# *The Structure of Overcrowded Aromatic Compounds. Part III.* The Crystal Structure of 3 : 4-Benzophenanthrene.*

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The crystal structure of 3 : 4-benzophenanthrene has been analysed by two-dimensional Fourier methods. The molecular orientation and position in the unit cell were fixed by a combination of the molecular Fourier transform method and the interpretation of non-space-group absences and near absences of certain zonal reflections. The atomic co-ordinates were refined by successive $F_o - F_c$ syntheses to *R* factors of 0·22, 0·23, and 0·26 in the *hk*0, 0*kl*, and *h*0*l* zones.

The final co-ordinates can be fitted, within a root-mean-square deviation of 0·03 Å, to a molecular model of symmetry 2, in which a separation of 3·0 Å between the centres of the overcrowded carbon atoms labelled 1 and 12 in Fig. 1 is achieved by distortion of the benzene rings. This model consists of two pairs of six-membered rings, related by a twofold axis, which are folded about their long diagonals through angles of 10° and 14°.

The distortions of the molecular skeleton have been related to the difference between the calculated and measured resonance energies and to the non-vanishing dipole moment; the nearly tetrahedral bond angles at four of the secondary carbon atoms to the close approach distance of 3·13 Å between two such atoms of neighbouring molecules, and to the preferential attack on these same atoms by electrophilic reagents.

THE analysis of the structure of 3 : 4-benzophenanthrene was undertaken in continuation of work outlined in Part I (*J.*, 1954, 3288). The distance of 2·4 Å between carbon atoms labelled 1 and 12 in Fig. 1 † in a conventional model of the molecule is shorter than the approach distances found in any of the overcrowded molecules discussed in Part I, and one may therefore expect the benzophenanthrene ring system to be distorted in order to achieve relief from overcrowding. To investigate quantitatively any such deformation we have determined the structure of 3 : 4-benzophenanthrene by *X*-ray crystallography, and now report the results of an analysis by two-dimensional Fourier methods.

A preliminary crystallographic investigation has been reported by Iball (*Z. Krist.*, 1938, **99**, *A*, 230), from which we cite the following data : $a = 14·60, b = 14·00, c = 5·76$ Å;

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* Part II, preceding paper.

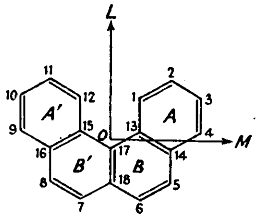
† In this paper the numbers used in references to the carbon atoms are those shown in Fig. 1 and not those strictly related to the name 3 : 4-benzophenanthrene.

$d$ (found) 1·265, $d$ (calc.) 1·278; $n = 4$. Absences: $h0l$ absent for $h + l$ odd, $0k0$ absent for $k$ odd. Possible space-groups: $P2_12_12_1$, $Pmn$, $Pmnm$, with $Pmn$ favoured on evidence referred to below.

The cell dimensions and space-group were now determined from zero- and first-layer Weissenberg photographs about the three principal axes. The lattice constants were corrected by extrapolation to $\theta = 90°$ (Buerger, "*X*-Ray Crystallography," J. Wiley and Sons, New York, 1942, Ch. 20) and are accurate to 0·1%: $a = 14{\cdot}69$, $b = 14{\cdot}19$, $c = 5{\cdot}76$ Å; $d$ (calc.) = 1·261. Absences: $h00$ absent for $h$ odd, $0k0$ absent for $k$ odd, $00l$ absent for $l$ odd. Space-group: $P2_12_12_1$.

The two sets of lattice parameters are in good agreement. Our Weissenberg photographs show that the $h0l$ reflections with $h + l$ odd are weak but not systematically absent. Thus the extinctions referred to by Iball as systematic are in fact pseudo-absences; the space-group is therefore unequivocally determined as $P2_12_12_1$. The significance of these pseudo-extinctions for the molecular shape and arrangement is discussed in detail below.

FIG. 1. *The planar model of the* 3 : 4-*benzophenanthrene molecule, showing the molecular axes and the nomenclature of atoms and rings used in this paper.*



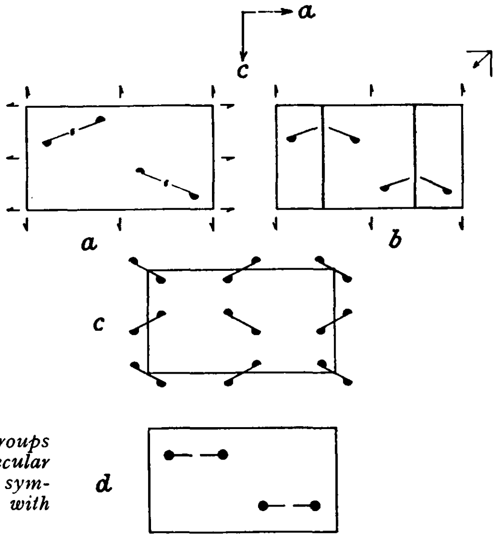


FIG. 2. *The* (010) *projections of the space-groups* (a) $P2_12_12_1$ *and* (b) $Pmn2_1$. *Possible molecular arrangements in* $P2_12_12_1$ *with the additional symmetry implied by the absences of* $h0l$ *spectra with* $h + l$ *odd are shown in* c *and* d.

In common with other workers, we prefer, for space-group $P2_12_12_1$, to choose origins for the three principal projections at the points of intersection of the corresponding twofold screw axes with the respective planes of projection. Hence, the origins of the (001), (100), and (010) projections are at the points ($\frac{1}{4}$00), (0$\frac{1}{4}$0), and (00$\frac{1}{4}$), respectively, in the co-ordinate system of the "Internationale Tabellen zur Bestimmung von Kristallstrukturen" (Gebr. Borntraeger, Berlin, 1935). For the sake of uniformity all co-ordinates mentioned in the following discussion are referred to the origin ($\frac{1}{4}$00).

The length of the $c$ axis permits only a single molecule to be accommodated along [001], with the molecular plane inclined at about 45° to (001). For additional information as to the molecular orientation, packing considerations are not very helpful because of the similarity of the $a$ and $b$ axes and the relatively symmetrical shape of the molecule; nor is the level of the unitary structure factors sufficiently high to favour the use of any of the analytical methods of sign determination. The correct molecular orientation was eventually derived by arguments based mainly on the molecular Fourier transform method and on the interpretation of the pseudo-absences in the zonal reflections.

In applying the Fourier transform method we have followed the procedure outlined by Klug (*Acta Cryst.*, 1950, **3**, 176) in the analogous instance of triphenylene and shall therefore restrict the following discussion to features peculiar to the present problem. The real and imaginary parts of the Fourier transform of 3 : 4-benzophenanthrene were calculated on the assumption of a planar molecule with atoms at the corners of regular hexagons of side 1·40 Å. The system of molecular axes is shown in Fig. 1.

Comparison of the weighted reciprocal lattice with the Fourier transform led to the conclusions that (1) $a^*$ must lie along the $OL$ axis of the transform, (2) $b^*$ must lie at about 45° to the plane of the transform, (3) the approximate co-ordinates $(u_0, v_0)$ of the molecular reference point $O$ are either (0·01, 0·25) or (0·26, 0·25), (4) the poor agreement between the Fourier transform and observed values of the structure factors beyond the low orders of F(*hk*0) suggests that the planar and regular model used for the computation of the transform represents only inadequately the structure of the real molecule.

A second clue to the molecular orientation is provided by the pseudo-absences in the *h*0*l* zone, which imply that the *b* axis projection of the unit cell approximates to that of space-group $Pmn2_1$ (Figs. 2, *a* and *b*). There are two possible molecular arrangements in $P2_12_12_1$ satisfying this condition of additional symmetry, of which one can be decisively ruled out. This orientation (Fig. 2, *c*) requires the projected molecule to have a pseudo-centre of symmetry at the point $u = 0$, $w = 0$. As the only possible centrosymmetric projection of benzophenanthrene is that down the molecular $OL$ axis it follows that $OL$ would necessarily lie parallel to $b$. This arrangement is contradicted by the evidence of the Fourier transform, according to which $OL$ is parallel to $a$. Moreover, it is ruled out by the value of F(230), which it would require to be small whereas in fact this reflection is the second strongest in the (*hk*0) zone. In his discussion of possible space-groups Iball put forward this molecular arrangement in $P2_12_12_1$ as the explanation for the extra *h*0*l* absences; he rejected it as an unlikely packing arrangement and concluded that the space-group could not be $P2_12_12_1$.

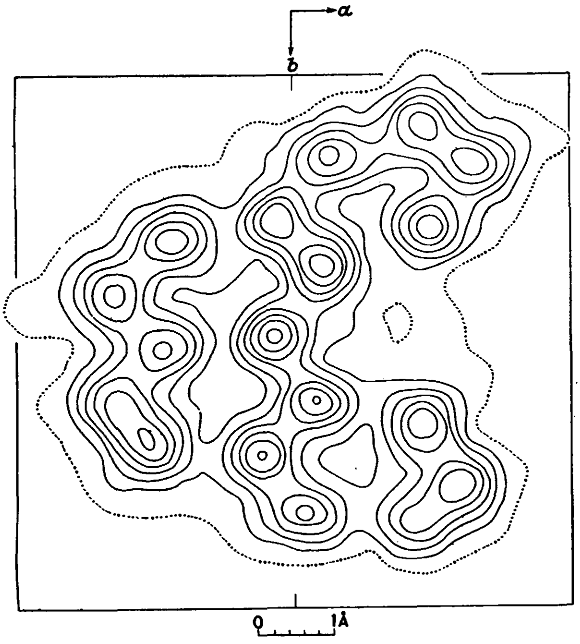


FIG. 3. *The electron-density projection on* (001), *calculated with* 144 *out of* 154 *observed terms. The contours are drawn at intervals of* 1 e.Å$^{-2}$, *with the one-electron line dotted.*

The second possible molecular arrangement (Fig. 2, *d*) requires the projected molecule to have a pseudo-mirror plane parallel to (001) at $w = 0·25$. This must coincide with the projected $OL$ axis, evidently a molecular twofold axis of symmetry. Thus, the information deduced from the pseudo-absences, together with the evidence from the Fourier transform, leads to the following conclusions: (1) the molecule has an approximate twofold axis of symmetry along $OL$, nearly parallel to the $a$ axis; (2) $OM$ is inclinded at about 45° to the $a$ axis; (3) the approximate co-ordinates of the point $O$ are $u_0 = 0·01$ or 0·26 (Fourier transform), $v_0 = 0·25$ (Fourier transform), $w_0 = 0·25$ (*h*0*l* pseudo-absences).

Conditions (1) and (3) together imply that the symmetry of the cell approximates to that of space-group $B22_12$; we should thus expect the pseudo-absences to extend throughout the reciprocal lattice. Indeed, Weissenberg photographs of the *hk*1 and *hk*4 spectra as well as of the three principal zones reveal that reflections with $h + l$ odd tend to be generally weaker than those with $h + l$ even.

The ambiguity in the $u_0$ parameter was resolved in favour of $u_0 = 0{\cdot}01$ from considerations of molecular packing; during the course of the analysis the second alternative was tested and ruled out on the basis of the *h*0*l* structure factors.

Atomic co-ordinates were calculated for a planar and regular molecule with $u_0 = 0{\cdot}01$, $v_0 = 0{\cdot}25$, $w_0 = 0{\cdot}25$, *OL* parallel to [100], and *OM* at 45° to (001). Refinement from this original set of co-ordinates was carried out by means of successive $F_O - F_C$ syntheses until the *R* factor had decreased to 0·22. There remained at this stage ten *hk*0 structure factors of uncertain sign, of which six had unitary scattering factors exceeding 0·05, the largest being U(14,2,0) = 0·16. However, as a further difference synthesis failed to improve the agreement for these reflections it was concluded that the atomic co-ordinates already determined were the best that could be derived from the present experimental data.

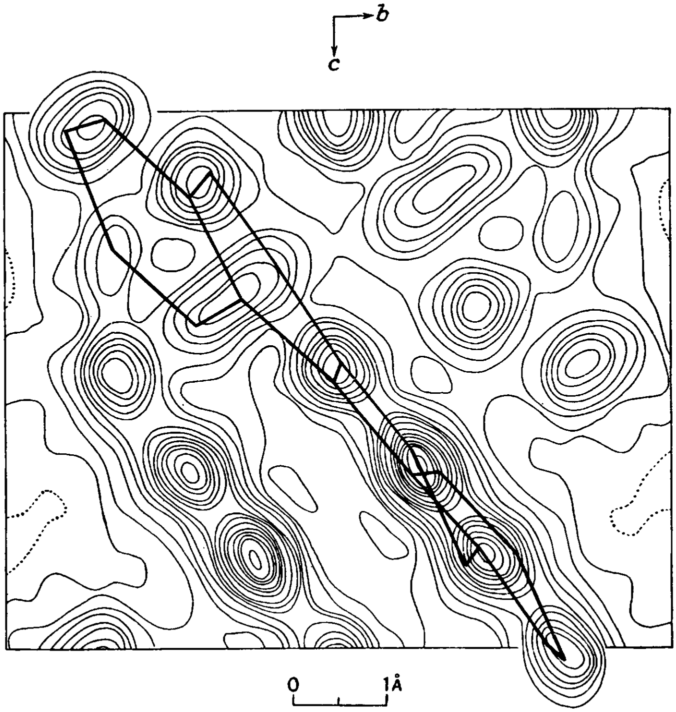


FIG. 4. *The electron-density projection on* (100).

A Fourier summation of 144 terms, out of 154 observed, was calculated at intervals of 120ths along *a* and *b* (Fig. 3). This projection shows that the molecule is not regular and probably not planar. By means of an adjustable wire model a non-planar molecular configuration was fitted to this projection, in which the mean plane of the molecule was inclined at about 45° to the projection plane. With the molecular reference point *O* located at $w_0 = 0{\cdot}25$, approximate *w* co-ordinates were obtained from this model, giving *R* factors for the 0*kl* and *h*0*l* zones of 0·42 and 0·34, respectively. Although the degree of overlap is smaller in the 0*kl* than in the *h*0*l* zone, the latter was refined first because of the smaller initial value of its *R* factor. After five difference syntheses *R*(*h*0*l*) had been reduced to 0·18; however, *R*(0*kl*) had risen to 0·47 and this set of *w* co-ordinates was therefore discarded.

Adjustment of the initial set of *w* co-ordinates produced a new molecular model which gave values of $R(0kl)$ and $R(h0l)$ of 0·26 and 0·30 for reflections up to $2 \sin \theta = 1·0$. Refinement of this model by difference syntheses on the $0kl$ reflections resulted after eight cycles in values for $R(0kl)$ and $R(h0l)$ of 0·023 and 0·26, at which point refinement ceased. The final Fourier projection on to (100), embodying 58 of the 62 observed $0kl$ structure factors, is shown in Fig. 4, and Table 1 lists the final $z$ co-ordinates in col. 4 and the spurious $z$ co-ordinates, derived from the $h0l$ zone only, in col. 5.

No attempt has been made to improve the rather high discrepancy factors (0·22, 0·23, and 0·26 in the $hk0$, $0kl$, and $h0l$ zones), which may be partly due to the exclusion of the hydrogen contributions from the calculated structure factors. That these contributions are not insignificant is shown by the appearance of a (001) projection obtained by one of us on $X$-RAC; this summation contains all observed $hk0$ structure factors, including the ten terms referred to above, whose signs were determined by means of the " negative-background criterion " (*e.g.*, Pepinsky, " Computing Methods and the Phase Problem in $X$-Ray Crystal Analysis," State College, Pa., 1952, p. 3). Although the carbon peaks are not significantly affected by these ten additional terms, the molecular outline is altered in the regions where hydrogen peaks may be expected. It is hoped later to refine this structure by a low-temperature technique whose usefulness as regards both accurate bond lengths and location of hydrogen atoms has been demonstrated in the structure of α-phenazine (Hirshfeld and Schmidt, *Acta Cryst.*, 1954, **7**, 129). In the meantime the general features of the crystal structure and of the molecular shape are quite clear on the basis of the present results.

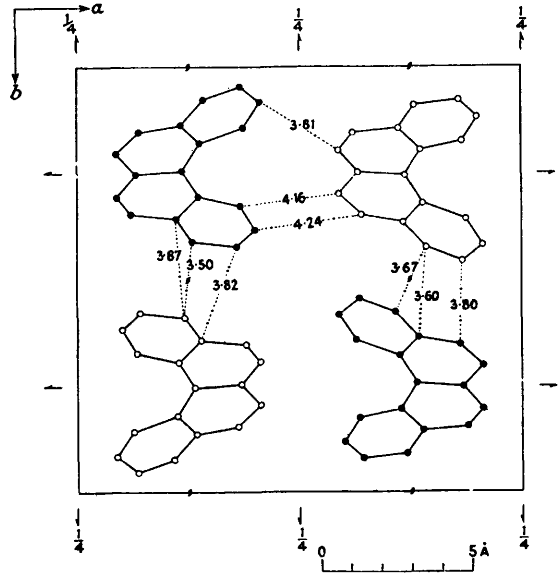


FIG. 5. *The projection of the unit-cell contents on* (001).

TABLE 1. *Experimentally-determined atomic co-ordinates* (*in* Å).

| Atom * | $x$ | $y$ | $z$ | Spurious $z$ co-ordinates | Atom * | $x$ | $y$ | $z$ | Spurious $z$ co-ordinates |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1·81 | 2·06 | 0·86 | 0·94 | 10 | 1·60 | 5·97 | 4·46 | 4·06 |
| 2 | 2·39 | 1·18 | 0·05 | −0·02 | 11 | 2·19 | 5·43 | 3·34 | 2·86 |
| 3 | 1·70 | 0·65 | −1·25 | −1·10 | 12 | 1·73 | 4·64 | 2·40 | 2·00 |
| 4 | 0·50 | 1·08 | −1·38 | −1·38 | 13 | 0·40 | 2·54 | 0·58 | 0·71 |
| 5 | −1·63 | 2·19 | −0·79 | −0·74 | 14 | −0·24 | 1·94 | −0·54 | −0·46 |
| 6 | −2·38 | 2·89 | 0·21 | 0·63 | 15 | 0·32 | 4·31 | 2·46 | 2·30 |
| 7 | −2·38 | 4·34 | 2·19 | 2·31 | 16 | −0·41 | 5·05 | 3·25 | 3·29 |
| 8 | −1·90 | 4·91 | 3·44 | 3·31 | 17 | −0·22 | 3·46 | 1·45 | 1·57 |
| 9 | 0·12 | 5·82 | 4·30 | 4·16 | 18 | −1·75 | 3·58 | 1·25 | 1·46 |

* Cf. Fig. 1 and footnote, p. 3303.

FIG. 6. *The projection of the unit-cell contents on* (100).

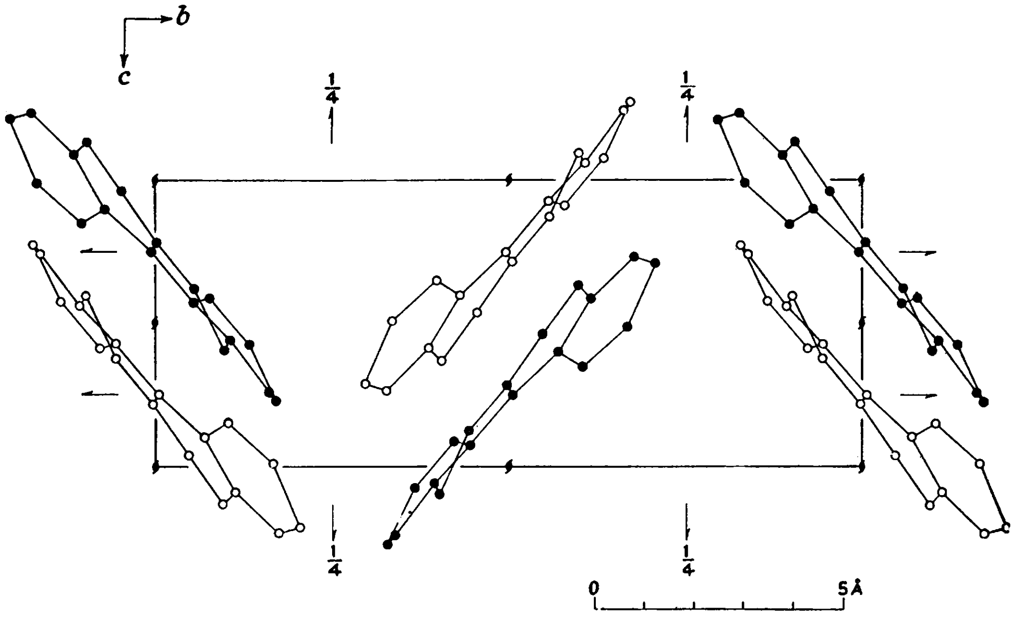


FIG. 7. *The projection of the unit-cell contents on* (010). *In the lower half of the projection two of the overlapping molecules have been omitted for greater clarity.*

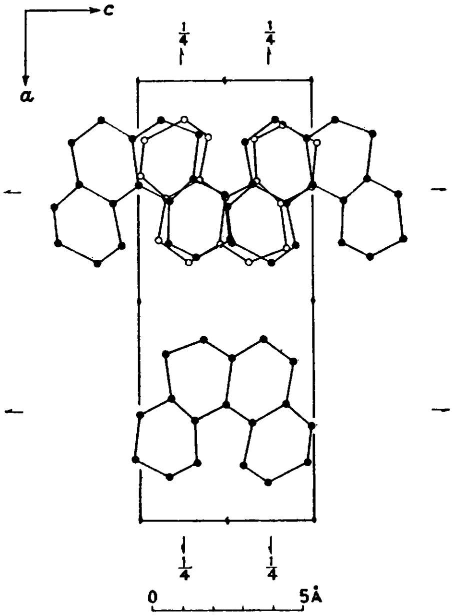
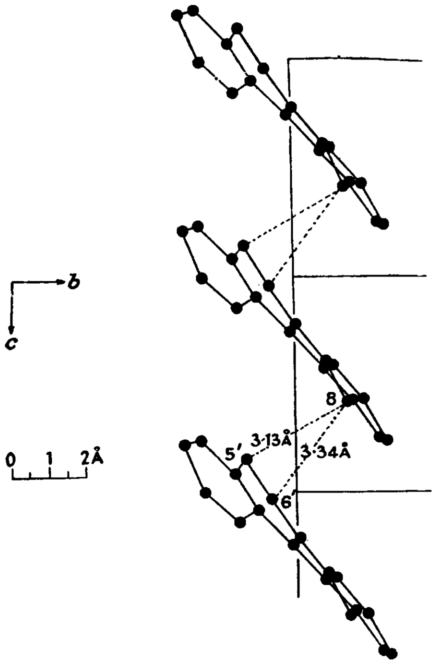


FIG. 8. *The molecular arrangement in one stack along* [001] *seen in the* (100) *projection, showing the short approach distances between neighbouring molecules.*



Despite the non-planarity of 3 : 4-benzophenanthrene, the packing arrangement of the molecule in the cell (Figs. 5—8) is similar to that observed in normal aromatic hydrocarbons such as coronene (Robertson and White, *J.*, 1945, 607). The molecules are arranged in stacks along the short axis of the unit cell; within each stack the molecules are parallel and inclined to this axis at about 40°, while the mean planes of molecules in different stacks, related by twofold screw axes, are nearly perpendicular.

A very similar arrangement has been postulated for 3 : 4-5 : 6-dibenzocarbazole (Iball, *Z. Krist.*, 1936, **95**, *A*, 282), an overcrowded molecule of the same general shape as 3 : 4-benzophenanthrene: *viz.*, $a = 14{\cdot}07$, $b = 6{\cdot}10$, $c = 15{\cdot}36$ Å. Space-group, $A2_122$; molecular symmetry, 2. There the situation is complicated by the appearance of extra reflections that indicate a superlattice with one axial length four times that of the main lattice. If these are ignored the packing of the molecules as deduced by Iball is seen to be identical with the arrangement, in space-group $B22_12$, to which 3 : 4-benzophenanthrene approximates. The similarity of the two structures is further emphasised by a general correspondence in the relative intensities of the low-angle spectra, allowance being made for the cyclic permutation of the crystallographic axes suggested by a comparison of the molecular orientations and axial lengths in the two crystals.

It is interesting that the packing in 3 : 4-benzophenanthrene, while approaching closely to the symmetry of $B22_12$, nevertheless deviates slightly from the arrangement of that more symmetrical space-group. Instead of an exact twofold axis parallel to [100] at $v = w = \frac{1}{4}$, the molecule has an approximate twofold axis inclined at about 7° to [100], with the geometric centre of the molecule located at $u = 0{\cdot}007$, $v = 0{\cdot}243$, $w = 0{\cdot}253$. This would appear to indicate that the lattice energy must be critically dependent on the precise disposition of the molecules in the cell; such a situation might be somewhat surprising were it not for certain short intermolecular contacts that also imply the presence of crystal forces unusual in fully aromatic hydrocarbons.

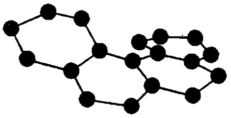


FIG. 9. *The molecular model viewed at about* 30° *to the twofold axis.*

Within each stack along [001], several pairs of atoms in successive molecules approach to within less than 3·7 Å (Table 2). The shortest intermolecular distances are between atoms 8 and 5′, which are 3·13 Å apart, and between atoms 8 and 6′, 3·34 Å apart. These close contacts are apparently related to an unusual valency structure of atoms 5 and 8, which will be discussed further below. The shortest contacts in the [100] direction are greater than those along [010] (Fig. 5); this probably indicates weaker binding forces in the [100] direction, in accordance with the observed cleavage of the crystals parallel to {100}.

TABLE 2. *Some short contact distances (in* Å*) between molecules separated by unit translation along the* c *axis.*

| Atoms | 8—5′ | 8—6′ | 16—5′ | 7—5′ | 16—14′ |
|---|---|---|---|---|---|
| Distance | 3·13 | 3·34 | 3·48 | 3·55 | 3·70 |

At the present stage of crystallographic refinement the following conclusions about the molecular shape are warranted. The centre-to-centre distance between the overcrowded carbon atoms 1 and 12 is 3·0 Å; 3 : 4-benzophenanthrene thus falls into line with previously-studied overcrowded compounds (see Part I, *loc. cit.*) as regards the minimum approach distance between non-bonded carbon atoms. The manner in which the molecule is distorted from planarity so as to achieve this separation between carbon atoms 1 and 12 may be seen in Fig. 9, which is a perspective view of a model based on the experimental co-ordinates. It is seen that rings *A* and *A′* are bent in opposite directions out of the mean plane of rings *B* and *B′*.

While the experimental co-ordinates do not conform precisely to the chemically-probable molecular symmetry 2, a molecule having exact twofold symmetry may be visualised, whose atomic co-ordinates, listed in Table 3, deviate from the experimental values by a root-mean-square difference of only 0·03 Å. This deviation is probably not significant, since structure factors calculated for the symmetrical model lead to *R* factors for the *hk*0, 0*kl*, and *h*0*l* zones of 0·23, 0·25, and 0·27, which are not much higher than for the experimental co-ordinates. Accordingly, in discussing the shape of the molecule and the manner in which it is deformed, we shall refer exclusively to the dimensions of the symmetrical model. On the assumption that the molecule does in fact possess symmetry 2, the observed deviations from this symmetry provide an estimate of the accuracy of the present analysis. Thus the experimental co-ordinates may be regarded as subject to a root-mean-square error of 0·05 Å, which is then also the root-mean-square error of the averaged bond lengths (except for bond 17—18, which occurs only once) shown in Fig. 10.

TABLE 3. *Atomic co-ordinates (in Å) adjusted to conform with molecular symmetry* 2.

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1·76 | 2·05 | 0·85 | 7 | −2·43 | 4·34 | 2·19 | 13 | 0·40 | 2·54 | 0·54 |
| 2 | 2·32 | 1·18 | 0·03 | 8 | −1·88 | 4·93 | 3·38 | 14 | −0·24 | 1·92 | −0·47 |
| 3 | 1·76 | 0·68 | −1·23 | 9 | 0·18 | 5·80 | 4·31 | 15 | 0·33 | 4·32 | 2·42 |
| 4 | 0·44 | 1·07 | −1·36 | 10 | 1·55 | 6·01 | 4·46 | 16 | −0·42 | 5·03 | 3·30 |
| 5 | −1·63 | 2·21 | −0·84 | 11 | 2·27 | 5·42 | 3·32 | 17 | −0·22 | 3·47 | 1·42 |
| 6 | −2·33 | 2·88 | 0·22 | 12 | 1·77 | 4·62 | 2·39 | 18 | −1·76 | 3·57 | 1·27 |

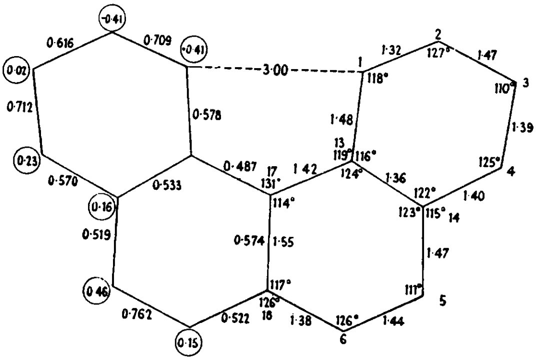


FIG. 10. *Dimensions of the symmetrical model fitted to the experimental co-ordinates. The bond lengths (in* Å*) and the bond angles are indicated on the right, the theoretical mobile bond orders (Berthier* et al., loc. cit.) *on the left. The circled figures are the distances of the atoms from a reference plane through atoms* 13, 15, 17, 18.

The most striking feature of this structure is the non-planarity of the " benzene " rings. Atoms 1, 2, 3, 4, 14, 13, constituting ring *A*, deviate from the best plane through these atoms by a root-mean-square distance of over 0·05 Å and a maximum of 0·08 Å, the deviations being systematic so that the ring may be regarded as folded, through an angle of 10°, along the diagonal joining atoms 3 and 13. The distortion of ring *B* is even greater, its atoms deviating from their best plane by a root-mean-square distance of 0·08 Å and a maximum of 0·10 Å. Here again the principal mode of deformation consists in a folding of the ring, through an angle of 14° along the diagonal 5—17. It seems certain that this folding of rings *A* and *B*, together with the corresponding folding of the symmetry-related rings *A'* and *B'*, accounts for most of the distortion of the molecular skeleton by which relief from overcrowding is achieved. Any other deformations of the skeleton appear to be of secondary importance, atoms 1, 2, 3, 4 being coplanar to within a root-mean-square deviation of 0·02 Å, while the groups comprising atoms 3, 4, 14, 5, 17, 13 and atoms 5, 6, 18, 7, 8, 17 are each planar to within a root-mean-square deviation of 0·04 Å.

The molecular properties likely to be affected by the distortions of the aromatic system include resonance energy, dipole moment, valency structure, and chemical reactivity; these will be discussed in turn.

The results of calculations, by the method of molecular orbitals, of theoretical resonance energies of all four-ring aromatic hydrocarbons $C_{18}H_{12}$ (Berthier, Coulson, Greenwood, and A. Pullman, *Compt. rend.*, 1948, **226**, 1906) are quoted in Table 4. The computations, for planar molecules, were made both with and without allowance for overlap between adjacent atomic orbitals, the results being given in terms of the empirical constants γ and β respectively. The corresponding experimental values have been determined by Magnus and Becker (*Erdöl und Kohle*, 1951, **4**, 115). By combining the theoretical and experimental results for all these compounds except 3 : 4-benzophenanthrene, we obtain values for γ and β of 37·64 ± 1·0 kcal./mole and 18·61 ± 0·15 kcal./mole, respectively. The resonance energy per mole of the planar model of 3 : 4-benzophenanthrene is thus calculated as 134·9 ± 3·5 kcal., from γ, or 133·8 ± 1·1 kcal., from β; both values are greater than the experimental value of 127·7 kcal. The energy defect of 6 or 7 kcal. must be related to the energy of intramolecular repulsion, neglected in the theoretical calculations, and to the deformation of the hypothetically-planar ring system.

TABLE 4. *Comparison of experimental and theoretical resonance energies of all four-ring aromatic hydrocarbons* $C_{18}H_{12}$.

| Compound | Exptl. resonance energy (kcal./mole) * | Quantum-mechanical resonance energy : † with overlap (γ) | Quantum-mechanical resonance energy : † without overlap (β) | γ ‡ (kcal./mole) | β ‡ (kcal./mole) | Quantum-mechanical resonance energy : γ = 37·64 | Quantum-mechanical resonance energy : β = 18·61 |
|---|---|---|---|---|---|---|---|
| 3 : 4-Benzophenanthrene | 127·7 | 3·5840 | 7·1874 | 35·63 | 17·77 | 134·9 | 133·8 |
| Tetracene .................. | 129·6 | 3·3400 | 6·9316 | 38·80 | 18·70 | 125·7 | 129·0 |
| 1 : 2-Benzanthracene ... | 130·4 | 3·5027 | 7·1012 | 37·23 | 18·36 | 131·8 | 132·2 |
| Chrysene .................. | 134·4 | 3·5872 | 7·1900 | 37·47 | 18·69 | 135·0 | 133·8 |
| Triphenylene ........... | 135·8 | 3·6658 | 7·2745 | 37·05 | 18·67 | 138·0 | 135·4 |

* Magnus and Becker, *loc. cit.* † Berthier *et al.*, *loc. cit.*

‡ Values derived from comparison of corresponding experimental and theoretical resonance energies.

The dipole moment of 3 : 4-benzophenanthrene has been reported as 0·7 D (Bergmann, Fischer, and B. Pullman, *J. Chim. phys.*, 1951, **48**, 356). The major contribution to this moment probably comes from the dipoles of the C–H bonds, which do not cancel in the deformed structure as they would in a regular planar molecule.

The folding of the rings is reflected in the abnormal bond angles at the carbon atoms on the axes of fold; the bond angles at the secondary atoms 3 and 5 are 110° and 111°, while the corresponding angles at the tertiary carbon atoms 13 and 17 are 116° and 114°. Although the individual values may not be too reliable, it is significant that they all deviate in the same direction from the trigonal bond angle of 120° and that those at the secondary carbon atoms approach the tetrahedral angle of 109½°. Thus it appears that the valency electrons of these secondary atoms do not occupy pure $(sp^2)p$ orbitals, appropriate to a planar aromatic structure, but more nearly approximate to the tetrahedral $sp^3$ hybridisation. This must imply an enhanced localisation of the π electrons that these atoms contribute to the aromatic system and may be expressed in a greater polarisability than would be expected in an undeformed molecule. Whether or not this localisation involves a decoupling of the electron spins should be deducible from magnetic data, which are unfortunately not available. A knowledge of the hydrogen positions would be of considerable value in specifying more exactly the type of hybridisation present.

The increased free valence that may be expected to accompany the apparent shift towards tetrahedral hybridisation probably accounts for the short approach distance between atoms 5 and 8 of neighbouring molecules in the crystal, which may indicate a tendency towards additional bond formation on the part of these " unsaturated " atoms. On the basis of the co-ordinates of the symmetrical model it is found that the line joining atoms 5 and 8 of neighbouring molecules makes, at one end, angles of 85° and 112° with bonds 5–6 and 5–14 respectively and, at the other end, angles of 94° and 91° with bonds 8–7 and 8–16 respectively.

The known chemical properties of 3 : 4-benzophenanthrene support the above view of the valency structure since the increased availability of negative charge at the distorted carbon atoms provides an explanation for the preferential substitution at the 5-position by bromine, nitric acid, and the Friedel–Crafts reagent (Newman and Kosak, *J. Org. Chem.*, 1949, **14**, 375). Also the tetrahedral hybridisation already evident at the reactive carbon atom in the unperturbed molecule would favour the formation of the activated complex, in which, supposedly, the entering substituent and the outgoing hydrogen are simultaneously bound to this carbon atom in a tetrahedral arrangement (*e.g.*, Waters, *J.*, 1948, 727). We

TABLE 5. *List of observed and calculated structure factors.*

(*a*) F(*hk*0) referred to origin (¼00).

| *hk*0 | $F_o$ | $F_c$ * |
|---|---|---|
| 200 | 67 † | 102 |
| 4 | 49 | −48 |
| 6 | 61 | 63 |
| 8 | 51 | 63 |
| 10 | 5 | 5 |
| 12 | 7 | − 9 |
| 14 | 12 | −13 |
| 16 | 4 | − 4 |
| 020 | 56 | −69 |
| 4 | 56 | −60 |
| 6 | 0 | 2 |
| 8 | 16 | −14 |
| 10 | 12 | −12 |
| 12 | 13 | 13 |
| 14 | 4 | 3 |
| 16 | 5 | 2− |
| 18 | 9 | −13 |
| 110 | 9 | 6 |
| 2 | 12 | 11 |
| 3 | 6 | − 3 |
| 4 | 16 | −16 |
| 5 | 0 | 0 |
| 6 | 4 | − 4 |
| 7 | 4 | − 5 |
| 8 | 4 | 4 |
| 9 | 0 | − 5 |
| 10 | 6 | − 6 |
| 11 | 2 | − 1 |
| 12 | 0 | − 4 |
| 13 | 3 | − 5 |
| 14 | 5 | 3 |
| 120 | 9 | − 5 |
| 2 | 17 | −20 |
| 3 | 2 | 0− |
| 4 | 3 | 2 |
| 5 | 5 | − 4 |
| 6 | 21 | −23 |
| 7 | 18 | −17 |
| 8 | 17 | −13 |
| 9 | 11 | − 9 |
| 10 | 0 | 1 |
| 11 | 0 | 4 |
| 12 | 3 | 1+ |
| 13 | 4 | 5 |
| 14 | 7 | 1+ |
| 15 | 4 | 4 |
| 130 | 13 | 14 |
| 2 | 68 | −77 |
| 3 | 20 | −16 |
| 4 | 16 | 13 |
| 5 | 7 | − 5 |
| 6 | 19 | 23 |
| 7 | 9 | 9 |
| 8 | 11 | −14 |
| 9 | 8 | − 2− |
| 10,30 | 3 | − 5 |
| 11 | 5 | − 8 |
| 12 | 0 | − 2 |
| 13 | 0 | − 1 |
| 14 | 4 | − 3 |
| 15 | 0 | 1 |
| 16 | 3 | 5 |
| 140 | 15 | −11 |
| 2 | 24 | −20 |
| 3 | 11 | − 8 |
| 4 | 13 | 10 |
| 5 | 9 | 2− |
| 6 | 12 | −12 |
| 7 | 0 | − 3 |
| 8 | 13 | −15 |
| 9 | 8 | − 1+ |
| 10 | 0 | 2 |
| 11 | 2 | − 2 |
| 12 | 3 | 4 |
| 150 | 0 | 22 |
| 2 | 15 | −13 |
| 3 | 2 | 3 |
| 4 | 6 | − 9 |
| 5 | 0 | − 2 |
| 6 | 5 | − 4 |
| 7 | 0 | 2 |
| 8 | 3 | − 3 |
| 160 | 5 | − 5 |
| 2 | 4 | − 3 |
| 3 | 7 | − 3− |
| 4 | 15 | −11 |
| 5 | 2 | 5 |
| 6 | 6 | − 6 |
| 7 | 4 | 2 |
| 8 | 5 | 4 |
| 9 | 6 | 1− |
| 10 | 5 | − 2− |
| 11 | 6 | 1− |
| 12 | 10 | − 8 |
| 170 | 5 | 3 |
| 2 | 6 | 1+ |
| 3 | 7 | 10 |
| 4 | 24 | −23 |
| 5 | 7 | − 7 |
| 6 | 6 | − 4 |
| 7 | 4 | − 1+ |
| 8 | 2 | 5 |
| 9 | 13 | 18 |
| 10 | 17 | −18 |
| 11 | 9 | 9 |
| 12 | 12 | −12 |
| 13 | 0 | − 1 |
| 14 | 0 | 4 |
| 15 | 0 | 4 |
| 16 | 0 | − 1 |
| 17 | 3 | 6 |
| 180 | 9 | − 8 |
| 2 | 0 | 1 |
| 3 | 6 | −10 |
| 4 | 0 | 4 |
| 5 | 0 | 2 |
| 6 | 0 | − 3 |
| 7 | 0 | 1 |
| 8 | 7 | 6 |
| 9 | 10 | −10 |
| 10 | 7 | 3 |
| 11 | 3 | − 6 |
| 12 | 0 | − 2 |
| 13 | 2 | 1+ |
| 14 | 3 | 7 |
| 15 | 0 | − 2 |
| 16 | 3 | 6 |
| 190 | 8 | − 8 |
| 2 | 20 | 15 |
| 3 | 0 | − 3 |
| 4 | 27 | 24 |
| 5 | 0 | 0 |
| 6 | 13 | 12 |
| 7 | 0 | − 2 |
| 8 | 11 | 10 |
| 9 | 0 | − 1 |
| 10 | 17 | 21 |
| 11 | 0 | 1 |
| 12 | 13 | 17 |
| 13 | 0 | 1 |
| 14 | 5 | 6 |
| 15 | 0 | 2 |
| 16 | 4 | 4 |
| 1,10,0 | 3 | 3 |
| 2 | 12 | − 9 |
| 3 | 5 | − 4 |
| 4 | 12 | 11 |
| 5 | 0 | 1 |
| 6 | 13 | 13 |
| 7 | 17 | 20 |
| 8 | 14 | −16 |
| 9 | 5 | 7 |
| 10 | 6 | − 9 |
| 11 | 6 | − 7 |
| 12 | 12 | 14 |
| 13 | 3 | 3 |
| 14 | 3 | 4 |
| 15 | 5 | 9 |
| 1,11,0 | 12 | −12 |
| 2 | 0 | 0 |
| 3 | 0 | 2 |
| 4 | 6 | − 6 |
| 5 | 4 | 6 |
| 6 | 0 | 2 |
| 7 | 6 | − 7 |
| 8 | 0 | 1 |
| 9 | 11 | −13 |
| 10 | 8 | − 9 |
| 11 | 2 | − 5 |
| 12 | 3 | − 2 |
| 1,12,0 | 7 | 5 |
| 2 | 11 | 8 |
| 3 | 7 | 5 |
| 4 | 0 | − 1 |
| 5 | 3 | − 3 |
| 6 | 3 | − 2 |
| 7 | 3 | − 1− |
| 8 | 5 | 7 |
| 9 | 6 | 7 |
| 10 | 2 | 6 |
| 11 | 0 | 3 |
| 12 | 3 | − 5 |
| 13 | 4 | − 4 |
| 14 | 2 | − 4 |
| 1,13,0 | 6 | 4 |
| 2 | 0 | − 2 |
| 3 | 0 | − 2 |
| 4 | 0 | 0 |
| 5 | 5 | 5 |
| 6 | 5 | 6 |
| 7 | 2 | 3 |
| 8 | 5 | − 7 |
| 9 | 4 | − 5 |
| 1,14,0 | 0 | − 1 |
| 2 | 0 | 1 |
| 3 | 0 | 2 |
| 4 | 0 | 1 |
| 5 | 0 | 1 |
| 6 | 0 | 1 |
| 7 | 7 | − 8 |
| 8 | 0 | − 1 |
| 9 | 3 | − 5 |
| 1,15,0 | 0 | 1 |
| 2 | 0 | 1 |
| 3 | 0 | − 2 |
| 4 | 0 | 2 |
| 5 | 0 | − 2 |
| 6 | 0 | − 1 |
| 7 | 0 | 2 |
| 8 | 2 | 1 |
| 9 | 0 | 1 |
| 10 | 3 | 3 |
| 1,16,0 | 2 | − 2 |
| 2 | 2 | 2 |
| 3 | 0 | 0 |
| 4 | 3 | 4 |
| 5 | 2 | 2 |
| 1,17,0 | 0 | 1 |
| 2 | 0 | 1 |
| 3 | 9 | 11 |
| 4 | 0 | − 1 |
| 5 | 4 | 5 |
| 1,18,0 | 0 | 0 |
| 2 | 6 | − 6 |

* Signs determined on *X*-RAC by means of the " negative-background criterion."
† Presumed secondary-extinction error.

TABLE 5. (*Continued.*)

(*b*) F(0*kl*) referred to origin (0¼0).

| 0*kl* | Fo | Fc | 0*kl* | Fo | Fc | 0*kl* | Fo | Fc | 0*kl* | Fo | Fc |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 002 | 13 | −11 | 012 | 8 | −10 | 073 | 0 | 1 | 015 | 10 | 15 |
| 4 | 0 | 3 | 2 | 20 | 20 | 8 | 6 | −10 | 2 | 3 | 7 |
| 6 | 12 | −20 | 3 | 11 | 10 | 9 | 18 | −16 | 3 | 0 | − 4 |
| | | | 4 | 23 | −24 | 10 | 8 | 5 | 4 | 0 | 1 |
| | | | 5 | 35 | 34 | 11 | 11 | − 9 | 5 | 8 | 6 |
| 011 | 0 | − 2 | 6 | 43 | −40 | 12 | 8 | 5 | | | |
| 2 | 10 | 13 | 7 | 26 | 26 | | | | 016 | 0 | − 2 |
| 3 | 8 | −11 | 8 | 9 | − 5 | | | | 2 | 3 | − 6 |
| 4 | 14 | − 5 | 9 | 3 | − 3 | 014 | 0 | − 2 | 3 | 0 | 1 |
| 5 | 25 | 18 | 10 | 8 | −13 | 2 | 12 | −15 | 4 | 3 | 4 |
| 6 | 27 | −23 | 11 | 18 | −18 | 3 | 5 | − 2 | 5 | 0 | − 1 |
| 7 | 6 | 7 | 12 | 9 | −12 | 4 | 15 | 17 | 6 | 0 | − 1 |
| 8 | 9 | 11 | 13 | 6 | − 9 | 5 | 14 | 19 | 7 | 0 | 1 |
| 9 | 0 | − 1 | | | | 6 | 30 | 37 | 8 | 0 | 1 |
| 10 | 4 | 1 | | | | 7 | 14 | 15 | 9 | 4 | 2 |
| 11 | 8 | 6 | 013 | 10 | −11 | 8 | 0 | − 2 | | | |
| 12 | 0 | 1 | 2 | 2 | 4 | 9 | 9 | − 4 | 017 | 0 | 5 |
| 13 | 0 | − 1 | 3 | 7 | 6 | 10 | 0 | − 4 | 2 | 0 | 2 |
| 14 | 8 | 8 | 4 | 10 | − 7 | 11 | 8 | − 8 | 3 | 0 | − 2 |
| 15 | 5 | − 5 | 5 | 10 | 8 | 12 | 11 | 7 | 4 | 0 | 2 |
| | | | 6 | 8 | − 5 | 13 | 7 | − 6 | 5 | 5 | −10 |

(*c*) F(*h*0*l*) referred to origin (00¼).

| *h*0*l* | Fo | Fc | *h*0*l* | Fo | Fc | *h*0*l* | Fo | Fc | *h*0*l* | Fo | Fc |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 101 | 24 | 24 | 402 | 7 | 2 | 803 | 0 | 3 | 105 | 3 | 7 |
| 2 | 3 | − 2 | 5 | 0 | 1 | 9 | 20 | 20 | 2 | 5 | − 4 |
| 3 | 8 | −13 | 6 | 16 | 19 | 10 | 0 | − 2 | 3 | 6 | − 7 |
| 4 | 0 | − 2 | 7 | 0 | − 5 | 11 | 25 | −28 | | | |
| 5 | 7 | − 9 | 8 | 11 | 16 | 12 | 0 | − 1 | 106 | 0 | 1 |
| 6 | 8 | − 7 | 9 | 5 | − 7 | 13 | 6 | 6 | 2 | 11 | −10 |
| 7 | 4 | − 4 | 10 | 15 | −16 | | | | 3 | 0 | 3 |
| 8 | 6 | 6 | 11 | 6 | 9 | 104 | 0 | − 5 | 4 | 9 | 5 |
| 9 | 0 | 2 | | | | 2 | 0 | − 5 | | | |
| 10 | 0 | 1 | 103 | 19 | 19 | 3 | 6 | − 7 | | | |
| 11 | 5 | 1 | 2 | 2 | − 9 | 4 | 0 | 7 | 506 | 0 | 2 |
| | | | 3 | 46 | −42 | 5 | 0 | 0 | 6 | 3 | − 5 |
| | | | 4 | 4 | − 2 | 6 | 0 | − 3 | 7 | 0 | − 1 |
| 102 | 4 | − 2 | 5 | 28 | 19 | 7 | 0 | 2 | 8 | 3 | 6 |
| 2 | 36 | −27 | 6 | 0 | 4 | 8 | 0 | − 1 | | | |
| 3 | 3 | 9 | 7 | 0 | 3 | 9 | 8 | 5 | | | |

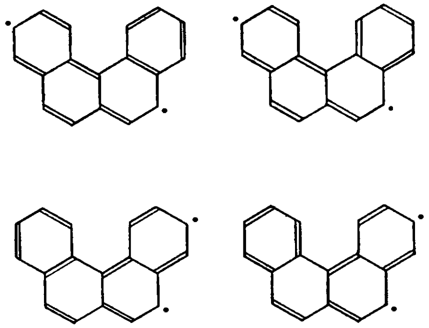
prefer this explanation to the one based on an analogy with the reactivity of phenanthrene at the 9-position, which would in any case not account for the preferential attack on the 5- rather than the 6-position in 3 : 4-benzophenanthrene. Two disubstitution products were also found in the nitration reaction but their constitution was not investigated further. Unless primary substitution fundamentally changes the structure of the molecule we should expect, on the above arguments, that the second substituent has entered at the 8-, 3-, or 10-position.

Although the present bond-length measurements are not sufficiently accurate to warrant detailed analysis, their general tendency is in accord with the proposed interpretation of the molecular valency structure. Some idea of the bond lengths to be expected on this hypothesis may be derived from a consideration of the eight biradical structures (Fig. 11) suggested by the tetrahedral bond angles at atoms 3, 5, 8, and 10. Although there is no evidence that the molecule is, in fact, a biradical, we should expect similar bond-length variations to occur even if the electron spins are not uncoupled since there are one Dewar long-bond and two ionic structures corresponding, in the distribution of single and double bonds, with each of the proposed biradical structures and these would probably contribute strongly, along with the eight Kekulé-type structures, to the resultant bond structure of a molecule with no unpaired electrons. Thus, the length of the central 17–18 bond, which is certainly exaggerated by the present data, is partly explained by the fact that it appears single in all the suggested non-Kekulé formulæ, as does bond 5–14, whose measured length is 1·47 Å. These formulæ would also indicate three-fourths double-bond character for bond 1–2, measured as 1·32 Å long. It may also be significant that bond 5–6, with a measured length of 1·44 Å despite its theoretical mobile-bond order of 0·762 calculated by Berthier *et al.* (*loc. cit.*), for a planar molecule, appears as a double bond in just half the biradical, or pseudo-biradical, formulæ under consideration. Thus the measured bond lengths, insofar as they are reliable, seem generally consistent with the other evidence as to the type of electronic structure to be associated with the distorted benzophenanthrene molecule.

The conclusions reached here provide a coherent interpretation of the known physical and chemical properties of 3 : 4-benzophenanthrene, as well as indicating several directions in which further work is needed. On the crystallographic side, comparison of these results with the analysis of the crystal structure of 5 : 4′-dimethyl-3 : 4-benzophenanthrene, which is already well under way, will be of particular interest.

The crystallographic evidence indicates resolution of 3 : 4-benzophenanthrene into (+)- and (−)-crystals. We have not yet succeeded in growing crystals either of large enough size or with sufficiently well-developed *hkl* faces to take advantage of this spontaneous resolution for the measurement of the optical activity of 3 : 4-benzophenanthrene; experiments in this direction are in progress.

FIG. 11. *Four of the eight biradical formulæ suggested by the tetrahedral bond configurations. The remaining four are related to these by the operation of the molecular two-fold axis of symmetry.*



*Experimental.*—Good crystals of 3 : 4-benzophenanthrene can be obtained by slow cooling of a solution in ethanol. They are colourless needles, elongated along [001], whose most prominent faces are {100} and {010}, with {110} and {011} frequently present. The crystals show a cleavage plane parallel to {100}.

All zonal reflections obtainable with Cu-*K*α radiation were recorded on Weissenberg photographs about the three principal axes, and their intensities measured visually by comparison with a series of standard spots. The roughly cylindrical outline of the crystals made spot-shape and absorption corrections in the *hk*0 zone unnecessary; for photographs about the [100] and [010] axes, a crystal was cut to approximately cubic shape. The absolute scale, originally estimated by Wilson's statistical method (*Nature*, 1942, **150**, 151), was later found, on comparison with the scale of the final calculated structure factors, to be about 10% higher in F(*hkl*) that the scale originally adopted. The accuracy of the observed structure factors is thought to be of the order of 10%.

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