iron garnet (Geller & Gilleo, 1957*b*) shows that the two structures are quite similar in detail. The differences in distances and angles can be accounted for by the increase in size of the Gd^{3+} ion over that of Y^{3+}. It is particularly interesting to note that the interionic angle $Fe^{3+}(a)$–O^{2-}–$Fe^{3+}(d)$ is 127·4° in gadolinium–iron garnet, compared to 126·6° in yttrium–iron garnet. The difference between these two angles is practically insignificant. This finding appears to support the conclusions reached by Pauthenet (1958) from his study of the paramagnetism and Curie temperatures of rare-earth–iron garnets, including gadolinium–iron garnet. He has found that the Curie temperatures of all of these garnets are very similar and close to that of yttrium–iron garnet. Because the paramagnetic behavior of the rare-earth ions indicates only weak interactions on them, the Curie points must be determined by interactions between Fe^{3+} ions, which are the same for the different iron garnets.

Possibly, the most significant differences between gadolinium–iron garnet and yttrium–iron garnet are in the O^{2-}–O^{2-} interionic distances in the oxygen dodecahedron about Gd^{3+}. These distances are such as to make the dodecahedron slightly more irregular in gadolinium–iron–garnet than in yttrium–iron garnet.

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References

Bertaut, F. & Forrat, F. (1956). *C. R. Acad. Sci., Paris*, **242**, 382.
Bond, W. L. (1959). *Acta Cryst.* **12**, 375.
Busing, W. R. & Levy, H. A. (1959). ORNL Central Files Memorandum 59-4-37.
Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.
Geller, S. & Gilleo, M. A. (1957*a*). *Acta Cryst.* **10**, 239.
Geller, S. & Gilleo, M. A. (1957*b*). *J. Phys. Chem. Solids*, **3**, 30.
Geller, S. & Gilleo, M. A. (1959). *J. Phys. Chem. Solids*, **9**, 235.
Geller, S. (1960). (To be published.)
James, R. W. (1953). *The Optical Principles of the Diffraction of X-Rays*. London: Bell.
Keith, M. L. & Roy, R. (1954). *Amer. Min.* **39**, 1.
Menzer, G. (1928). *Z. Kristallogr.* **69**, 300.
Nielsen, J. W. & Dearborn, E. F. (1958). *J. Phys. Chem. Solids*, **5**, 202.
Pauthenet, R. (1958). *J. Appl. Phys.* **29**, 253.
Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.
Yoder, H. S. & Keith, M. L. (1951). *Amer. Min.* **36**, 519.

Acta Cryst. (1961). **14**, 1056

An Attempt to Determine the Structure Parameters of Condensed Ring Hydrocarbons Using the Electron-Diffraction Method in Gas Molecules

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Electron diffraction studies have been carried out to determine the molecular structure of naphthalene, anthracene, and coronene, using least-squares refinement. For naphthalene a set of structure parameters are obtained of approximately the same accuracy as those from the X-ray crystallographic studies (Table 2). For anthracene the present study leads to ambiguity, and no single set of parameters can be presented (Table 4). For coronene the investigation leads to a unique set of values for the C–C bond distances, but the standard deviations are so large that at least two of the distance values must be considered as rather uncertain (Table 6).

Introduction

The ambitions of molecular structure chemists as to the accuracy of bond-distance determination seem to continue to increase. In particular the problem of accurate bond-distance determination of aromatic molecules is continually attracting the interest of both theoreticians and experimentalists. The simple one-ring aromatic molecules, benzene, pyridine, and furan, have been studied using Raman spectroscopy (Stoicheff, 1954; Stoicheff & Langseth, 1956), microwave spectroscopy (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958), and electron diffraction (Almenningen, Bastiansen & Hansen, 1955; Almenningen, Bastiansen & Fernholt, 1958), and the bond distances have been determined with an accuracy of 0·001–

0·005 Å. For larger aromatic molecules, consisting of condensed rings, practically only X-ray crystallographic methods have been applied. For a survey of the large number of papers published in the latter field reference may be made to a recent article by Cruickshank & Sparks (1960).

In the present work attempts have been made to study whether the electron-diffraction gas technique may be used on the condensed ring molecules. The molecules studied are naphthalene, anthracene, and coronene. This work should not be considered the final study on the use of electron diffraction for these three molecules. Further investigation is needed before a final statement about the accuracy of the method can be made. In spite of the promising results obtained for benzene by the electron-diffraction method on gas molecules, electron diffractionists have found reasons for doubting whether the method can be successfully applied to large aromatic molecules. The doubts arise from the fact that the intensity values as well as the radial distribution curve, as studied in electron-diffraction work, represent one dimensional descriptions. For benzene this does not introduce particular difficulties, as all three C–C distances in benzene show up with separately resolved peaks in the radial distribution curve. In molecules like naphthalene, anthracene, and coronene practically all the peaks of the radial distribution curve are composed of contribution from two or more distances of slightly different values. For instance the first C–C peak at approximately 1·4 Å is, for the three molecules in question, composed of contributions from all the C–C-bond distances, and these distances lie so close together that they cannot be directly resolved. The electron-diffraction method should be able to give the *average* bond distance of each molecule with the same accuracy as for benzene. The problem, however, is to obtain the different individual bond distances. Our approach has been to determine the bond distances indirectly from all the observable interatomic distances of the molecule. In practice only the C–C distances are used. The method is to choose a set of structure parameters and express the positions of all the peaks in the radial distribution curve as functions of these parameters. For each of the three compounds under investigation, this leads to an overdetermined set of equations. These equations are all mathematically independent, but unfortunately there will often occur 'quasi degeneracy', i.e. two equations are so similar that they are nearly identical. The number of equations will not be much greater than the number of unknowns, so it is fairly simple to obtain the parameters for

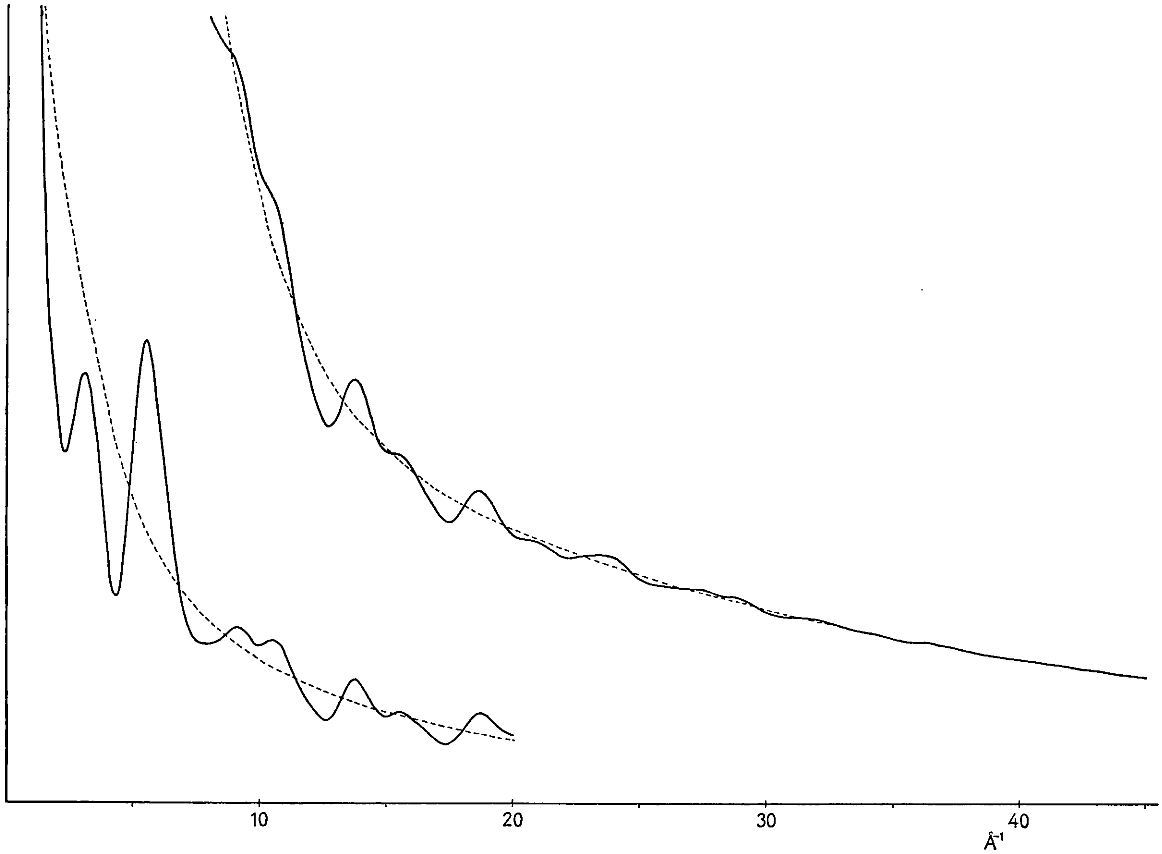

Fig. 1. Naphthalene. Intensity curve with theoretical background.

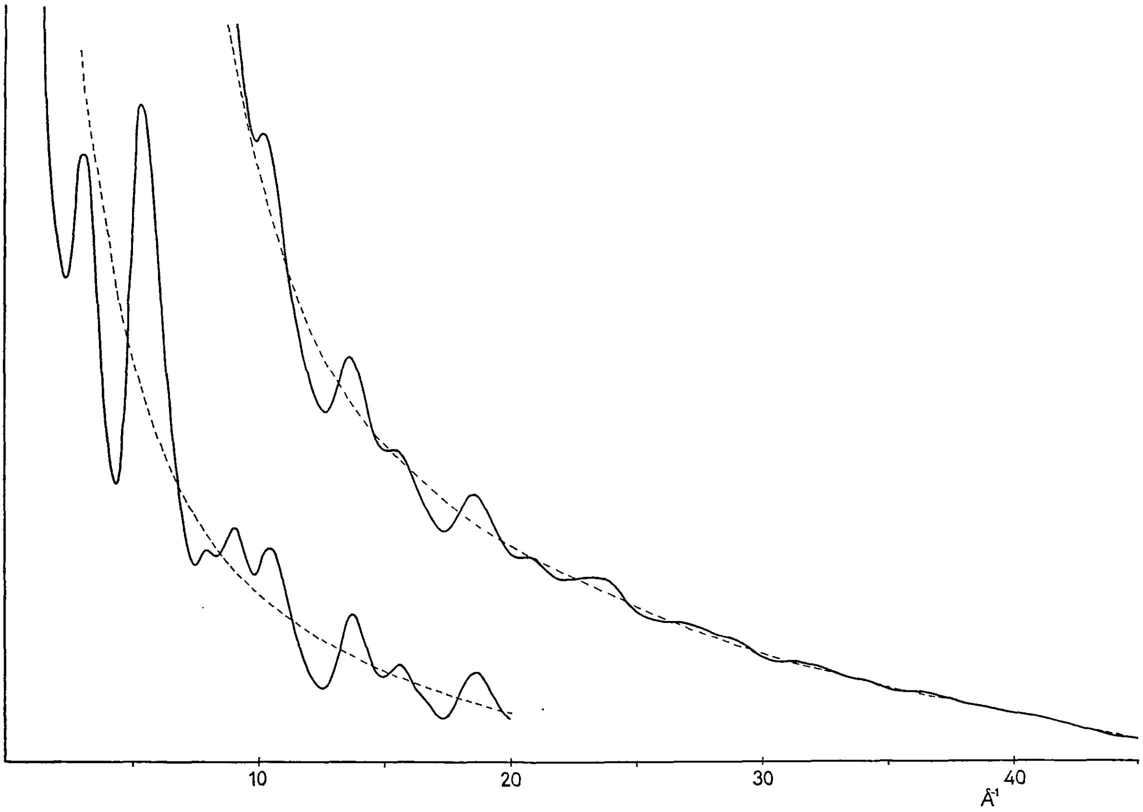

Fig. 2. Anthracene. Intensity curve with theoretical background.

instance by a least-squares calculation. The results are, however, very sensitive to errors in the determination of the maximum positions of the peaks of the radial distribution curves, which should therefore be determined with the greatest possible accuracy.

Intensity curves

Electron-diffraction diagrams were taken for all three compounds at three different distances between the diffraction point and the photographic plate, namely approximately 48 cm., 18 cm., and 11 cm. A series of plates were exposed for each of the compounds at each distance. The intensity values thus obtained range from about $s = 1{\cdot}5$ Å^{-1} to about $s = 60$ Å^{-1} ($s = 4\pi/\lambda . \sin \theta/2$). The sector used has an opening that increases with s by a factor approximately proportional to s^3. Figs. 1, 2, and 3 show the intensity curves, on an arbitrary scale, obtained for the two largest distances between diffraction point and photographic plate. The curves were obtained from the photometer traces after the necessary corrections had been carried out. The dashed curves are the theoretical backgrounds. Though these theoretical backgrounds follow the intensity curves reasonably well, corrections have to be made. This is usually done in the following way: a preliminary background is subtracted from the experimental curve and the difference is multiplied by the proper modification factors to obtain the molecular intensity curve. After Fourier transformation, the first radial-distribution curve is calculated and used to obtain the first approximate model. From this model a theoretical intensity curve is obtained and used as a basis for the background correction. The background thus corrected will usually be sufficiently good to form the basis for the final radial-distribution calculations.

In Fig. 4 the final experimental molecular intensity curves [multiplied by the factor $\exp(-0{\cdot}0009s^2)$] are presented out to s approximately equal to 45 Å^{-1}. The theoretically calculated curves, that have not been reproduced in the figure, follow the experimental curves very closely.

Radial-distribution curves

The molecular intensity curves obtained after the correction of the background formed the basis for the radial-distribution curve calculation. For each compound three radial-distribution curves were calculated using three different damping constants [$k = 0$, $0{\cdot}0009$, and $0{\cdot}0036$ Å^2 in the expression $\exp(-ks^2)$]. Fig. 5 shows the radial-distribution curves for the three compounds on arbitrary scales ($k = 0{\cdot}0009$ Å^2). The peaks marked with Roman numbers are the C–C-distance peaks. The other peaks are C–H-distance

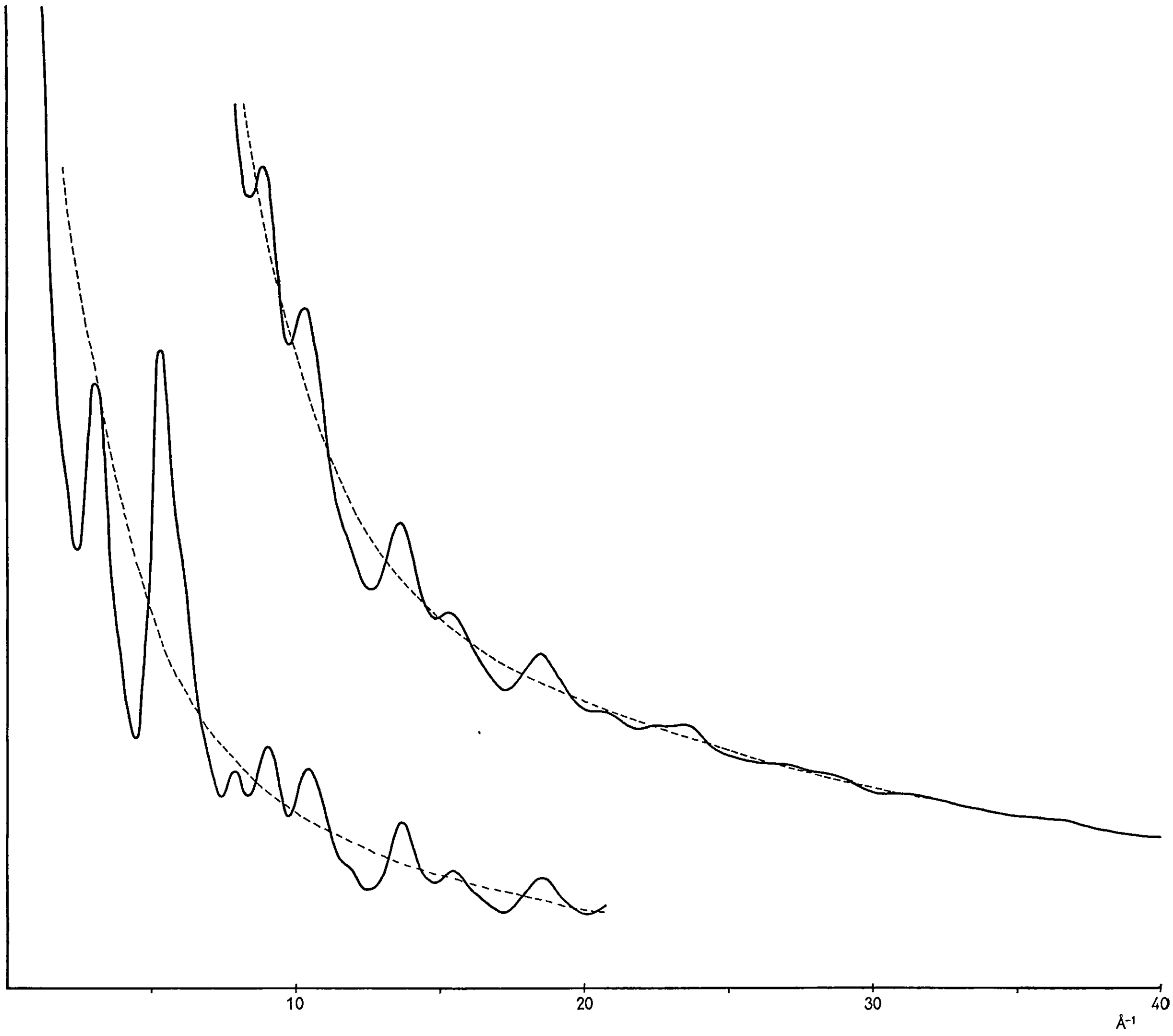

Fig. 3. Coronene. Intensity curve with theoretical background.

peaks. The numbering of the C–C peaks is explained in Tables 1, 3, and 5 and in Figs. 6, 7, and 8. It is seen that practically all the C–C peaks are composed of two or more C–C distances. For the determination of the structure of the carbon skeleton only the C–C distances have been used. The effects of the C–H distances have been subtracted. This C–H subtraction was based upon the following assumptions: (1) All C–C bond distances equal to the observed average C–C bond distance. (2) All C–C–C angles and C–C–H valency angles equal to 120°. (3) All C–H bond distances equal to the observed average C–H bond distance. Of course these assumptions are only approximations and the C–H subtraction may therefore give raise to errors. On the other hand the positions of the C–H peaks do not give confident indications as to the exact positions of the hydrogen atoms, and furthermore the contributions of the C–H distances are comparatively small. In the outer part of the radial distribution curve the C–H contribution is relatively larger than in the inner part, but the larger C–H peaks are much flattened out by the intramolecular vibrations. Therefore, the C–C peaks are very little influenced by slight variations in the C–H distances.

The C–H bond distance itself was found to be approximately 1·09 Å for all the three compounds. This is within the error limits the same value as obtained for benzene.

In setting up the equations connecting the geometric structure parameters and the positions of the maximum of the peaks in the radial distribution curve, the theoretical maxima were assumed to coincide with the weighted arithmetic mean of the C–C distances contributing to each of the peaks. To check the validity of this approximation theoretical peaks composed of contributions from the actual distances were

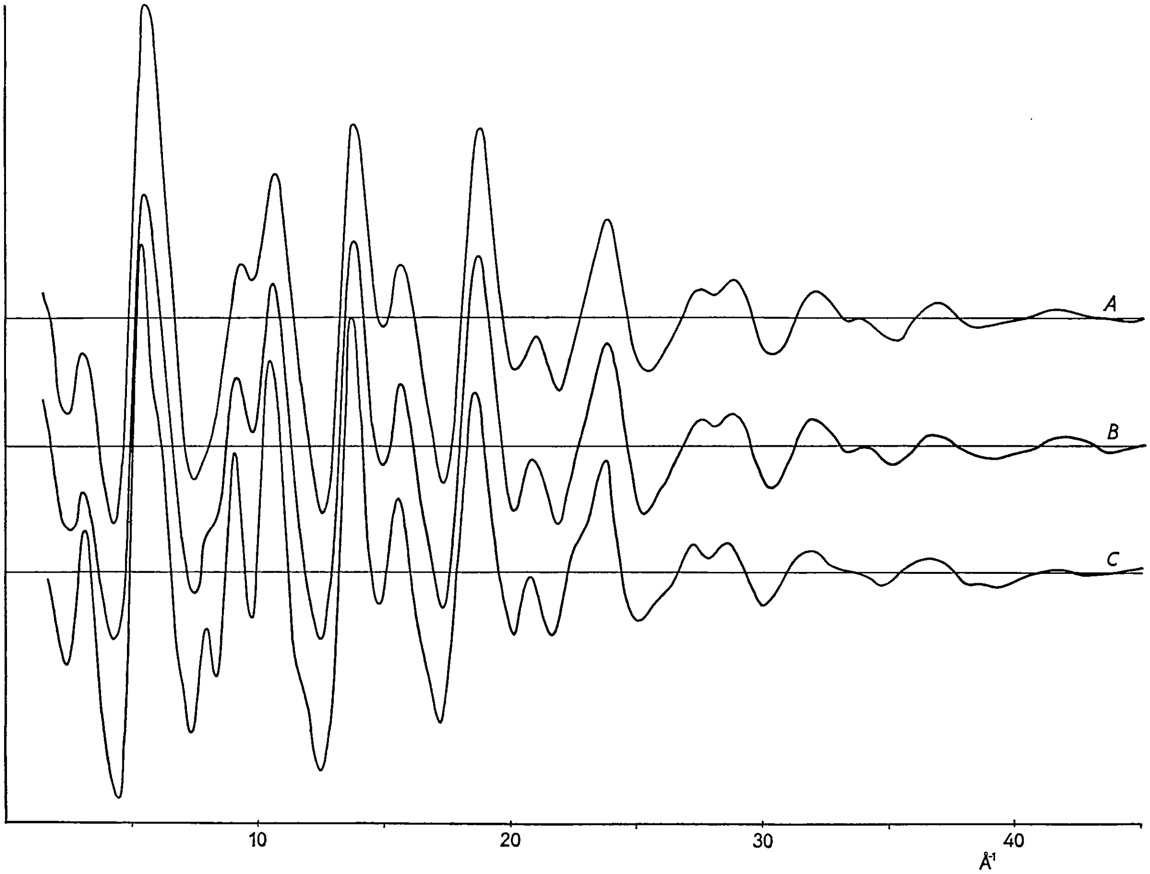

Fig. 4. Molecular intensity curves for naphthalene (*A*), anthracene (*B*), and coronene (*C*).

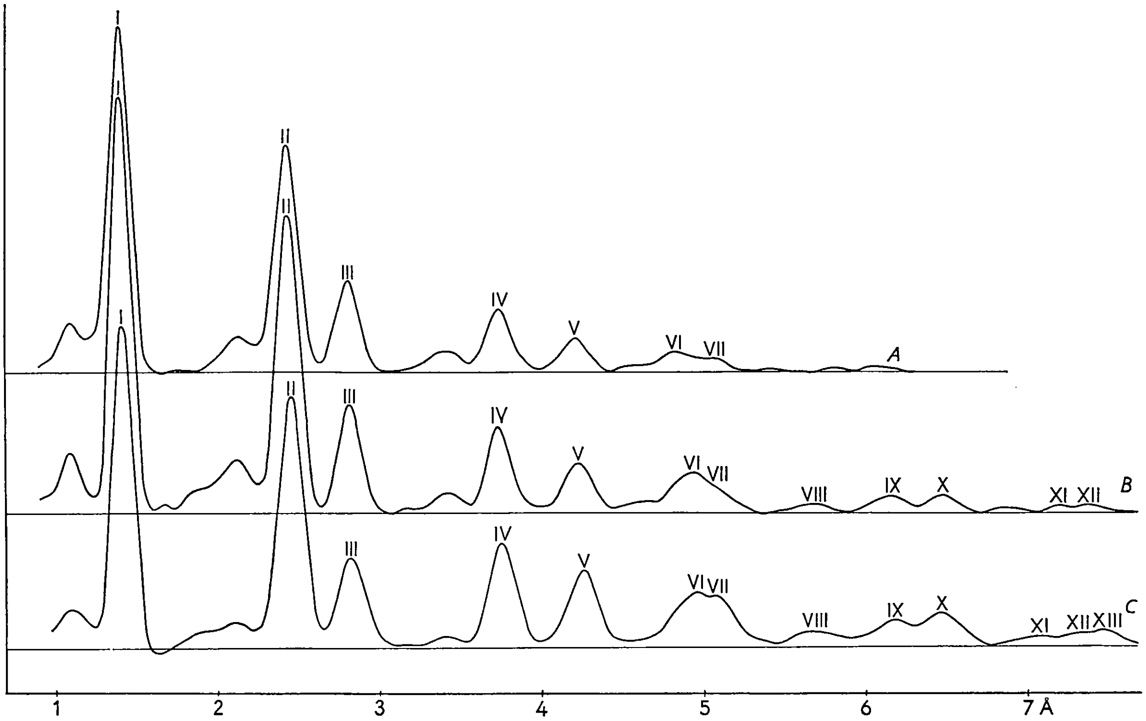

Fig. 5. Radial distribution curves ($k = 0{\cdot}0009$) for naphthalene (*A*), anthracene (*B*), and coronene (*C*).

constructed, and the errors were found to be less than 0·0001 Å.

One particular difficulty in this kind of investigation is the insensitivity of the mean value of the distances in the various distance groups. A reasonable change in the structure parameters generally leads to a shortening of some distances and a lenghtening of others in the same group, so that the group average is much less altered than the individual distances.

Least-squares calculations

The least-squares calculation can be based on the intensity curve (Bastiansen, Hedberg & Hedberg, 1957) or on the radial distribution curve. Many arguments can be presented in favour of both. In the present work we have based our least-squares calculations mainly on the radial distribution curves. Today no electronic computer programme has been tried out on electron-diffraction intensity curves for molecules as large as those dealt with here. A programme is being set up by Hedberg & Iwasaki at Oregon State College. As soon as this programme is in operation least-squares calculations on naphthalene, anthracene, and coronene should be tried out.

In the study of the radial distribution curves, the least-squares calculations may be used for various purposes: (*a*) to determine the exact position of the maxima of the various peaks, (*b*) to resolve overlapping peaks, and (*c*) to determine the structure parameters from the deduced C–C distance peaks. The determination of the maximum positions is done by fitting in Gaussian peaks. To resolve overlapping peaks, a direct trial-and-error procedure often seems more adequate.

One disadvantage in the application of least-squares to radial distribution curves is that the small number of equations (one for each reliable C–C peak in the curve) makes the values of the standard deviations rather dubious. The standard deviations obtained from radial distribution curve calculations should, therefore, be taken with considerable reservation.

For the use of least-squares calculations the choice of weight factors often obscures the method. Special attention should therefore be paid to the influence of the weight factors.

All the refinements and standard deviation calculations in the present article were calculated with full least-squares matrix.

Naphthalene

The positions of the maxima of the various peaks are given in Table 1. The values obtained are the weighted averages from the various radial distribution curves. The table also describes how the peaks are composed of contribution from the various C–C distances in the molecule. The numbering of the atoms and the definition of the structure parameters *a*, *b*, *c*, *d*, and φ are explained in Fig. 6.

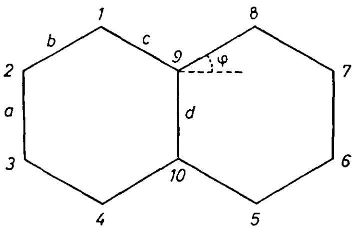

Fig. 6. Naphthalene. Notation for atoms and bonds.

To start a least-squares refinement, one has to choose a zeroth order model. A model free of any presumptions as to special values for the various bond distances is one with all C–C distances equal and with all valency angles equal to 120°. Starting from this zeroth order model and performing two successive least-squares refinement calculations (of which the second only leads to small changes) the values given in second column of Table 2 were obtained. (The values in parentheses are those of the zeroth order model). To study the influence of the zeroth order model another initial model was tried, namely the one given by Cruickshank (1957).* The result of this attempt is given in third column of Table 2 with the zeroth order values in parentheses. The correspondence between these two sets of structure parameters is very satisfactory.

Table 1. *Naphthalene*

Average internuclear distances (Å) obtained from the radial distribution curves

Peak no.	Distances	Multiplicity of distances	Obs. max. positions
I	*a*	2	1·401
	b	4	
	c	4	
	d	1	
II	1–10	4	2·435
	1–3	4	
	2–9	4	
	1–8	2	
III	1–4	2	2·810
	2–10	4	
IV	2–8	4	3·734
	1–5	2	
V	2–5	4	4·219
VI	2–7	2	4·825
VII	2–6	2	5·045

Least-squares refinements based upon intensity curves were also carried through. The values obtained are in fairly good agreement with the results presented in Table 2. The influence of the C–H distances and the problem of properly weighting the various parts of the intensity curve lead to special difficulties that are hard to overcome without an elaborate computer programme. The calculation was not carried on to self-

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* When this calculation was performed the final results of Cruickshank & Sparks (1960) were not known.

Table 2. *Naphthalene*

Structure parameters obtained from electron diffraction and X-ray studies. Distances in Å

Structure parameters	1st set of el.dif. data	2nd set of el.dif. data	Standard deviations	Average of el.dif. data	X-ray data (Cruickshank & Sparks, 1960)
a	1·412 (1·400)	1·413 (1·421)	0·014	1·412	1·415
b	1·371 (1·400)	1·371 (1·361)	0·009	1·371	1·364
c	1·421 (1·400)	1·423 (1·425)	0·004	1·422	1·421
d	1·422 (1·400)	1·418 (1·410)	0·007	1·420	1·418
φ	29·37° (30°)	29·48° (29·23°)	0·22°	29·42°	29·13°

consistency and the obtained parameters were therefore not included in the table. The standard deviations obtained from intensity least-squares calculations are, however, listed in Table 2. Though these standard deviations are not quite adequate in this connection, they may give an indication of the order of magnitude of the errors. The fact that the standard deviation for distance *a* comes out as the largest and for distance *c* as the smallest is in good accord with expectation. The influence of bond *a* upon the larger C–C distances is considerably less than that of bond *c*.

In the fifth column of Table 2 the average values of the best electron-diffraction calculations are compared with the latest results of X-ray crystallography (Cruickshank & Sparks, 1960). These latest X-ray values were brought to knowledge of the authors after the completion of the refinement calculations. It is interesting to note that the electron-diffraction values are in better agreement with this latest set than with the X-ray values used for the least-squares calculations.

The fact that the two initial models seem to lead to the same unique set of structure parameters indicates that in this case the electron-diffraction method leads to no ambiguity. The rather small standard deviations seem also to indicate that the values obtained for naphthalene are comparable in accuracy with the X-ray values which they strongly support.

Anthracene

Table 3 and Fig. 7 for anthracene correspond to Table 1 and Fig. 6 for naphthalene. No observed value is given for the three peaks VII, XI, and XII, as due to overlap, their positions are not determined with sufficient accuracy for inclusion in the least-squares calculations. Table 4 shows the results of two least-squares refinement calculations using two different zeroth order models, the parameters of which are given in parentheses. In this case the two results are not in satisfactory agreement. This shows that the function of the structure parameters to be minimized in the least-squares calculations does not have a unique minimum. It must have at least two different, well separated, minima. As these two attempts already demonstrated an ambiguity, no further calculation was performed in order to reveal other possible minima. It may be pointed out that the average of the two electron-diffraction sets correlates fairly well with the latest values of Cruickshank & Sparks. Both the average of the two sets and Cruickshank & Sparks' latest values are given in Table 4. This correlation should, however, not be taken too seriously.

Table 3. *Anthracene*

Average internuclear distances (Å) obtained from the radial distribution curves

Peak no.	Distances	Multiplicity of distances	Obs. max. positions
I	*a*	2	1·408
	b	4	
	c	4	
	d	2	
	e	4	
II	2–11	4	2·444
	2–4	4	
	1–12	4	
	1–10	4	
	11–13	2	
	5–11	4	
III	2–12	4	2·826
	1–4	2	
	12–13	2	
	5–10	1	
IV	2–10	4	3·731
	1–13	4	
	1–5	4	
V	2–5	4	4·236
	1–14	4	
VI	2–13	4	4·898
	1–9	2	
VII	2–14	4	
VIII	1–6	2	5·672
IX	2–9	4	6·157
X	2–6	4	6·487
XI	2–8	2	
XII	2–7	2	

The proper conclusion is that the electron-diffraction method, as applied here, at the present stage of development is not able to give values of an accuracy comparable with the X-ray values. This pessimistic conclusion is reinforced by the results of a study of the least-squares technique in an ideal case with no experimental errors. The test was done as follows: An arbitrarily chosen model was defined as the 'correct' one, and the theoretical values for all the C–C distances in this 'correct' model were calculated.

Table 4. *Anthracene*

Structure parameters obtained from electron diffraction and X-ray studies. Distances in Å

Structure parameters	1st set of el.dif. data	2nd set of el.dif. data	Average of el.dif. data	X-ray data (Cruickshank & Sparks, 1960)
a	1·409 (1·408)	1·429 (1·419)	1·419	1·419
b	1·404 (1·408)	1·377 (1·366)	1·390	1·368
c	1·425 (1·408)	1·415 (1·433)	1·420	1·436
d	1·407 (1·408)	1·444 (1·436)	1·425	1·428
e	1·407 (1·408)	1·400 (1·399)	1·404	1·399
φ_1	29·96° (30°)	28·60° (28·71°)	29·28°	29·00°
φ_2	29·73° (30°)	29·11° (29·49°)	29·42°	29·51°

The zeroth order model for the least-squares calculation was taken to have all bond distances equal and all valency angles equal to 120°. Using four significant figures in the 'observed' distances, the results obtained showed considerably larger deviations from the 'correct' values than the standard deviations of the X-ray values of Cruickshank & Sparks.

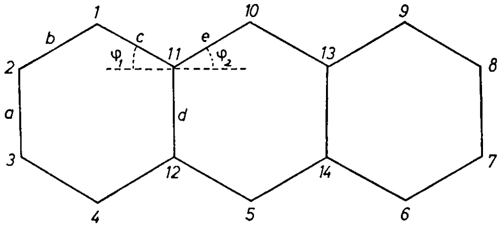

Fig. 7. Anthracene. Notation for atoms and bonds.

A least-squares calculation based on intensity curves may perhaps give greater hopes for future electron-diffraction studies on anthracene. The present investigation does, however, also seem to demonstrate the need of further improvements in both the calculation procedures and the experimental electron-diffraction technique.

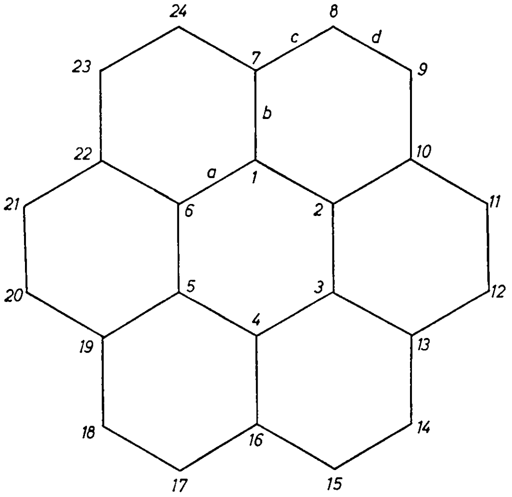

Fig. 8. Coronene. Notation for atoms and bonds.

Coronene

Table 5 and Fig. 8 give the necessary description as to the parameters, C–C distances and maxima of the radial-distribution curves. The positions of the three last peaks could not be determined with sufficient accuracy and were omitted in the least-squares calculation.

In Table 6 three sets of least-squares calculation results are given based upon three different zeroth order models. The average standard deviations are also

Table 5. *Coronene*

Average internuclear distances (Å) obtained from the radial distribution curves

Peak no.	Distances	Multiplicity of distances	Obs. max. positions
I	a	6	1·415
	b	6	
	c	12	
	d	6	
II	1–3	6	2·456
	1–8	12	
	7–9	12	
	1–10	12	
	9–11	6	
III	1–4	3	2·829
	1–9	12	
	7–10	6	
IV	1–13	12	3·758
	1–11	12	
	8–11	12	
V	1–16	6	4·263
	7–11	12	
	1–12	12	
VI	8–12	6	4·901
	1–14	12	
	7–13	6	
VII	1–15	12	5·099
	7–12	12	
VIII	8–21	6	5·677
	7–16	3	
IX	7–14	12	6·168
X	7–15	12	6·479
	8–14	12	
XI	8–15	6	
XII	8–18	6	
XIII	8–17	6	

Table 6. *Coronene*

Bond distances (Å) obtained from electron diffraction and X-ray studies

Distances	1st set of el.dif. data	2nd set of el.dif. data	3rd set of el.dif. data	Average standard deviations	Average of el.dif. data	X ray data (Robertson & White, 1945)
a	1·441 (1·415)	1·437 (1·430)	1·435 (1·438)	0·009	1·438	1·430
b	1·374 (1·415)	1·382 (1·430)	1·388 (1·381)	0·019	1·381	1·430
c	1·446 (1·415)	1·445 (1·415)	1·440 (1·444)	0·016	1·444	1·415
d	1·361 (1·415)	1·360 (1·385)	1·365 (1·362)	0·017	1·362	1·385

given. The correspondence between the three sets is good, which indicates a unique minimum of the square-sum function. On the other hand the average standard deviation is considerably larger than for naphthalene. In this case the standard deviations are based on radial distribution curve calculations. The comparison with naphthalene is therefore not quite fair.

The average electron-diffraction result is compared with the X-ray result (Robertson & White, 1945). In the case of bond distance *a* where the standard deviation has the lowest value the correspondence is satisfactory. For the bond distances *c* and *d* the discrepancy is large but not unreasonable compared with the large standard deviations. For bond distance *b* the deviation is approximately three times as large as the standard deviation. This is so much that reasons other than a pure accidental deviation might be looked for. As mentioned earlier, not too much confidence should be attached to the standard deviations. A more detailed analysis shows that the two distances *b* and *c* are particularly sensitive to errors in the larger internuclear distances of the molecule and may deviate so that one of the two distances may come out too large and the other one too small, the sum $b+2c$ being approximately constant. This fact does not, as it ought to, show up sufficiently in the standard deviations of the bond distances. It ought to be mentioned that the X-ray results for coronene are rather old and based upon two dimensional data. They are, therefore, unlikely to be as accurate as those of naphthalene and anthracene.

Conclusion and discussion

The main conclusions of this work can be briefly stated: The present electron-diffraction studies lead to satisfactory results for naphthalene but to an ambiguity for anthracene. For coronene the results are unambiguous but not of great use as the probable errors, particularly for the distances *b* and *c*, are rather large.

One interesting conclusion is that the average bond distance increases with the size of the molecule. For the four molecules benzene, naphthalene, anthracene, and coronene the average bond distances as determined from electron-diffraction studies are: 1·397, 1·401, 1·408, and 1·415 Å respectively.

It is of the greatest importance for possible future work in this field to study the various limitations of the method and to decide which of these are intrinsic and which may be removed by improvement of the method. One intrinsic limitation is connected with the intramolecular vibration of the molecules. In carrying out the least-squares calculations as discussed earlier, a high molecular symmetry has been tacitly assumed; for instance, a hexagonal symmetry in coronene. Another tacit assumption is that the molecules are planar. Both these assumptions are reasonable, but even if the equilibrium conformations of the molecules are highly symmetric and planar, molecular vibration may lead to an apparent deviation from planarity. An analogous effect, known as the 'shrinkage effect', is familiar in studies of linear molecules like dimethyldiacetylene, allene, and butatriene (Almenningen, Bastiansen & Trætteberg, 1959). This effect makes the larger interatomic distances look shorter than in a stiff molecular model. The effect is very difficult to correct for and is particularly serious in larger molecules. It may be that this is the reason for the lack of success in anthracene and coronene. For naphthalene the effect should not be so critical. It is possible that the effect of the out-of-planarity vibrations can be handled in a way analogous to that worked out by Morino (1960) for linear molecules.

It may well be that the limiting factor is the present accuracy of the intensity curve measurement. It seems most important to improve the inner part of the intensity curve. This part of the curve is particularly important for the determination of the larger C–C distances, the values of which are of decisive significance for the final results. A new electron-diffraction camera especially intended for small *s*-values is under construction.

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References

Almenningen, A., Bastiansen, O. & Hansen, L. (1955). *Acta Chem. Scand.* **9**, 1306.

Almenningen, A., Bastiansen, O. & Fernholt, L. (1958). *K. Norske Vidensk. Selsk. Skr.* No. 3.

Almenningen, A., Bastiansen, O. & Trætteberg, M. (1959). *Acta Chem. Scand.* **13**, 1699.

Bak, B., Hansen-Nygaard, L. & Rastrup-Andersen, J. (1958). *J. Mol. Spectr.* **2**, 361.

Bastiansen, O., Hedberg, K. & Hedberg, L. (1957). *J. Chem. Phys.* **27**, 1311.

Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504.

Cruickshank, D. W. J. & Sparks, R. A. (1960). *Proc. Roy. Soc.* A, **258**, 270.

Morino, Y. (1960). *Acta Cryst.* **13**, 1107.

Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.*, p. 607.

Stoicheff, B. P. (1954). *Canad. J. Phys.* **32**, 339.

Stoicheff, B. P. & Langseth, A. (1956). *Canad. J. Phys.* **34**, 350.

Acta Cryst. (1961). **14**, 1065

The Crystal Structures of $IrAs_3$ and $IrSb_3$

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The compounds $IrAs_3$ and $IrSb_3$ have the $CoAs_3$-type structure (space group $Im3$) with

$IrAs_3$: $a = 8{\cdot}4691$ Å, $y = 0{\cdot}350 \pm 0{\cdot}002$, $z = 0{\cdot}146 \pm 0{\cdot}002$, density $= 9{\cdot}03$ g.cm.$^{-3}$,
$IrSb_3$: $a = 9{\cdot}2495$ Å, $y = 0{\cdot}343 \pm 0{\cdot}001$, $z = 0{\cdot}157 \pm 0{\cdot}001$, density $= 9{\cdot}26$ g.cm.$^{-3}$.

The shortest interatomic distances are

$$\text{Ir–6As} = 2{\cdot}445 \pm 0{\cdot}012,\ \text{As–As} = 2{\cdot}473 \pm 0{\cdot}034 \text{ and } 2{\cdot}541 \pm 0{\cdot}034 \text{ Å},$$
$$\text{Ir–6Sb} = 2{\cdot}613 \pm 0{\cdot}006,\ \text{Sb–Sb} = 2{\cdot}904 \pm 0{\cdot}018 \text{ Å}.$$

The compounds have almost zero magnetic susceptibility.

The structure parameters have been refined by a trial-and-error method. Three different reliability indices R_1, R_2 and R_3 have been calculated to check the agreement between I_o and I_c for every shift of the atoms. Systematic improvement of the coordinates is discussed on the basis of $R(y, z)$ maps.

Introduction

In recent studies of the iridium antimonides (Žuravlev & Ždanov, 1956; Kuzmin *et al.*, 1957) a compound $IrSb_3$, was identified by means of X-ray and metallographic methods. According to Žuravlev & Ždanov the structure is of the skutterudite, $CoAs_3$, type, and in making their structure determination they used Oftedal's (1928) parameter values for $CoAs_3$. Oftedal's values were based on the postulated relation $y+z=\frac{1}{2}$ between the independent parameters y and z, which makes all distances between immediately coordinating arsenic atoms equal. This relation has also been used by Rosenqvist (1953) for $CoSb_3$ and by Žuravlev & Ždanov (1956) for $CoSb_3$ and $RhSb_3$. In order to check this assumption a reinvestigation of $IrSb_3$ was carried out. As a preliminary study of the iridium–arsenic system indicated the existence of an isostructural compound $IrAs_3$, this compound was also investigated.

The $IrAs_3$ and $IrSb_3$ samples were made by heating weighed quantities of iridium and arsenic or antimony at about 850 °C. in pure alumina crucibles placed inside silica tubes which were evacuated and sealed. The samples were heated at this temperature for one month and cooled slowly to room temperature. Heat treatment at temperatures above 1200 °C. indicates that $IrAs_3$ and $IrSb_3$ are formed peritectically. For $IrSb_3$ this is in agreement with the result by Kuzmin *et al.* (1957), who found that this compound has a peritectic temperature between 800 and 950 °C.

Crystallographic data

Powder photographs of $IrAs_3$ and $IrSb_3$ were taken with filtered Cu K-radiation ($\lambda_{\alpha_1} = 1{\cdot}54050$ Å) in cameras with 114·6 mm. effective diameter and indexed on the basis of a cubic unit cell, *cf.* Tables 1 and 2. The extrapolated lattice constants (Nelson & Riley, 1945) of $IrAs_3$ and $IrSb_3$ are listed in Table 3, together with the lattice constant for $IrSb_3$ determined by Žuravlev & Ždanov (1956). The agreement between this value and the new one is very satisfactory.

On the basis of the observed densities at 25·00 °C., *cf.* Table 3, the unit cell contains 8 AB_3-groups ($Z_c = 7{\cdot}92$ for $IrAs_3$ and $Z_c = 7{\cdot}91$ for $IrSb_3$).

The systematic missing reflections were of the type (hkl) absent when $h^2+k^2+l^2 = 2n+1$. This condition also characterized the possible space groups of $CoAs_3$ (Oftedal, 1928). According to Oftedal the atomic arrangement in the skutterudite, $CoAs_3$, structure in terms of the space group $Im3(T_h^5)$ is as follows:

8 Co in (e) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ etc.
24 As in (g) $0, y, z$ etc.