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Structure of a novel form of carbon: dehydropolycondensed adamantane?

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The paper presents synchrotron X-ray diffraction and complementary transmission IR spectroscopy data on a series of products of adamantane in an attempt to elucidate the detailed nature of their structure. Although qualitative similarities between this work and earlier studies have been identified, the X-ray diffraction measurements, when coupled with IR absorption analysis, argue for a very different interpretation of the structural changes associated with the chemical processes involved in generating this suite of materials. It is clear that 1,3,5,7-tetrabromoadamantane has indeed been formed from the adamantane precursor, but that there are some Br sites that are occupied by carbon atoms. 'Polymerisation' of these units into an amorphous network with no residual long-range ordering may then be induced through chemical processes; the C_{10} carbon units are broken up to form an amorphous network (or 'patchwork') of unit fragments. The corroborating presence of short hydrocarbon chains is also revealed. Once the material is heat treated it begins to revert to a graphitic structure, with the hydrocarbon chains being eliminated.

Carbon is probably the most widely studied of the known elements. Various forms of amorphous carbon, and in particular amorphous hydrogenated carbon (sometimes referred to as 'diamond-like' carbon, a-C:H), have become of increasing significance in recent years following the development of CVD-based deposition techniques.[1–3] This family of materials contains a mixture of sp^3, sp^2 and (sometimes) sp^1 carbon bonding, with the nature of the mixture of bonding depending on the conditions under which the a-C:H was prepared; the incorporated hydrogen plays an important role and has itself been the subject of much study.[4–6] A paper by Kasatochkin *et al.*[7] claiming a 'wet chemistry' route to an amorphous carbon, which they termed dehydropolycondensed adamantane, using adamantane as the precursor and based on its polymerisation through the removal of hydrogen, was therefore of considerable intrinsic interest. Their work presents an outline description only of the preparative chemistry involved, and the structural study is limited to IR transmission spectroscopy and the use of a low intensity laboratory X-ray source which, with some additional electron diffraction, provides qualitative data only. Given the suggested novelty of the material itself it is important to establish the nature of its structural parameters with precision: the work reported here was undertaken with this aim.

The precursor for the materials studied here is adamantane. The essence of the adamantane molecule's structure[8] is that the 10 carbon atoms form a cage as depicted in Fig. 1(*a*); it consists of two distinct carbon atom sites: four C_A atoms which lie at the vertices of a tetrahedron and six C_B atoms which lie at the vertices of an octahedron. The overall cage has tetrahedral symmetry. Four-fold coordination of the carbon atoms is maintained with the addition of the 16 hydrogen atoms as depicted in Fig. 1(*b*).

Although (highly crystalline) polyadamantane was first prepared more than 30 years ago[9] by heating 3,3-dibromo-1,1-diadamantane with metallic sodium, the route adopted here and by Kasatochkin *et al.*[7] avoids the problems of steric hindrance generated by the size of the bromine atoms, which are used to replace hydrogen atoms, and allows a more complete removal of hydrogen by employing a repeated process of bromination (initially to 1,3,5,7-tetrabromoadamantane) followed by the removal of the halogen using metallic sodium. It is therefore expected that a large degree of bonding between the C_{10} cages will be possible, resulting in a three-dimensional (3D) polymer network.

Sample Preparation

Adamantane (99+%), aluminium bromide (98+%) and bromine were purchased from Aldrich, and the bromine was dried by distillation from phosphorus(v) oxide before use. A 30% m/m dispersion of sodium metal in toluene was purchased from Fluka. Glacial acetic acid, ethanol and toluene were 'AnalaR' grade and purchased from BDH.

The first stage of the sample preparation process is the formation of tetrabromoadamantane from the adamantane precursor:[10]

$$C_{10}H_{16} + 4\,Br_2 \rightarrow C_{10}H_{12}Br_4 + 4\,HBr$$

Adamantane (10.0 g) was added to a stirred mixture of aluminium bromide (17.6 g) and dry bromine (40 cm^3) in an ice bath. After the addition was complete and the initial reaction had subsided, the mixture was heated to reflux at 60 °C for 24 h with stirring. The excess bromine was then distilled from the reaction flask, and the remaining solids were treated with aqueous sodium metabisulfite to remove the last traces of bromine and hydrolyse the aluminium bromide. The product was collected, washed with water and recrystallised from glacial acetic acid (a yield of 61%) to give a light tan product. This was shown to be 1,3,5,7-tetrabromoadamantane by its IR spectrum (see below) and with supportive evidence from mass spectroscopy measurements and C,H,N combustion analysis. This is referred to as sample 1.

The second stage is centred on the Wurtz reaction:[11]

$$nC_{10}H_{12}Br_4 + 4nNa \rightarrow (C_{10}H_{12})_n + 4n\,NaBr$$

Tetrabromoadamantane (16.0 g) was added to a stirred dispersion of sodium (6.5 g) in toluene (60 cm^3) and heated to reflux for 48 h with stirring. After allowing the reaction mixture to cool, ethanol (50 cm^3) was added to remove the sodium, and the solids were collected and washed with toluene. The sodium bromide was removed by stirring the solids in warm (50 °C)

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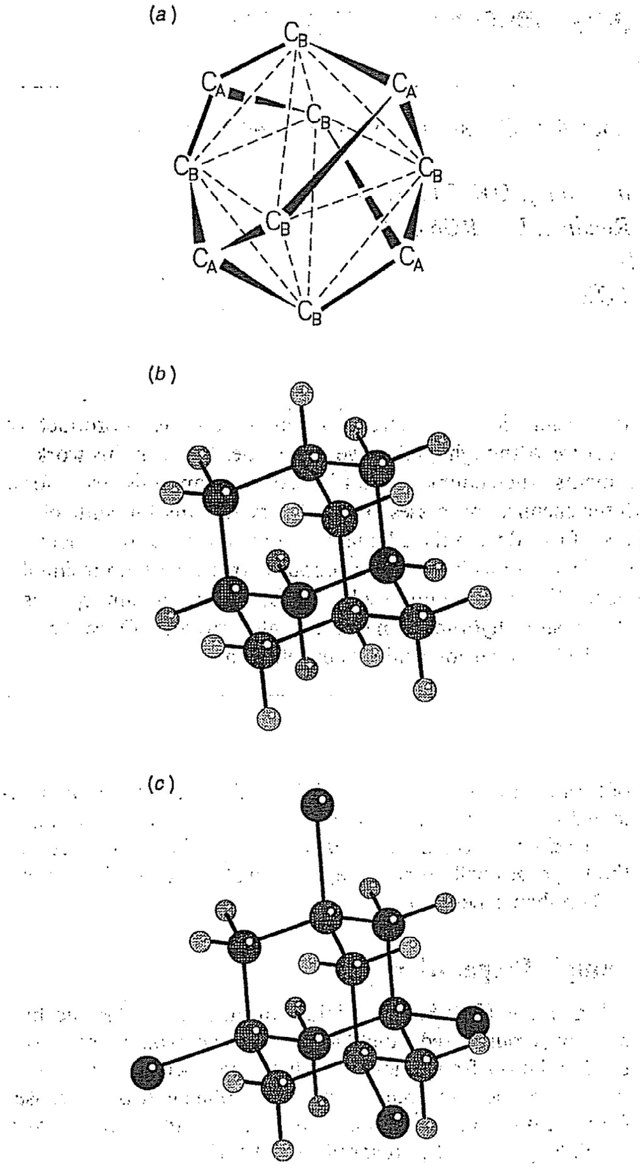

Fig. 1 (*a*) Diagrammatic representation of the adamantane C_{10} cage structure (after ref. 8); (*b*) conventional ball-and-stick view of adamantane, showing the decoration of the C_{10} cage structure with hydrogens; (*c*) the analogous view of the principal intermediate stage, tetrabromoadamantane

water for 20 min, after which the remaining product was collected and dried. This product (an off-white solid; yield 75.5%) is insoluble in toluene and ethanol, and according to Kasatochkin *et al.*[7] it is the product of the 3D polymerisation of adamantane at its four apices (we dispute their interpretation, see below). This is referred to as sample 2.

A third stage involved heating sample 2 in argon by placing it in a Pyrex boat and heating it in a horizontal tube furnace at 400 °C for 2 h, with a steady stream of argon passing through. The powder darkened and lost about one-third of its mass (*i.e.* a yield at this stage of 67.2%. Note that if heated further to 450 °C, the powder turns black, but its mass remains constant). This product is referred to as sample 3.

In the final stage, sample 3 (1.05 g) was heated at reflux in bromine (60 cm^3) for 24 h, and the residual bromine removed as in stage 1. This dark powder (brominated polyadamantane, 2.37 g) was stirred under an argon atmosphere in a bath of liquid sodium (17 g) at 140 °C for 1 h. This is intended to remove the bromine atoms and to cross-link the polymer further. The sodium was removed with ethanol, and then water was added, and the resultant solid was collected. The product was finally heated to 400 °C in a tube furnace under vacuum for 2 h to yield a dark powder; this observation is in immediate contrast to that of Kasatochkin *et al.*[7] who cite the product as being white.

Experimental Methods

The X-ray diffraction experiments were performed at the SRS, Daresbury Laboratory, UK, using a high intensity line with the synchrotron radiation being produced through a 5 T superconducting wiggler. The diffraction experiment was performed on flat-plate samples in θ–2θ transmission geometry, and at an X-ray wavelength of 0.62 Å (which was calibrated using the K-shell absorption edge of molybdenum). This transmission geometry was chosen as it simplifies many of the necessary corrections. The 2θ angular range measured was chosen to be 2–130° in 0.2° steps, giving a nominal Q range [$Q=(4\pi \sin\theta)/\lambda$, the wavevector transfer] of 0.4–23 Å^{-1}. The sample itself was held in a flat-plate container of 0.5 mm thickness with Kapton foil windows.

The diffraction data were normalised to allow for variations in incident flux, corrected for beam polarisation, background scattering effects and sample illuminated volume variation on rotation. The correction and normalisation procedures adopted were broadly those described by Huxley,[12] though much simplified here given the dominance of Bragg scattering in all but one of the samples studied. General data analysis is based upon the text by Warren.[13] One important feature of the experimental method is that the Warren–Mavel method[14,15] was adopted in order to suppress Compton scattering: in this case a molybdenum foil (K-edge at $\lambda=0.620$ Å) was used at the position normally occupied by the X-ray detector (see Fig. 2) and the fluorescence intensity then measured. In this way, to a good approximation, only elastic scattering events are recorded since those X-rays scattered incoherently with an associated energy loss will be unable to excite the Mo K-edge fluorescence.

IR spectra were measured on a Perkin-Elmer 1720-X FT IR spectrometer. The IR samples were prepared by grinding a small amount of the powder with dried potassium bromide, which was then pressed into 13 mm discs.

Results and Discussion

The X-ray diffraction and IR absorption spectra for sample 1 are shown in Fig. 3(*a*), (*b*) respectively. The diffraction pattern

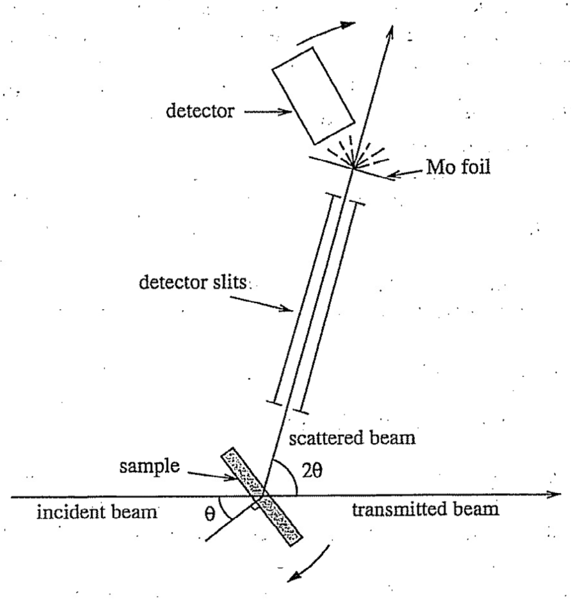

Fig. 2 Warren–Mavel experimental geometry

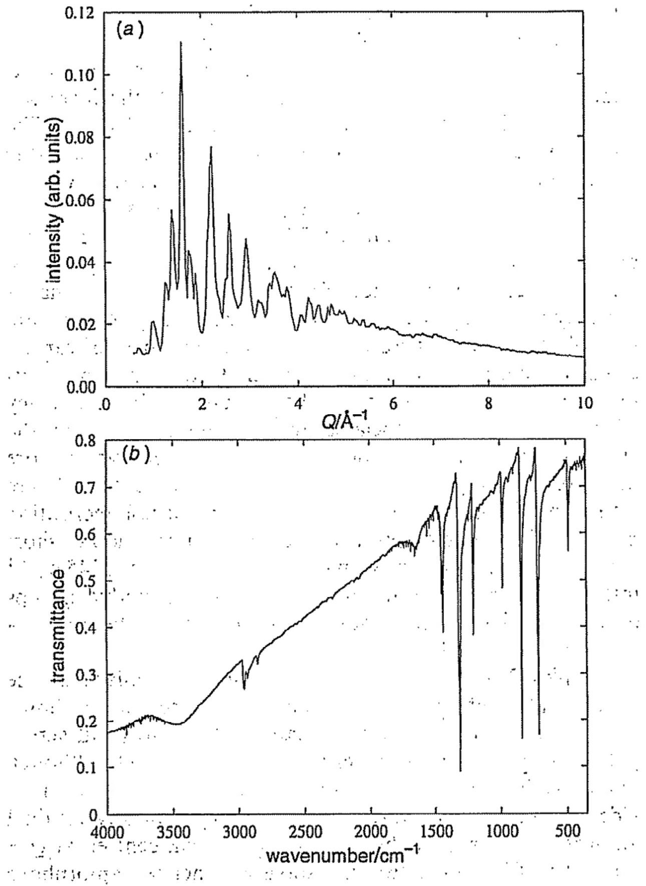

Fig. 3 (*a*) Diffraction spectrum for sample 1; (*b*) IR absorption spectrum for sample 1

is easily interpreted in terms of the expected dominance of 1,3,5,7-tetrabromoadamantane. The associated bond lengths and pairwise separations, derived by applying Bragg's equation to the observed diffraction peaks, are listed in Table 1 together with their chemical assignments; these may be compared to published crystallographic values for tetrabromoadamantane.[16,17] The one peak that does not easily fit into this interpretation is that associated with a distance of 3.86 Å; this feature is present in the data of Kasatochkin *et al.*[3] also, but was not discussed by them. However, the difficulty may be resolved in a relatively straightforward way if one assumes that some of the (nominally) Br sites are in fact occupied by carbon atoms, since the calculated distance from this carbon atom to those in the nearest C_{10} 'cage' is 3.89 Å.

The IR data for sample 1 was interpreted largely on the basis of existing work on adamantane,[18] though bearing in mind the obvious fact that the presence of the relatively massive Br atoms will cause some shift to peak positions. The band at 716 cm^{-1} derives from the CH_2 rocking frequency and appears in all aromatic hydrocarbons containing more than four methylene-like groups.[19] Note the absence of a strong band at 2900 cm^{-1} which confirms that the majority of the methine groups have been removed by bromination. The doublet at 1450 and 1441 cm^{-1} is the associated CH_2 deformation which normally appears at 1465 cm^{-1}, but when derived from a many-ring system[20] may be seen with components in the regions 1450–1485 and 1436–1450 cm^{-1}. The non-adamantane feature at 486 cm^{-1} is the Br—C fundamental stretching mode. Note the weakness of the CH_2 stretching mode band shown in the range 2850–2930 cm^{-1}; this is probably due to the nature of the carbon ring structure in bromoadamantane given the inverse correlation noted by Boobyer and Weckherlin[21] between the size of other such structures and the observed absorption band intensity. Other than the usual water/CO bands, the remaining features in the spectrum are associated with C—C skeleton vibrations. Note the similarity between the spectrum shown here and that measured for 1,3,5,7-bromoadamantane by Sollot and Gilbert,[22] we therefore confirm the general nature of the compound as outlined in the original Russian paper with the small differences noted above.

The diffraction data and IR absorption spectrum for sample 2 are shown in Fig. 4(*a*) and (*b*) respectively. All traces of the ordered structure have disappeared with the removal of bromine and we are left with diffuse scattering from what is now an amorphous network. After removing the underlying background and self-scattering terms from the spectrum it may be Fourier transformed to reveal the pair correlations in real-space shown in Fig. 4(*c*). Only two broad features are evident, centred at 1.4 and 2.48 Å, which are strongly suggestive of a highly disordered network based on graphitic bonding. This sample corresponds reasonably well to the disordered polyadamantane model suggested by Kasatochkin *et al.*,[7] though it is

Table 1 Synopsis of diffraction data from all samples

sample	Q/Å^{-1}	$d(=\lambda/2\sin\theta)$/Å (Bragg) measured [tables/calculated]	correlation length/Å (amorphous)	assignment
1	1.38	4.55 [4.25, 4.73]		C–Br
	1.60	3.93 [3.883]		C–C (*extra*-C_{10} unit)
	1.75	3.59 [3.567]		C–C
	2.22	2.83 [2.85]		C–Br
	2.52	2.49 [2.522]		C–C
	2.93	2.14 [2.167]		C–H
	3.20	1.96 [1.93]		C–Br
	ca. 3.5	1.8 [1.78]		(H–H?)
	ca. 4.2	1.5 [1.545]		C–C
2	*ca.* 2.9, *ca.* 4.9		2.5, 1.4	C–C–C, C–C (disordered graphitic)
3, 4	1.1	5.7 (absent from 4)		approx. graphitic, see text
	1.82	3.41 [3.36]		graphite {0.02}
	2.11	2.98 [2.84]		(across graphitic ring)
	2.98	2.11 [2.13, 2.03]		graphite {100}, {101}
	3.49	1.80 [1.80]		graphite {102}
	3.64	1.73 [1.68]		graphite {004}
	4.22	1.49 [1.54]		graphite {103}
	4.59	1.37		
	4.71	1.33		
	5.15	1.22 [1.23]		graphite {110}
	5.48	1.15 [1.16, 1.14, 1.12]		graphite {112}, {105}, {006}
	5.96	1.05		graphite {201}
			5.2, 4.2, *ca.* 2.6, 1.42	disordered graphitic (sample 3 only)

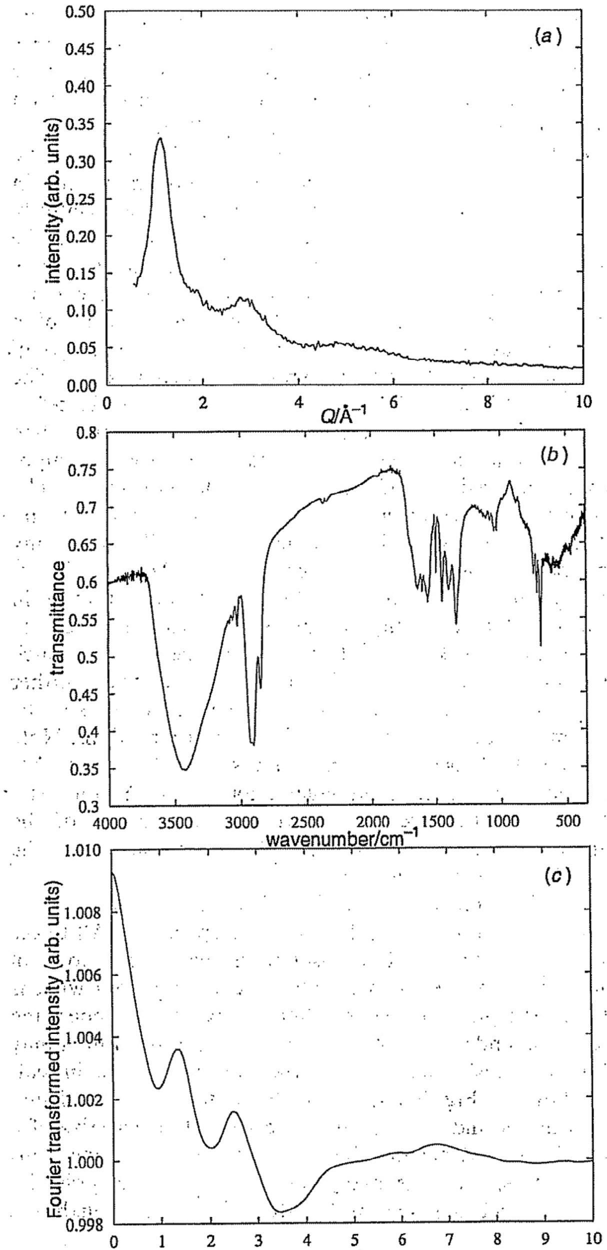

Fig. 4 (*a*) Diffraction spectrum for sample 2; (*b*) IR absorption spectrum for sample 2; (*c*) Fourier transform of the spectrum shown in (*a*) after the removal of the underlying 'background' intensity using a low-order polynomial

evident that the data presented here is of substantially higher quality since the correlation lengths these determined cannot easily be related directly to any likely physical model. Furthermore, there is clear evidence in their diffraction data of residual crystallinity whilst the data we present here has no such crystalline contaminant phase. Given the intrinsic form factor weighting of the X-ray diffraction data towards correlations involving the (high atomic number) bromine atoms, the absence of any indication of the primary 1.93 Å Br—C separation is strong evidence for the successful removal of all the bromine atoms: and this in its turn might at first sight be said to provide the evidence that the mechanism associated with the polymerisation process centres on the linking of adamantane cages at one or more of the 1,3,5,7-apices. However, the amorphous nature of the spectrum (which was also noted by Kasatochkin *et al.*[7]) must actually rule out this simple model since the continued existence of well defined C_{10} units would, however disordered the inter-unit angular correlation, yield diffraction features associated with the intra-unit correlations (much as we observe for sample 1).

As might be anticipated the IR spectrum now has no Br—C band at 486 cm^{-1}, and this is consistent with the increased intensity of the CH_2 stretching band at 2850–2930 cm^{-1}. The feature which appeared at 716 cm^{-1} in Fig. 3(*b*), and was due to the presence of several CH_2 groups associated with a broadly aromatic ring structure, has disappeared and is replaced by three peaks (at 754, 729 and 702 cm^{-1}). These are also assigned to rocking modes associated with CH_2 groups, but in this case the presence of the feature at 729 cm^{-1} makes it highly likely that these groups, or at least many of them, are part of chain-like structures with varying numbers of carbon atoms involved. It is well known[23,24] that the frequency of this mode depends strongly on the chain length, with a frequency of 770 cm^{-1} being associated with a single unit, and the frequency falling rapidly towards 720 cm^{-1} when two or more units form the chain; the presence of the bands observed here is therefore further evidence for the nature of the polymerisation process, which would appear to include the formation of short chain-like hydrocarbon segments. The band at 1345 cm^{-1} might conceivably be due to the presence of methyl groups (symmetric deformation), but it is more likely to be due to a C—H rocking mode.[19]

Samples 3 and 4 appear to have strong similarities; the experimental diffraction and IR absorption spectra are shown in Fig. 5(*a*), (*b*) and 6(*a*), (*b*) respectively. The X-ray diffraction pattern shows a strong increase in ordering, which, although qualitatively similar to the work of Kasatochkin *et al.*,[7] provides evidence for a more complete removal of any residual amorphous phase. The broad diffraction peak centred at $Q = 1.1$ Å^{-1} in Fig. 5(*a*) shows that some well defined amorphous phase material remains at this penultimate stage, and it is instructive to generate a Fourier transform of this spectrum [Fig. 5(*c*)] and to compare it with that shown for sample 2 in Fig. 4(*c*). The presence of graphitic short-range ordering is present in both, but it is clear that the pair correlations (see Table 1) exist over much longer length scales in sample 3, with distances reminiscent of those expected for an extended graphite-like or hexagonal structure. Indeed, a comparison of the published graphite interplanar distances[17] with the present data for both samples 3 and 4 (Table 2) is revealing, particularly when combined with the fact that the bulk graphite interlayer distance of 3.36 Å and the cross-ring distance of 2.84 Å may also be associated with features in the data [at 3.41(7) and 2.96 Å respectively for sample 3 (and 4)].

Kasatochkin *et al.*[7] attempted to fit their own data using a quadratic equation to describe the system in terms of a generic hexagonal system, which they then assign to a 'hexagonal crystalline phase' of polyadamantane. Our diffraction data does not agree with theirs, and given the close correspondence of the major part of our spectra to that expected from bulk graphite we are drawn to the conclusion that the material is actually a distorted graphitic structure rather than a polymeric network of well defined adamantane C_{10} units, with the initial adamantane-like units being broken up beginning at the stage associated with sample 2. The distortion of the graphitic layers

Table 2 Comparison between measured and literature (ref. 17) graphite interplanar distances (*d*/Å)

measured	ref. 17
3.41	3.36
2.11	2.13
1.80	1.80
1.73	1.68
1.49	1.54
1.22	1.23
1.14	1.12
1.05	1.05

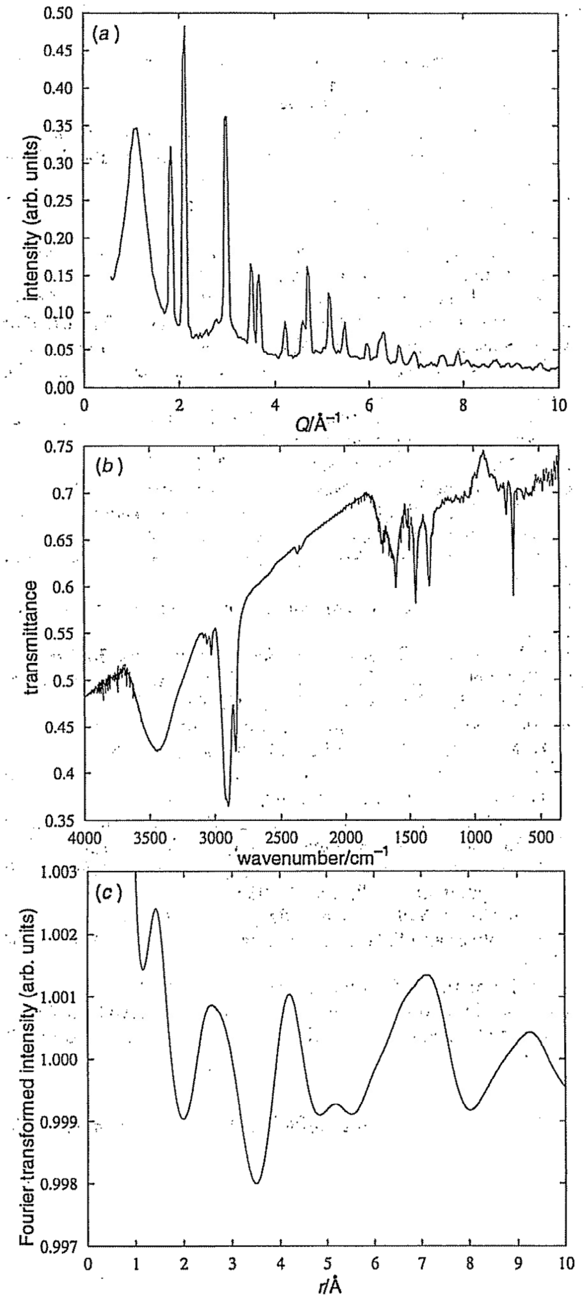

Fig. 5 (*a*) Diffraction spectrum for sample 3; (*b*) IR absorption spectrum for sample 3; (*c*) Fourier transform of the spectrum shown in (*a*) after the removal of the underlying 'background' intensity using a low-order polynomial

would appear to be greater for sample 3 than for sample 4, as might be expected if we interpret the structural change as being due to a progressive graphitisation of sample 2 due to the heat treatment.

The IR absorption data for samples 3 and 4 supports these conclusions. For sample 3, the disappearance of the *ca.* 730 cm^{-1} features (and the relative strength of the aromatic CH_2 features at 701 and 750 cm^{-1}) serves as evidence for the reduction in CH_2 hydrocarbon chains and the growth of more graphitic/aromatic structures. The CH_2 stretching mode at *ca.* 2900 cm^{-1} is now very intense (relative to other bands), and the associated deformation mode at 1448 cm^{-1} is also clearly seen, as is the C—H rocking mode at 1346 cm^{-1}; all of which supports the model of a return to (graphitic/aromatic) crystallinity. The absorption spectrum from sample 4 shows the continuing trend, but with weaker features due to the decrease in the overall hydrogen content (see Table 3). Note that although the combustion analysis is able to reveal quantitative information only on the volatile/combustible carbon and hydrogen, it is possible to summize additional information related to the 'residual' mass percentage. A clear example of this is in relation to sample 1 where this mass corresponds well, within errors, to the expected bromine fraction; for other samples where reliable data were obtained the residual mass is assumed to be associated with impurities of bromine and/or unreacted reagents) and with some C—O stretching contamination at 1719 cm^{-1}. The feature at 870 cm^{-1} is a deformation mode associated with C—H, and those at 1615 cm^{-1} and 1040 cm^{-1} are associated with C—C modes.[19] The presence of these well defined absorption features is strongly indicative of a graphite-like material, though clearly with some residual hydrogen (the presence of which may be related to our observation of some methyl groups in sample 1: they would affect the polymerisation process since the methyl groups would not cross-link).

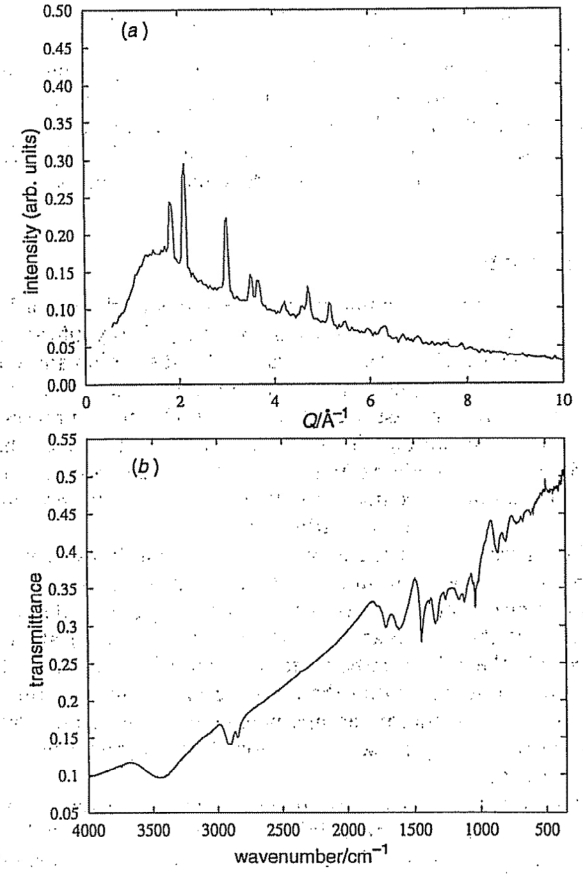

Fig. 6 (*a*) Diffraction spectrum for sample 4; (*b*) IR absorption spectrum for sample 4

Table 3 C, H, N combustion analysis of the samples; sample 4 provided data with a high degree of variability (±0.01), but samples 1, 2 and 3 yield errors in the H:C ratio of ±0.003 or lower

sample	H:C (mass%)
1	0.10:1
2	0.12:1
3	0.10:1
4	(0.06:1)

Neutron diffraction and incoherent inelastic neutron spectroscopy (IINS) would provide additional information on these structural transformations since neutron scattering methods are highly sensitive to correlations and vibrations involving hydrogen; in addition, neutron diffraction offers a wider dynamic range and therefore improved real-space resolution, which would be of value in the detailed study of the amorphous components, and IINS provides direct access to the true vibrational density of states. The structural changes suggested by the X-ray diffraction and IR data may be associated with macroscopic effects such as the formation and collapse of voids within the material; small angle X-ray scattering (SAXS) studies are underway in an attempt to understand such effects.

Conclusions

Although qualitative similarities between this work and earlier studies have been identified, the more precise X-ray diffraction measurements, when coupled to careful IR absorption analysis, have served to argue for a different interpretation of the structural changes associated with the chemical processes involved in generating this suite of materials. It is clear that 1,3,5,7-tetrabromoadamantane has indeed been formed from the adamantane precursor, but that there are some bromine sites that are occupied by carbon atoms.

'Polymerisation' of these units into an amorphous network with no residual long-range ordering may then be induced through chemical processes, with the data suggesting that it is in fact not the case that C_{10} carbon units are linked at their apices *via* the 1,3,5,7-carbon sites (the model currently in the literature), but rather that the units are broken up to form an amorphous network (or perhaps 'patchwork') of unit fragments. The corroborating presence of short hydrocarbon chains is also revealed.

Once the material is heat treated it begins to revert to a graphitic structure, though initially with a small amorphous component remaining. The hydrocarbon chains are eliminated.

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