Structure of Naphthalene and Anthracene

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NAPHTHALENE and anthracene have perhaps been studied more intensively and for a longer time than most other organic crystals. It seems appropriate that we should review their structures, because the thermal vibrations of the atoms and the distribution of the electronic charge density in these structures have now been very carefully examined.

When W. H. Bragg first applied the x-ray diffraction method to the study of organic crystals, these two compounds were among his earliest examples.[1] By 1920 he had solved the crystal structures in the sense that, the dimensions of the unit cells and the number and relative positions of the molecules in them had been correctly determined (Fig. 1).

The *c* axis increases in length by about 2.5 A in passing from naphthalene to anthracene, while the other dimensions remain almost the same. Now, if the extra ring of carbon atoms required by the chemical formula has about the same dimensions as the rings in diamond and graphite, this can be explained. In this way and by various other measurements[2] Bragg was able to demonstrate that the organic molecule had a real existence in the crystal; a conclusion which did not by any means follow from the earlier work on inorganic crystal structures.

Bragg's measurements were made by means of his original ionization spectrometer. It is a melancholy reflection that they were probably more accurate than the majority of the measurements on which our recent work is based. They were not, however, sufficiently extensive for a full determination of the structures, in the sense of finding the positions of all the atoms. This did not come until 1932, when the photographic method was used to make complete surveys of all the principal zones of reflection.[3] By means of various trial structures, and guided by the optical and magnetic properties of the crystals, the positions of all the atoms were at last deduced. These rough positions were then refined by an application of the two-dimensional Fourier method, which gives electron density maps of the molecule as seen in various projections (Fig. 2).

Careful measurements on these maps were able to place the atoms to within a few hundredths of an A. Within these limits the rings were shown to be planar, and the average C–C bond length 1.41 A. The orientation of the molecule in the crystal could be found to within about 1°. The long axes of the molecules are not

exactly coincident with the crystal *c* axes, as at first supposed, the deviation for naphthalene being about 14° and for anthracene about 9°. In both cases the molecular planes are steeply inclined at about 64° to the projection plane (010), a fact which obscures the resolution and reduces the accuracy. Figure 3 shows in some detail the arrangement of the molecules in the anthracene unit cell.

Further interesting details may, however, be observed even at this rather crude stage of the analysis. Particularly in anthracene, there is a notable falling off in the peak values of the electron densities on the carbon atoms as we move outwards from the center of the molecule. In 1932 this effect was attributed to a rigid body oscillation of the whole molecule about its center, although it was pointed out that series termination errors might account for some of the observed density variation. Recent work has fully verified this result, the amplitude of angular oscillation for the long axis in anthracene being about 3°.

With regard to interatomic distances we were content in 1932 to assess the average C–C distance as 1.41 A. However, in discussing the dependence of interatomic distance on single-bond double-bond resonance Pauling reported in 1935 that our maps did show small variations in the distances of about 2 to 3% in the directions required by theory.[4]

However, to proceed further and establish the significance of these interesting effects it was clearly necessary to use more complete data and a more comprehensive analysis. This task was not attempted until 15 years later. There were two reasons for this rather long delay. In the first place, computing facilities were meager in 1932. Our laboratory at the Royal Institution did not possess even a desk adding machine, and aids like the Beevers-Lipson strips had not been
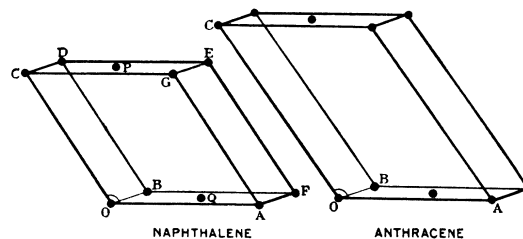

FIG. 1. Unit cells of naphthalene and anthracene (Bragg).

	$OA=a$	$OB=b$	$OC=c$	$AOC=\beta$
Naphthalene	8.24	6.00	8.66A	122.9°
Anthracene	8.56	6.04	11.16	124.7°

[1] W. H. Bragg, Proc. Phys. Soc. (London) **34**, 33 (1921); **35**, 167 (1922).

[2] W. H. Bragg, Z. Krist. **66**, 22 (1928).

[3] J. M. Robertson, Proc. Roy. Soc. (London) **A140**, 79 (1933); **A142**, 674 (1933).

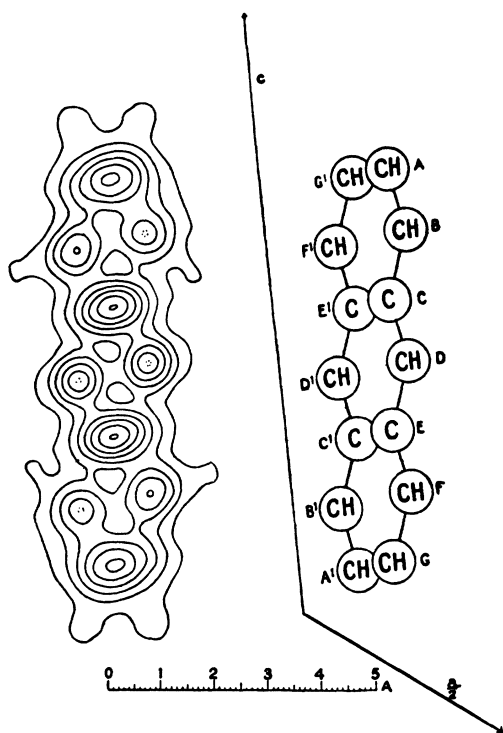[4] Pauling, Brockway, and Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

FIG. 2. Electron density projection of one anthracene
molecule on (010).

invented. Even a computation like that involved in
Fig. 2 represented rather a formidable amount of work.
In the second place, with the technique of x-ray
analysis developed even to this two-dimensional stage,
there were many other exciting structures to explore
in the field of organic chemistry. For example, the
phthalocyanine compounds had just been discovered,
and our work on these structures began shortly
afterwards.

However, between 1947 and 1950 we came back to
the naphthalene-anthracene problem and carried the
analysis into the third dimension, with a complete
survey of all the measurable reflections.[5] For the first
time, in relation to these crystals, this now represented
the x-ray diffraction method at its full power. Out of
the large mass of results obtained the most interesting
are probably the electron density sections through the
mean planes of the molecules, evaluated by summing
the appropriate triple Fourier series. These sections
are shown in Fig. 4.

All the carbon atoms are now resolved with a precision
which enables the positions of their centers to be
estimated to within a few thousandths of an A, and
most of the hydrogen atoms are also clearly visible.
Some series termination errors are still present in these
diagrams, but their effect is not large because the

Fourier series used was very complete. The corrections
have been found by Ahmed and Cruickshank[6] and
after these are applied the bond lengths are in fair
agreement with theory.[7] The estimated standard
deviations in the measured values are between 0.004
and 0.010 A. The distribution of electron density, and
especially the falling off in peak heights noted in 1932
and now confirmed, shows that considerable anisotropic
thermal motion is present.

It is important to emphasize that up to this stage
nothing at all has been assumed regarding the exact
form of the atomic scattering curves or the existence
of temperature factors, and no hydrogen atoms have
been postulated as present in the structure. The phase
constants of the structure factors were determined
from the 1932 analysis, and in these calculations a
pure empirical f curve based on graphite was em-
ployed. Even the latest refinements of these structures
have not altered the phase constants to any significant
extent, and so it can be said that these electron density
maps are a very direct representation of the experi-
mental results. They can only be altered if more
accurate or more complete intensity measurements
become available.

Having reached this stage, however, we now want
to go further and try to interpret these experimental
results in terms of the thermal vibrations of the atoms
and the distribution of the electronic charge density
in the atoms. This is obviously a difficult matter
because the thermal motion must inevitably blur the
picture of the electron distribution, and our experi-
ments, which have so far been carried out at only one
temperature, do not provide any direct means of
separating these two effects.

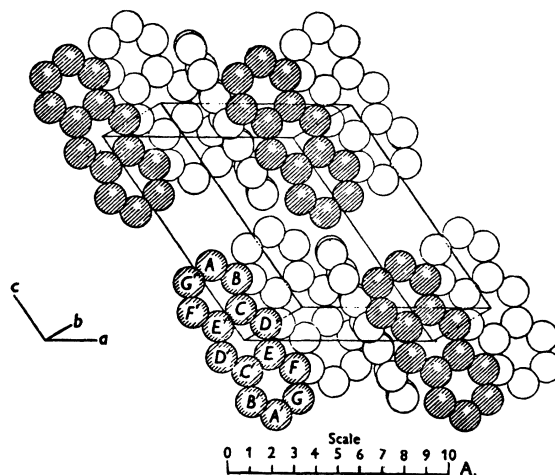Recourse must therefore be had to theoretical

FIG. 3. Positions of the anthracene molecules in the
unit cell.

[5] Abrahams, Robertson, and White, Acta Cryst. 2, 233, 238
(1949); Mathieson, Robertson, and Sinclair, Acta Cryst. 3, 245,
251 (1950).

[6] F. R. Ahmed and D. W. J. Cruickshank, Acta Cryst. 5, 852
(1952).

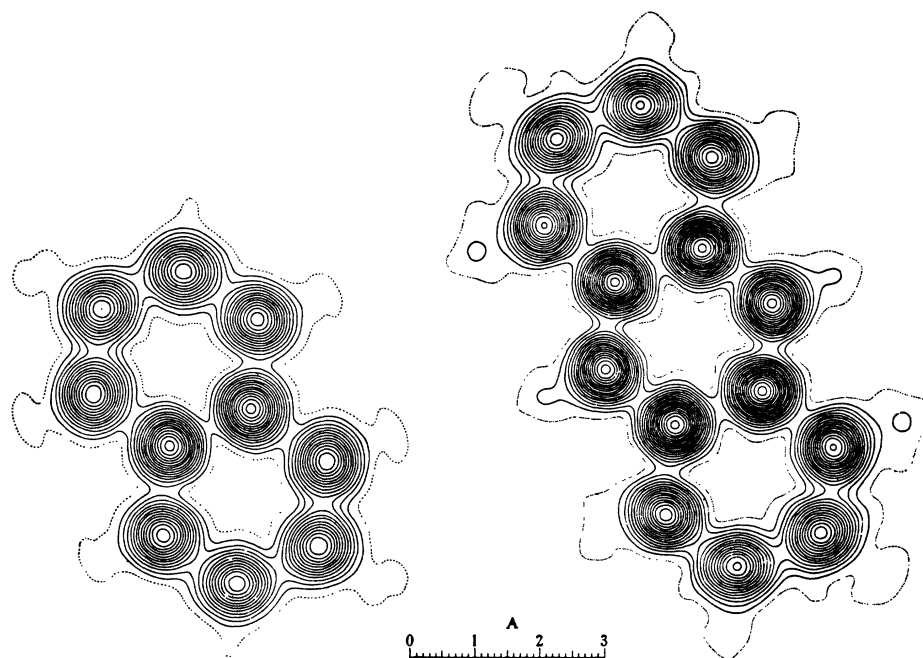[7] Coulson, Daudel, and Robertson, Proc. Roy. Soc. (London)
A207, 306 (1951).

FIG. 4. Electron density sections through the central molecular planes.

knowledge of the electron distribution in an isolated carbon atom. If this is compared with the observed distribution a measure of the thermal movement may be obtained (Debye factor $B = 8\pi^2 \bar{u}^2$). Assuming the form factor of McWeeny,[8] Cruickshank[9] has found, after four cycles of refinement on the Manchester electronic computer, that the temperature factors (assumed to be isotropic at this stage) have values which vary from $B = 4.0$ A^2 on the outermost carbon atoms to $B = 2.5 - 2.8$ A^2 for the atoms of the central ring.

If we now subtract the calculated carbon atom distributions, corrected for temperature in this way, from our experimentally observed electron distribution, the result is shown in Fig. 5. This difference synthesis gives a very much improved definition of all the hydrogen atoms, which are now separately resolved and appear very close indeed to their expected locations. We also find considerable peaks of electron density situated on the bonds between the carbon atoms. These cannot be caused solely by the bonding electrons, however, because the peaks are in some cases greater than those due to the hydrogen atoms themselves. It is clear that they must in large part be caused by certain anisotropic thermal movements of the atoms, of which we have not yet taken account.

The next step is to correct for this anisotropic thermal motion. Methods for doing this have been devised by Cochran[10] and by Cruickshank.[11] In the

three-dimensional case a symmetric tensor with six independent components is required for each atom to characterize its vibrations; and the criteria for determining these thermal parameters are that the six second derivatives of the observed and calculated electron densities should be equal at each atomic position. Elaborate and lengthy calculations are thus
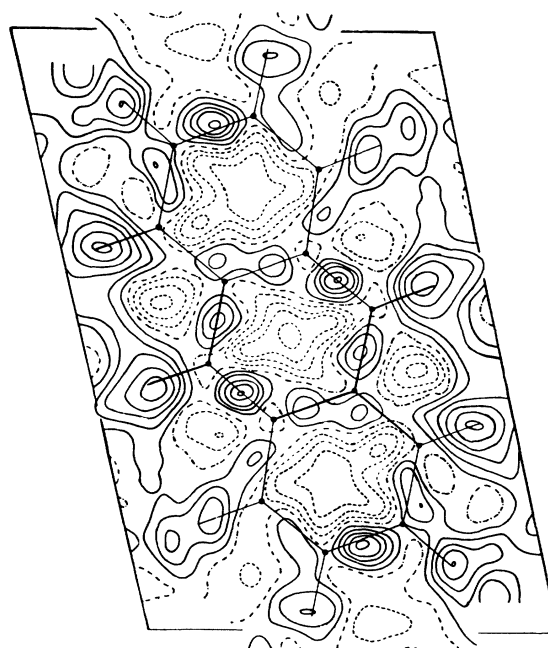

[8] R. McWeeny, Acta Cryst. 4, 513 (1951).
[9] D. W. J. Cruickshank, Acta Cryst. 9, 915 (1956).
[10] W. Cochran, Acta Cryst. 4, 408 (1951).
[11] D. W. J. Cruickshank, Acta Cryst. 9, 747 (1956).

FIG. 5. Anthracene difference map in the central plane. Isotropic carbons subtracted.
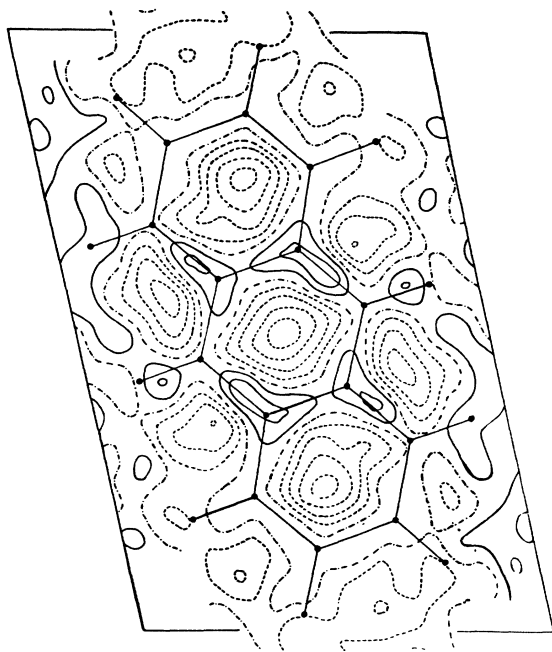
FIG. 6. Anthracene difference map in the central plane.
Anisotropic carbons and isotropic hydrogens subtracted.

required, but Cruickshank has been able to program these for the electronic computer. Without this aid the work would have been virtually impossible. Had it been attempted even 10 years ago the numerical work required for this refinement would have taken about 100 man-years to complete.

At this point, however, a new difficulty confronts us. We are interested in the details of the outer electron distribution and what lies between the atoms. Now, in the mathematical methods devised for treating this problem of thermal anisotropy, the difference between the calculated and observed density curvatures at the atom sites is attributed exclusively to the thermal motion, whereas some of it may be due to bond formation. Obviously if we subtract away such fully corrected atoms the result may be exactly zero and our problem of finding evidence for the bonding electrons is not advanced.

Cruickshank's method of overcoming this difficulty is to determine the temperature parameters from the high-order reflections only.[12] For these, the major part of the x-ray scattering is due to the inner electrons only (K shell) which are not involved in bonding. Expressed otherwise, the more smeared-out bonding electrons will not have much effect on the intensities scattered from the very small spacing planes (high-order reflections).

[12] G. A. Jeffrey and D. W. J. Cruickshank, Quart. Rev. Chem. Soc. (London) 7, 335 (1953).

There are many difficulties in applying this elaborate technique, one of the greatest being to ensure that the absolute scale of the F values is correct over the wide range of reflections involved. On the whole, however, these difficulties appear to have been fairly successfully overcome and the final result obtained by Cruickshank in the molecular plane is given in Fig. 6. This map shows what is left when the anisotropically corrected carbons and the hydrogen are subtracted away from our experimentally observed electron density section. In other words, we have taken away a set of 14 vibrating but nonbonded carbon atoms and 10 hydrogen atoms as defined by their appropriate wave functions. The result seems to indicate a small but rather distinct channeling of the electrons along the bonds and around the rings.

At this level the accuracy is certainly not what we might desire. Cruickshank estimates the standard deviation of the difference map density at about 0.11 electron/A^3, so that the variation in the densities at the different atom positions and at the mid points of the bonds is not significant. Nevertheless, we have now for the first time obtained rather definite evidence regarding the existence of the outer electrons in these crystals. Further progress should be possible when we obtain more accurate intensity measurements, and preferably measurements at a much lower temperature.

A discussion of the bond lengths found in this latest refinement of the anthracene structure is outside the scope of this paper. But one structural result may perhaps be mentioned, because for the chemists at least it is a rather startling conclusion. The molecule which we proved planar in 1932 and much more accurately planar in 1950 is now found to be nonplanar. It is true that the deviations from the mean plane are just about the same as we found in 1950, of the order of 0.01 A, but with the refinements and corrections which Cruickshank has applied to the analysis these deviations now turn out to be highly significant, instead of being within the limit of possible error. And the distortion can be most neatly explained. Atom D (Fig. 3) is the one which deviates most from the mean plane (by 0.012 A). This is the only carbon atom which is approached directly by a hydrogen atom from a neighbouring molecule, the hydrogen of atom F of the molecule at ($\frac{1}{2}$, $-\frac{1}{2}$, 0) being only 2.67 A distant and lying almost directly above the carbon atom D. All other interatomic approaches of this order are between hydrogen atoms only. The molecule is wedged at its ends and the pressure of this hydrogen is causing a slight distortion of the skeleton. It is a case of a very small force causing a very small distortion in something which has after all a certain degree of flexibility. This very beautiful result well illustrates the degree of refinement which has now been achieved.