Calculated Bond Lengths in Some Cyclic Compounds. Part II. Benzanthrone, Acedianthrone, and Flavanthrone.*

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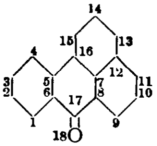
With the help of the methods developed in Part I the energy levels, bond orders, and bond lengths in benzanthrone, acedianthrone, and flavanthrone have been deduced by the molecular-orbital method. Bond orders and bond lengths in benzanthrone have also been derived by the two simple valence-bond approximations of the previous paper. For the second and the third compound the observed and the calculated interatomic distances agree very satisfactorily within the experimental uncertainty except for a very few bonds. The crystallographic examination of benzanthrone is not yet complete but the present calculations have been used in suggesting refinements.

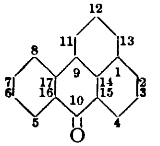
In this paper the methods of calculation developed in Part I have been applied to benzanthrone (I), acedianthrone (IV), and flavanthrone (V). Experimental and calculated bond lengths have already been compared for acedianthrone by Friedlander, Goodwin, and Robertson (*Acta Cryst.*, 1954, **7**, 127) without noting the assumed parameters or the energy levels, the bond orders or the electron distribution. For flavanthrone the crystal structure has been described by Stadler (*ibid.*, 1953, **6**, 540). The crystallographic examination of benzanthrone is not yet complete but the present calculations have already been of assistance in the refinement of the projection along one axis.

Benzanthrone

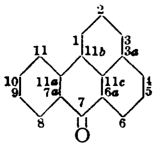
Molecular-orbital Method.—The secular equations of benzanthrone (I), $C_{17}H_{10}O$, with its eighteen π-electrons, were set up in the ordinary way using the following parameters: Coulomb integrals for carbon $= \alpha$, for oxygen $= \alpha + \beta$; exchange integrals between neighbouring carbon atoms $= \beta$, between neighbouring C and O atoms $= 2\beta$, between all other pairs of atoms $= 0$; overlap integrals $= 0$. They lead to an eighteenth-order secular determinant which cannot readily be factorised but which, when treated by the methods indicated in Part I, yields first the energy levels E_i listed in Table 1, then the electron distribution (q) noted in Table 2, and finally the bond orders (p_{12}) and the bond lengths L_1 and L_2 of Table 3. The values L_1 and L_2 were derived from the correlation curves *DGBE* and *DQCE* forming Fig. 1 of Part I.



(I*a*) (Numbering used for mathematical calculations.)



(I*b*) (Numbering based on anthracene)



(I*c*) (Ring Index No. 2812.)

TABLE 1. *Molecular-orbital energy levels for benzanthrone in order of increasing energy.*

i	E_i	i	E_i	i	E_i	i	E_i
1	$\alpha + 2{\cdot}9928\beta$	6	$\alpha + \beta$	11	$\alpha - 0{\cdot}8693\beta$	15	$\alpha - 1{\cdot}5718\beta$
2	$\alpha + 2{\cdot}3125\beta$	7	$\alpha + \beta$	12	$\alpha - \beta$	16	$\alpha - 1{\cdot}9654\beta$
3	$\alpha + 2{\cdot}0439\beta$	8	$\alpha + \beta$	13	$\alpha - \beta$	17	$\alpha - 2{\cdot}1270\beta$
4	$\alpha + 1{\cdot}6212\beta$	9	$\alpha + 0{\cdot}5534\beta$	14	$\alpha - 1{\cdot}3446\beta$	18	$\alpha - 2{\cdot}6523\beta$
5	$\alpha + 1{\cdot}40349\beta$	10	$\alpha - 0{\cdot}3968\beta$				

Valence-bond Methods.—Again, by using techniques described in Part I, the bond orders

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* Part I, preceding paper.

p_3 and p_4 were evaluated by valence-bond approximations and the corresponding bond lengths L_3 and L_4 were obtained from the curves of Fig. 2 of that reference. These results have also been included in Table 3.

TABLE 2. *Electron distribution* (q) *in benzanthrone* (*molecular-orbital method*).

Atom, numbered according to :				Atom, numbered according to :				Atom, numbered according to :			
(I*a*)	(I*b*)	(I*c*)	*q*	(I*a*)	(I*b*)	(I*c*)	*q*	(I*a*)	(I*b*)	(I*c*)	*q*
1	5	8	0·973	7	14	11*c*	0·991	13	13	3	0·978
2	6	9	1·002	8	15	6*a*	1·032	14	12	2	0·998
3	7	10	0·979	9	4	6	0·964	15	11	1	0·967
4	8	11	0·992	10	3	5	1·010	16	9	11*b*	0·986
5	17	11*a*	0·960	11	2	4	0·967	17	10	7	0·830
6	16	7*a*	1·024	12	1	3*a*	1·001	18*	O	O	1·345

* Oxygen.

TABLE 3. *Mobile bond orders* (p) *and bond lengths* (L) *in benzanthrone.*

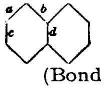
Bond, numbered according to :			Molecular-orbital method			Valence-bond methods			
						Method 1		Method 2	
(I*a*)	(I*b*)	(I*c*)	p_{12}	L_1	L_2	p_3	L_3	p_4	L_4
1–2	5–6	8–9	0·668	1·390	1·386	0·50	1·39	0·50	1·379
1–6	5–16	7*a*–8	0·638	1·397	1·394			0·44	1·387
2–3	6–7	9–10	0·649	1·394	1·391			0·43	1·389
3–4	7–8	10–11	0·673	1·389	1·384			0·52	1·377
4–5	8–17	11–11*a*	0·600	1·404	1·406			0·41	1·391
5–6	16–17	7*a*–11*a*	0·573	1·411	1·416			0·35	1·403
5–16	9–17	11*a*–11*b*	0·372	1·454	1·479	0	1·50	0·13	1·468
6–17	10–16	7–7*a*	0·321	1·463	1·484			0	1·50
7–8	14–15	6*a*–11*c*	0·561	1·413	1·420	0·33	1·42	0·39	1·395
7–12	1–14	3*a*–11*c*	0·533	1·420	1·431			0·17	1·455
7–16	9–14	11*b*–11*c*	0·507	1·426	1·440			0·31	1·413
8–9	4–15	6–6*a*	0·684	1·387	1·381	0·67	1·37	0·46	1·384
8–17	10–15	6*a*–7	0·303	1·466	1·486	0	1·50	0	1·50
9–10	3–4	5–6	0·627	1·399	1·397	0·33	1·42	0·41	1·391
10–11	2–3	4–5	0·723	1·379	1·374	0·67	1·37	0·48	1·382
11–12	1–2	3*a*–4	0·558	1·414	1·421	0·33	1·42	0·35	1·403
12–13	1–13	3–3*a*	0·551	1·416	1·423			0·41	1·391
13–14	12–13	2–3	0·709	1·382	1·376	0·67	1·37	0·43	1·389
14–15	11–12	1–2	0·616	1·401	1·400	0·33	1·42	0·46	1·384
15–16	9–11	1–11*b*	0·642	1·395	1·392	0·67	1·37	0·41	1·391
17–18 *	10–O	7–O	*0·884*	*1·188*	*1·188*	*1·00*	*1·185*	*1·00*	*1·185*

* Oxygen.

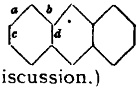
Discussion.—The discussion of accuracies in the preceding paper (p. 1688) shows that the molecular-orbital calculation of bond length ought to be accurate to ±0·03 Å, except perhaps for the bonds attached to carbonyl carbon. Three decimal places are given for bond orders and bond lengths simply to permit their more accurate use in subsequent work.

For benzanthrone the results obtained by the molecular-orbital method (either curve : the figures quoted below refer to *DQCE*) may be regarded as satisfactory pending completion of *X*-ray measurements. The bonds 5–16, 6–17, and 8–17, which are all single bonds on the first valence-bond approximation, are found to be 1·479, 1·484, and 1·486 Å respectively. These are greater than the characteristic length of *ca.* 1·39 Å found in aromatic compounds and shorter than pure single bonds, but virtually identical with the 1–2 bond in *p*-benzoquinone (see Part I, p. 1686). These results therefore represent an acceptable compromise between the wholly aromatic character of the compound and the general importance of structures of the Kekulé type in explaining the properties of condensed ring compounds.

(II)



(III)



(Bond symbolism used in the discussion.)

Bonds 5–6, 7–8, 7–12, and 7–16, the internal bonds, vary from 1·416 to 1·440 Å, being of the same order as the internal bonds *d* of naphthalene (II) and anthracene (III). The remaining twelve peripheral bonds vary from 1·374 to 1·423 Å though only three exceed

1·400 Å; there is no marked classification into links of the types *a*, *b*, and *c* of naphthalene and anthracene, which show significant differences in the Table in Part I. It is true that there is an alternation in the lengths of the peripheral bonds in the chains between atoms 5 and 6, 8 and 12, and 12 and 16, but the differences are very small and of doubtful significance in view of the coarseness of the fundamental approximations: further, two " long " bonds meet at atom 12.

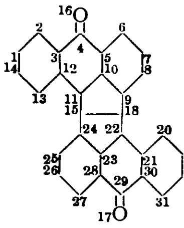
There is a marked alternation of electron density from atom 1 to atom 18 (Table 2), thus illustrating the law of alternating polarity pointed out by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **192**, 16) for hetero-molecules; the sequence of numbering the atoms for the calculations emphasises the alternation. The chemistry, however, does not point to any marked concentration or deficiency of electrons anywhere in the molecule though it seems that anionic and cationic reagents are respectively rather more active at atoms 9 and 13; these, however, both appear, from the calculations, to be electron-deficient atoms.

Of the two valence-bond approximations the first is particularly inadequate and the second, though a marked improvement, still suffers from the deficiencies inherent in the method. It was attempted solely to try to circumvent the difficulty that the first, although generally leading to reasonable predictions of order and length, requires that in benzanthrone (and all aromatic quinones) some of the bonds shall be regarded as pure single bonds. It did not seem worth while to attempt the more rigorous full application of the valence-bond method (*e.g.*, Wheland and Pauling, *J. Chem. Phys.*, 1933, **1**, 362; Sherman, *ibid.*, 1934, **2**, 488) to this compound.

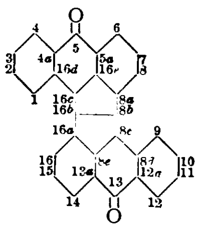
The crystallographic examination of benzanthrone has proved unusually difficult but is now well advanced. The calculations given above have been used in carrying out the refinement of the first zone as follows. At a certain stage the atoms were located approximately. There are three characteristic bond directions at 120° to each other in the molecule. The ratios of the projected to the predicted bond lengths in each of these directions were calculated. Three atoms (numbered 10, 16, and 17) were involved in bonds giving anomalous ratios and it was possible to suggest the directions and amounts by which they should be displaced to improve the ratios substantially. These deductions were excellently confirmed by a difference $(F_o - F_c)$ synthesis and are now being applied in seeking further refinements.

ACEDIANTHRONE

Acedianthrone (IV) has thirty-two π-electrons in a centrosymmetrical molecule; the thirty-second order secular determinant of the molecular-orbital method therefore factorises at once into two sixteenth-order ones according as $c^i_r = \pm c^i_{33-r}$. The values assumed for the various integrals were the same as for benzanthrone and, by using the methods of expansion and solution given in Part I, the energy levels were obtained which are listed in Table 4 in order of increasing energy, the symbols S and A indicating respectively the symmetry and antisymmetry of the molecular orbitals and hence the need for the + and − signs relating c^i_r and c^i_{33-r}. Table 5 gives the electron distribution in acedianthrone, while Table 6 gives for the twenty symmetrically independent bonds their mobile orders p_{12}, their lengths L_1 and L_2 derived from these by use of the curves *DGBE* and *DQCE* respectively, and their lengths L_M measured by Friedlander, Goodwin, and Robertson (*loc. cit.*)



(IV*a*) (Numbering used for mathematical calculations.)



(IV*b*) (Ring Index No. 3865.)

TABLE 4. *Molecular-orbital energy levels for acedianthrone.*

i	Symmetry	E_i	i	Symmetry	E_i	i	Symmetry	E_i
1	S	$\alpha + 3{\cdot}0127\beta$	11—14	S, S, A, A	$\alpha + \beta$	24	A	$\alpha - 1{\cdot}307\beta$
2	A	$\alpha + 2{\cdot}9872\beta$	15	S	$\alpha + 0{\cdot}5334\beta$	25	S	$\alpha - 1{\cdot}458\beta$
3	S	$\alpha + 2{\cdot}5613\beta$	16	A	$\alpha + 0{\cdot}5103\beta$	26	A	$\alpha - 1{\cdot}810\beta$
4	A	$\alpha + 2{\cdot}1136\beta$	17	S	α	27	A	$\alpha - 1{\cdot}837\beta$
5	A	$\alpha + 2{\cdot}0422\beta$	18	A	$\alpha - 0{\cdot}598\beta$	28	S	$\alpha - 1{\cdot}923\beta$
6	S	$\alpha + 2{\cdot}0180\beta$	19	S	$\alpha - 0{\cdot}794\beta$	29	S	$\alpha - 2{\cdot}07\beta$
7	S	$\alpha + 1{\cdot}6104\beta$	20	A	$\alpha - 0{\cdot}927\beta$	30	A	$\alpha - 2{\cdot}27\beta$
8	A	$\alpha + 1{\cdot}5337\beta$	21, 22	S, A	$\alpha - \beta$	31	A	$\alpha - 2{\cdot}55\beta$
9	S	$\alpha + 1{\cdot}2216\beta$	23	S	$\alpha - 1{\cdot}089\beta$	32	S	$\alpha - 2{\cdot}66\beta$
10	A	$\alpha + 1{\cdot}1511\beta$						

TABLE 5. *Electron distribution* (q) *in acedianthrone* (*molecular orbital method*)

Atom, numbered according to :			Atom, numbered according to :			Atom, numbered according to :			Atom, numbered according to :		
(IV*a*)	(IV*b*)	q	(IV*a*)	(IV*b*)	q	(IV*a*)	(IV*b*)	q	(IV*a*)	(IV*b*)	q
1	3	0·982	5	5*a*	0·992	9	8*a*	0·996	13	1	0·979
2	4	0·976	6	6	0·987	10	16*e*	1·030	14	2	0·989
3	4*a*	1·016	7	7	0·981	11	16*c*	0·919	15	16*b*	1·093
4	5	0·809	8	8	0·982	12	16*d*	0·996	16 *	O	1·279

* Oxygen.

TABLE 6. *Mobile bond orders* (p) *with calculated and measured bond lengths in acedianthrone* (*molecular-orbital method*).

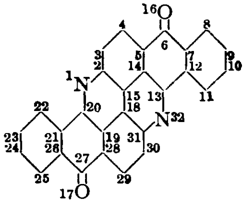
Bond, numbered according to :						
(IV*a*)	(IV*b*)	p_{12}	L_1	L_2	L_M	ΔL_2
1–2	3–4	0·665	1·390	1·387	1·32	−0·07
1–14	2–3	0·673	1·389	1·384	1·44	0·06
2–3	4–4*a*	0·653	1·393	1·389	1·41	0·02
3–4	4*a*–5	0·301	1·466	1·486	1·40	−0·09
3–12	4*a*–16*d*	0·579	1·409	1·413	1·42	0·01
4–5	5–5*a*	0·307	1·465	1·485	1·49	0
4–16 *	5–O	*0·862*	*1·195*	*1·195*	*1·20*	*0*
5–6	5*a*–6	0·634	1·397	1·395	1·41	0·01
5–10	5*a*–16*e*	0·580	1·409	1·413	1·37	−0·04
6–7	6–7	0·654	1·393	1·389	1·35	−0·04
7–8	7–8	0·654	1·393	1·389	1·38	−0·01
8–9	8–8*a*	0·621	1·400	1·399	1·42	0·02
9–10	8*a*–16*e*	0·542	1·418	1·427	1·39	−0·04
9–18	8*a*–8*b*	0·396	1·450	1·476	1·48	0
10–11	16*c*–16*e*	0·427	1·443	1·471	1·49	0·02
11–12	16*c*–16*d*	0·442	1·440	1·467	1·49	0·02
11–15	16*b*–16*c*	0·622	1·400	1·399	1·41	0·01
12–13	1–16*d*	0·608	1·403	1·403	1·41	0·01
13–14	1–2	0·686	1·386	1·381	1·30	−0·08
15–18	8*b*–16*b*	0·507	1·426	1·440	1·59	0·15

* Oxygen.

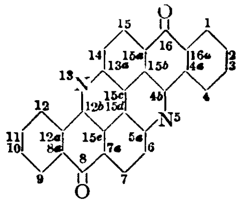
who consider them to be subject to an error of ±0·06, owing to the overlap of the molecules in the *b*-axis projection and to the non-resolution of certain atoms in other projections; $\Delta L_2 = L_M - L_2$ is also included. Neither the figures L_1 nor the values of ΔL are quite the same as those recorded in the above paper in which the calculated lengths were derived from a curve not quite identical with *DGBE* but ΔL of that paper is nearly $L_M - L_1$ of this. As these authors hope to re-examine this compound by *X*-rays to resolve the rather large discrepancies between a few of the observed and the calculated bond lengths, detailed comment is unnecessary at present. Again the bond lengths ought to be accurate to ±0·03 Å except for C–C bonds adjacent to the carbonyl groups. Of the twenty symmetrically independent interatomic distances it is very satisfactory to note that twelve have $|\Delta L|$ not greater than 0·03 Å and that only five have $|\Delta L|$ equal to or greater than the indicated experimental uncertainty of 0·06 Å. Three of these are the bonds 2–1, 1–14, 14–13, and it is not unreasonable to attribute part of their discrepancies to the failure to resolve atoms 1 and 14, especially as ΔL is negative for bonds 1–2 and 13–14 but positive for 1–14. Indeed bonds 1–2 and 13–14 are quoted as shorter than pure double bonds so that re-examination of their lengths is certainly called for. A similar remark applies to bond 3–4, which is recorded as being of about average aromatic length as compared with 1·49 Å required by the present calculations and 1·50 Å if regarded as a single bond in accordance with the simplest valence-bond approximation. As for bond 15–18, there is no doubt that a little of the discrepancy noted must be due to failure to allow for either a difference in hybridisation or a reduction of overlap in the five-membered rings where not all the angles can have the value of 120° required if maximum overlap of sp^2 orbitals is to occur. Change of hybridisation cannot be great since the molecule is planar. In chemical language we may say that this portion of the molecule must show strain tending to lengthen the central bond and in so far as the present calculations make no allowance for this they are inadequate. The simple molecular orbital theory used implies that all bonds in which the π-electrons can participate must be shorter than pure single bonds, so that it is difficult to believe that an allowance for strain (change of hybridisation or reduction of overlap) can increase the calculated interatomic distance from 1·44 to 1·53 Å, the minimum allowed by the *X*-ray measurements. Again further discussion must await refinement of the *X*-ray results and perhaps also of these calculations.

FLAVANTHRONE

Flavanthrone (V) has thirty-two π-electrons in its centrosymmetrical molecule and again the secular determinant factories into two sixteenth-order ones. The values of the various integrals in the secular equations were supposed to be the same as in benzanthrone with the addition of a Coulomb integral for nitrogen of $\alpha + \frac{1}{2}\beta$, the exchange integral between adjacent carbon and nitrogen being set equal to β as between neighbouring carbon atoms.



(V*a*) (Numbering used for mathematical calculations.)



(V*b*) (Ring Index No 3887)

On expansion and solution by the methods of Part I, the secular determinant gave first the values recorded in Table 7 for the sixteen lowest energy levels in increasing order of energy then the electron distribution (Table 8) and (Table 9) the bond orders and interatomic distances L_1 and L_2. Also in Table 9 are the interatomic distances L_M measured by Stadler (*loc. cit.*) along with $\Delta L_2 = L_M - L_2$.

If only the calculated interatomic distances are considered the same general comments could be made as for benzanthrone (subject to modifications caused by the nitrogen) but it is more useful to compare observed and calculated bond lengths, noting that as before the calculations should not be in error by more than *ca.* 0·03 Å, except perhaps for bonds attached to the keto-groups and for C–N bonds. It is then very satisfactory to find that for fifteen of the twenty symmetrically independent bonds $|\Delta L_2| \leqslant 0{\cdot}03$ Å. The calculated standard deviation of the observed co-ordinates is 0·032 Å, that of the bond lengths is thus 0·05 Å; seventeen of the bonds have $|\Delta L| \leqslant 0{\cdot}05$ Å. Of the others, bond 1–20 (equivalent to 13–32) involves the nitrogen (1 or 32) but even so is remarkably short; however, bond

TABLE 7. *Lowest energy levels in flavanthrone (molecular-orbital method).*

i	Symmetry	E_i	i	Symmetry	E_i	i	Symmetry	E_i
1	S	$\alpha + 3{\cdot}01149\beta$	6	A	$\alpha + 1{\cdot}9726\beta$	11	A	$\alpha + 1{\cdot}1120\beta$
2	A	$\alpha + 2{\cdot}9849\beta$	7	A	$\alpha + 1{\cdot}8341\beta$	12, 13	S, A	$\alpha + \beta$
3	S	$\alpha + 2{\cdot}5532\beta$	8	S	$\alpha + 1{\cdot}4578\beta$	14	A	$\alpha + 0{\cdot}8552\beta$
4	A	$\alpha + 2{\cdot}22451\beta$	9	S	$\alpha + 1{\cdot}3170\beta$	15	S	$\alpha + 0{\cdot}7984\beta$
5	S	$\alpha + 2{\cdot}0507\beta$	10	S	$\alpha + 1{\cdot}2729\beta$	16	A	$\alpha + 0{\cdot}52748\beta$

TABLE 8. *Electron distribution* (q) *in flavanthrone.*

Atom, numbered according to :			Atom, numbered according to :			Atom, numbered according to :			Atom, numbered according to :		
(V*a*)	(V*b*)	q	(V*a*)	(V*b*)	q	(V*a*)	(V*b*)	q	(V*a*)	(V*b*)	q
1 †	13 †	1·209	5	15*a*	1·004	9	2	0·984	13	4*b*	0·892
2	13*a*	0·951	6	16	0·813	10	3	0·984	14	15*b*	0·993
3	14	0·987	7	16*a*	1·003	11	4	0·977	15	15*c*	0·980
4	15	0·964	8	1	0·874	12	4*a*	0·992	16 *	O	1·290

* Oxygen. † Nitrogen.

TABLE 9. *Mobile bond orders* (p) *with calculated and measured bond lengths in flavanthrone* (*molecular-orbital method*).

Bond, numbered as :						
(V*a*)	(V*b*)	p_{12}	L_1	L_2	L_M	ΔL_2
† 1–2	13–13*a*	*0·515*	*1·374*	*1·374*	*1·37*	*0*
† 1–20	12*b*–13	*0·489*	*1·379*	*1·379*	*1·30*	*—0·08*
2–3	13*a*–14	0·583	1·408	1·412	1·44	0·03
2–15	13*a*–15*c*	0·515	1·424	1·438	1·43	—0·01
3–4	14–15	0·682	1·387	1·382	1·37	—0·01
4–5	15–15*a*	0·628	1·399	1·397	1·42	0·02
5–6	15*a*–16	0·307	1·465	1·485	1·50	0·01
5–14	15*a*–15*b*	0·593	1·406	1·409	1·33	—0·08
6–7	16–16*a*	0·303	1·465	1·486	1·54	0·05
6–16 *	16–O	*0·866*	*1·194*	*1·194*	*1·21*	*0·02*
7–8	1–16*a*	0·645	1·395	1·392	1·40	0·01
7–12	4*a*–16*a*	0·585	1·408	1·411	1·40	—0·01
8–9	1–2	0·665	1·390	1·387	1·36	—0·03
9–10	2–3	0·655	1·392	1·389	1·46	0·07
10–11	3–4	0·675	1·389	1·384	1·41	0·03
11–12	4–4*a*	0·614	1·401	1·401	1·40	0
12–13	4*a*–4*b*	0·476	1·433	1·455	1·48	0·02
13–14	4*b*–15*b*	0·278	1·470	1·487	1·47	—0·02
14–15	15*b*–15*c*	0·536	1·419	1·430	1·43	0
15–18	15*c*–15*d*	0·511	1·421	1·433	1·48	0·05

* Oxygen. † Nitrogen.

12–13 has $\Delta L = +0{\cdot}02$ though bond 13–14 has $\Delta L = 0{\cdot}02$. Thus a small displacement of atom 13 might yield a general improvement in these lengths although the centre marked for this atom seems to be that indicated by the contours of the published Fourier projection. Bonds 9–10 and 15–18 are much too long, although since the latter contains the centre of symmetry only half its length can be measured: it is therefore less reliable. However, too great significance should not be attached to the few large discrepancies, since the *X*-ray examination was not effected primarily to measure the interatomic distances with very great accuracy.

Conclusion.—Although there is some uncertainty as to the magnitude of the Coulomb and exchange parameters in hetero-compounds, and although all wave-mechanical derivations of bond lengths in molecules as large as those discussed here are approximations, it is reasonable to conclude that, provided there are not more than about two hetero-atoms to fourteen carbon atoms, bond lengths can be predicted to about ±0·03 Å in these large polynuclear compounds. It should therefore be possible to correlate calculated and observed bond lengths while *X*-ray work is in progress and so help in determining how to adjust molecular models in refining atomic co-ordinates (as with benzanthrone).

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