous » carbons it would be of interest to investigate whether the ordered or disordered part is attacked préferentially in combustion or other reactions. In the case of carbons showing some 3-dimensional order it may be asked whether or not planes showing the 3,44 Å spacing are substantially more available to attack than those which have the true graphite spacing of 3,35 Å.

DISCUSSION SUR LES DEUX COMMUNICATIONS PRÉCÉDENTES

M. Riley. — In an amorphous structure, it is not permissible to leave valency bonds unsatisfied, in other words, it is not merely a chaotic jumble of carbon atoms. A structure is involved, but one which is not sufficiently ordered to give coherent scattering of X-rays. Miss Franklin's paper suggests that we must identify the suggested three-dimensionally, cross-linked, aromatic structure with the disordered phase in the samples studied.

M. Bangham. — The studies of fuel carbons by X-ray methods made by Riley, Franklin and others have indicated that ordered crystallites of graphite form only part of the whole structure. It is a little tempting to identify the « amorphous » carbon as the portion which contributes most to the « reactivity ». Instead of doing so, however, I would like to offer the suggestion that the most reactive carbon atoms are those *in transition* between the amorphous (or other metastable) state and the stable graphitic phase. Whilst it is known that above a certain temperature the ordered portion increases at the expense of the disordered, it is well-nigh impossible to obtain data as to the *rate* at which this process takes place ; this is because one cannot, in practice, readily change the temperature of a sample of carbon from one steady value to another in an instant of time. Some data of H. L. Riley make it probable that the change associated with a marked rise of temperature occurs fairly rapidly — in a matter of minutes, perhaps, but not of days.

In considering how the more ordered structure is evolved from the less ordered, it appears necessary to suppose that migration, either of carbon atoms or of small groups thereof, can take place. These migrating atoms (or groups) will surely contribute very much to the reactivity towards gases. I would emphasise the importance of this transition state, bearing in mind the distinction made by Crone between the reactions undergone by a fuel particle which is being heated up, and those associated with its burning out ; with technical fuels the carbon generally has not been previously heated to temperatures such as are attained in fuel beds.

It would perhaps be interesting (though difficult) to study, from the theoretical point of view, the magnitudes of the energy barriers separating (say) amorphous from graphitic carbon, making different assumptions as to the size of the migrating unit. It might be found, for example, that the migration of individual carbon atoms is the most probable mechanism of the change ; or, alternatively, that several atoms move as a group.

The progress of the combustion of a sample of commercial carbon must provide conditions which *favour* the production of these migrating fragments. We are thus led, as in the study of homogeneous gas-phase reactions, to think in terms of the elementary events which may control (*a*) the formation and (*b*) the destruction of these *migrating* reaction centres. Viewed from this stand point, the « reaction vessel » becomes a two-dimensional mobile surface phase in which the simple gas-phase species (O_2, CO, etc...) are somewhat concentrated by the action of ordinary Van der Waals adsorption. One must remember that in such a phase — approximating to a condensed phase — dissipation of energy by three-body collisions would be frequent.

M. Goldfinger. — Il résulte de ces discussions, que les théoriciens aussi bien que les expérimentateurs admettent que le graphite réagit d'une manière un peu semblable à celle des radicaux libres. Plus précisément, les indices de valence libre de M. Daudel indiqueraient qu'il s'agit d'une réactivité intermédiaire entre celle des radicaux libres et des molécules saturées. Il semble que de tels radicaux « semi-libres » existeraient aussi en phase gazeuse et nous espérons pouvoir publier prochainement des résultats à ce sujet. Serait-il possible d'étudier cela par la conversion H_2-para ? ou bien a-t-on déjà fait des mesures de conversion sur du graphite traité de différentes manières, ou de réactivité différente ?

M. Duval. — *Réponse à M. Goldfinger.* — Il semble bien d'après les expériences de Bonhoeffer, Farkas et Rummel qu'il existe une conversion ortho-para due seulement aux propriétés paramagnétiques des atomes de carbone non saturés. Il faut seulement craindre qu'à basse température la réaction ne soit perturbée par des traces d'oxygène paramagnétique (adsorbé moléculairement). Aux températures supérieures à la température ordinaire, d'autre part, la réaction peut être accompagnée de la conversion par dissociation de l'hydrogène (par adsorption activée), dans laquelle les impuretés peuvent jouer un rôle.

M. Brusset. — Les communications précédentes viennent d'insister sur l'importance de l'état cristallin et la complexité de la structure dans le cas du carbone amorphe.

Il faut tenir compte dans la comparaison de réactions d'oxydation du carbone non seulement de l'état général cristallin mais aussi d'effets locaux d'orientation privilégiée. Là encore l'examen aux rayons X peut être d'un certain secours.

Avec du carbone vraiment à l'état de graphite on voit que les facteurs qui permettent de caractériser l'état et l'architecture du solide carbone soumis à l'oxydation sont moins nombreux et plus facilement déterminables.