The Structure of Overcrowded Aromatic Compounds. Part I. A Preliminary Survey.

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The configurations of compounds showing " intramolecular overcrowding " cannot be predicted by conventional methods owing to lack of data on the effects of repulsion between non-bonded atoms. Where such repulsion leads to observable deformation of an aromatic system, the distorted molecule may provide information about the nature of interatomic repulsion and also about the manner in which the aromatic system reacts to mechanical stresses. Four groups of overcrowded aromatic structures are considered, and the published data surveyed for an indication of the kinds of distortions observed. Such deviations from the conventional molecular structure include abnormal bond angles and non-planarity of aromatic systems. An approach of 3·0 Å or less between non-bonded carbon atoms frequently results in repulsion forces sufficient to produce detectable distortions within the molecule.

A preliminary crystallographic investigation of several overcrowded compounds has yielded information on their molecular shape, but only complete structure analyses can reveal the nature and extent of the deformations present.

As a result of much work on the structure of organic molecules, mainly by *X*-ray and electron-diffraction methods, and of parallel progress in the theoretical interpretation of the forces responsible for chemical bonding, it has become possible to predict the bond lengths and bond angles of many such molecules with fair accuracy. Nevertheless, it must be recognised that our information on molecular structure is still incomplete since the nature and effect of intramolecular repulsion forces between non-bonded atoms have not yet been investigated systematically. The successful calculation of bond lengths and angles in planar aromatic systems of the type of anthracene, coronene, etc., suggests that in such compounds at any rate these intramolecular repulsion forces can largely be ignored; on the other hand, both chemical and structural evidence has accumulated to demonstrate that in many compounds the influence of these repulsion forces on molecular structure is not negligible. One class of such compounds has been termed " overcrowded " (Bell and Waring, *J.*, 1949, 2689; Harnik, Herbstein, and Schmidt, *Nature*, 1951, **168**, 158). In its wider aspects this phenomenon has been rather loosely ascribed to the operation of " steric effects."

The work described in this and subsequent papers represents a systematic study of overcrowded aromatic compounds in an attempt to close the gap in the experimental data. Part I presents a brief discussion of the information to be sought from such a study and a summary of some already available data as well as the results of an *X*-ray crystallographic survey of a number of overcrowded compounds; Parts II, III, and IV describe the crystallographic analyses of dianthronylidene, 3 : 4-benzophenanthrene, and tetrabenzonaphthalene. The crystal structures of 5 : 4′-dimethyl-3 : 4-benzophenanthrene and of the β-modification of 3 : 4-5 : 6-dibenzophenanthrene will be reported later.

In many aromatic overcrowded molecules the compression of non-bonded atoms may be partly relieved through the adoption by the aromatic system of a non-planar configuration. Such molecules are of interest in that they permit a direct observation of the equilibrium between interatomic repulsion and the chemical forces tending to maintain planarity. Thus we may hope, on the one hand, for information about the nature of short-range repulsion forces between non-bonded atoms, which should be useful for an understanding of steric influences in general. On the other hand, the organic chemist may expect information about the manner in which a conjugated molecule reacts to static mechanical stresses. Thus, where measurable distortions are produced by repulsion forces in an overcrowded compound, the distorted molecule, regarded as an elastic mechanical system, permits a

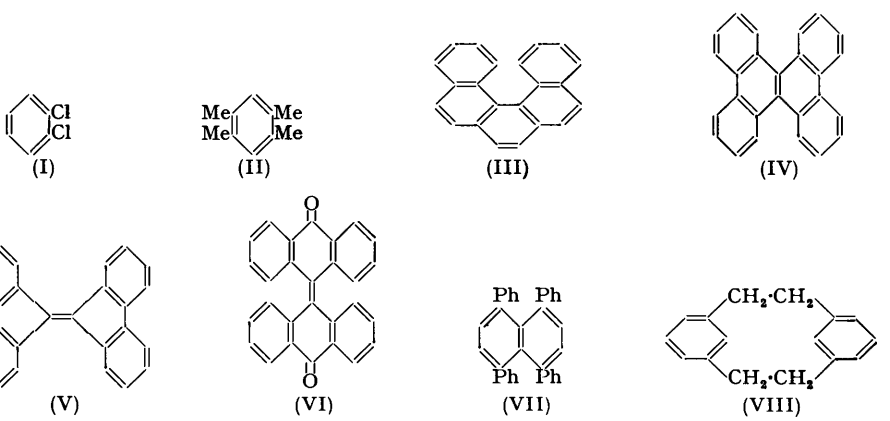
direct intercomparison of the bending force constants of the distorted bonds. These force constants which, except in fairly simple molecules, cannot be derived from infra-red spectra, are of particular interest because of the possibility that they may eventually be correlated with such molecular properties as bond orders and resonance energies.

Furthermore, one would expect the distortion of bond angles in an aromatic molecule to affect the state of hybridisation of the atoms involved; *e.g.*, it will be instructive to determine the degree of bending to which an exocyclic bond of a benzene ring may be subjected before the planarity of the six-membered ring itself is affected. Of particular interest also is the manner in which the effects of overcrowding in one part of a highly conjugated molecule may be transmitted to distant parts of the conjugated system.

Such distortions of aromatic ring systems must lead to wider variations in bond lengths and electron-density distribution than have so far been found in " normal " molecules like naphthalene, anthracene, etc.; correlation of these variations with the chemical properties of the overcrowded compounds may possibly lead to a better understanding of the relation between structure and reactivity.

Finally, the static deformations of the aromatic system within an overcrowded molecule owing to intramolecular compression may be expected to serve as models for the dynamic distortions produced by the approach of a reagent molecule towards the normal aromatic system in the course of a chemical reaction. These distortions are not, of course, susceptible to direct observation; nevertheless, the mode of deformation of an aromatic system produced by the penetration of its van der Waals envelope, by an uncharged (free-radical) reagent in particular, and the structure of the activated complex formed by the coalescence of the two components may well become deducible by analogy with overcrowded structures.

In our examination of the distortions produced in overcrowded aromatic compounds, we begin with certain molecules exhibiting close contact between benzene rings or their substituents. Four general types of such molecules will be considered. These are : *Group I : Substituted benzenes, e.g.*, *o*-dichlorobenzene (I), durene (II). *Group II : Aromatic polycyclics, e.g.*, 3 : 4-5 : 6-dibenzophenanthrene (III), tetrabenzonaphthalene (IV). *Group III :*



(I) (II) (III) (IV) (V) (VI) (VII) (VIII)

Tetraphenylethylenes bridged at all 2-positions, e.g., difluorenylidene (V), dianthronylidene (dianthrone) (VI). *Group IV : Molecules containing overcrowded phenyl rings, e.g.*, 1 : 4 : 5 : 8-tetraphenylnaphthalene (VII), di-*m*-xylylene (VIII). The following review of previous work conforms to the foregoing classification.

Group I.—In studies of hexachloro- and hexabromo-benzene by electron diffraction (Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489) the exocyclic bonds of both molecules were found to be bent out of the planes of the benzene rings by about 12°. In the corresponding *o*-dihalogeno-derivatives the same authors found that the distances between the substituents were consistent with an 18° bending of the carbon–halogen bonds out of the planes of the rings but could also be accounted for by a smaller out-of-plane bending together with a slight in-plane bending towards the unsubstituted positions. Their findings for

1 : 2 : 3 : 5-tetrabromobenzene also fell into line, with an apparent 15° out-of-plane bending of the exocyclic bonds to the three overcrowded bromine atoms, again with the possibility that the actual bending was less than this, being supplemented by a slight displacement of the 1- and the 3-bromine atom away from the 2-substituent.

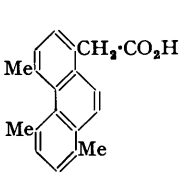
These electron-diffraction results appear to be contradicted, however, by an *X*-ray crystallographic structure analysis of hexachlorobenzene (Lonsdale, *Proc. Roy. Soc.*, 1931, *A*, **133**, 536). Although only one Fourier projection was obtained, down an axis roughly perpendicular to the molecular plane, this map is quite incompatible with the configuration reported by Bastiansen and Hassel (*loc. cit.*) for the molecules in the vapour. Lonsdale's co-ordinates for the chlorine atoms may be fitted, with a root-mean-square deviation of 0·013 Å, to a regular planar hexagon inclined at 23° to the plane of projection. Unless the structure she published is wrong by more than 0·1 Å *parallel to the plane of projection* it cannot be reconciled with an out-of-plane displacement of about 0·35 Å such as is implied by Bastiansen and Hassel's interpretation of their electron-diffraction data. It seems very unlikely that the molecules in the vapour could have the shape indicated by the electron-diffraction spectra and yet be compressed into a planar configuration by packing forces in the crystal. It is more probable that they are in fact planar, in the ground state, but that a strong correlation between the out-of-plane vibrations of the chlorine atoms, which are probably markedly anharmonic, accounts for the greater average separation between *ortho*-substituents observed in the vapour. The alternative explanation, that the ground-state configuration is non-planar and that the apparent planarity in the crystal is a statistical effect due to thermal oscillation between two mirror-image configurations, receives no support from the peak shapes in the published electron-density projection and seems inherently improbable. If any of these explanations is correct, however, it would indicate that there is a strong repulsion between neighbouring chlorine atoms which tends to stabilize the non-planar configuration. Similar considerations probably apply to hexabromobenzene, whose crystals are isomorphous with those of hexachlorobenzene (Plummer, *Phil. Mag.*, 1925, **50**, 1214).

Crystallographic structure analyses of hexamethylbenzene (Lonsdale, *Proc. Roy. Soc.*, 1929, *A*, **123**, 494; Brockway and Robertson, *J.*, 1939, 1324) and durene (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 659) indicate that in each of these compounds the carbon atoms are all coplanar. Well-resolved projections of both structures show the molecules sufficiently inclined to the planes of projection so that an out-of-plane displacement of as little as 0·1 Å could scarcely escape detection, although the incompleteness of the Fourier series used in the durene analysis makes it difficult to estimate the true limits of error in this structure. The distance between the *ortho*-substituents is given as 2·9 Å in hexamethylbenzene and as 3·0 Å in durene, the greater separation in the latter arising apparently from a bending of the exocyclic carbon–carbon bonds towards the unsubstituted positions. The extent of this bending, originally reported as 3°, is reduced to about 1° if the distance from the centre of the molecule to the methyl carbons is taken as 2·92 Å (Brockway and Robertson, *loc. cit.*) instead of 2·88 Å as given originally. Such a small bending could easily lie within the limits of error; thus there seems to be no conclusive evidence of any deformation resulting from repulsion between the methyl groups although there is no reason to doubt that some such deformation does occur.

Group II.—To this category belongs the classical work of Newman and his school on the optical activity of 4 : 5-dimethylphenanthrenes (IX) (Newman and Hussey, *J. Amer. Chem. Soc.*, 1947, **69**, 3023) and 5-methyl-3 : 4-benzophenanthrenes (X) (Newman and Wheatley, *ibid.*, 1948, **70**, 1913). However, while the existence of optical enantiomorphs demonstrates the non-planarity of these molecules, the type of distortion, whether of the substituents out of the plane of the nucleus or of the ring system itself, cannot be deduced from the optical evidence.

The situation is similar with regard to 4 : 5-dimethylphenazone, whose non-planarity has recently been proved by the optical resolution of (XI) (Theilacker and Baxmann, *Annalen*, 1953, **581**, 117). That 3 : 4-5 : 6-dibenzophenanthrene is also non-planar follows from the partial optical resolution of (XII) (Bell and Waring, *loc. cit.*). A direct structure analysis of the hydrocarbon has been carried out by McIntosh, Robertson, and Vand (*Nature*, 1952, **169**, 322), who report that " the steric effect has resulted almost entirely in

distortion from a planar arrangement with little change in the hexagonal form of the benzene rings." The distance between the overcrowded atoms is given as approximately 3·0 Å, but the precise nature of the distortions is unknown.



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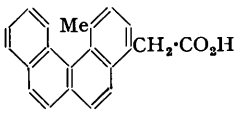

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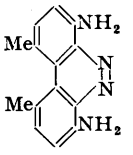

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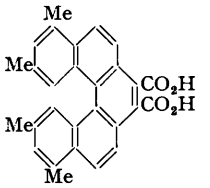

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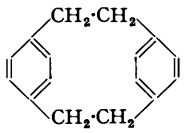


(XIII)

In octamethylnaphthalene the 1- and 8-methyl carbon atoms would approach to within 2·4 Å if the molecule were planar and regular. A crystallographic analysis (Donaldson and Robertson, *J.*, 1953, 17) has shown that they are displaced by 0·73 Å from the mean molecular plane and that the 2-methyl carbons also deviate from the mean plane, their displacement being estimated as 0·25—0·40 Å. There is, in addition, some indication that the naphthalene nucleus itself may be non-planar, but this is much less definitely established than the displacements of the substituents. These displacements, which must be assumed to alternate in direction around the nucleus, cause the approach distances between neighbouring methyl carbons all to be greater than 2·9 Å. That the 2-methyl groups are displaced from the mean molecular plane although their approach distances are at least as great as those between *ortho*-substituents in hexamethylbenzene, which is planar, may be due largely to the fact that the overcrowding of the 1- and 8-methyl groups destroys the planarity of the molecule and causes the repulsion between the 1- and 2-methyl groups, even at a separation of about 3·0 Å, to have an appreciable component normal to the mean plane such as is lacking in hexamethylbenzene. We conclude tentatively that repulsion between methyl groups is considerable at distances up to 3·0 Å at least, although in molecules of high symmetry it may not result in any observable deformation.

Group III.—The only representative of this group whose structure has been reported is difluorenylidene (Fenimore, *Acta Cryst.*, 1948, **1**, 295). An incomplete three-dimensional analysis has yielded a centrosymmetric model described as approximately planar; the overcrowded atoms are said to be 2·5 Å apart. It is doubtful whether the structure has been refined sufficiently to permit significant conclusions with regard to the molecular dimensions. The high discrepancy factors, $R(hk0) = 0{\cdot}31$ and $R(hkl) = 0{\cdot}36$, indicate that the structural details have not been fully established. The approach distance of 2·5 Å, which is considerably shorter than any observed in similar overcrowded structures, must therefore be regarded as questionable.

Group IV.—In di-*p*-xylylene (XIII) (Brown, *J.*, 1953, 3265) analysis from three-dimensional data shows that the separation between the unsubstituted carbon atoms of the two rings is 3·09 Å, and the substituted carbons are 2·83 Å apart. Thus the substituted atoms in each ring are displaced by 0·13 Å from the plane of the four unsubstituted carbons, giving the rings a folded, or "boat" shape. The bond angles at the aliphatic carbon atoms are 114° 37′. In addition, the three bonds to each substituted carbon atom are not coplanar, the exocyclic bond making an angle of about 13½° with the plane of the two aromatic bonds. Nevertheless, all benzene bond lengths are said to be 1·39 or 1·40 Å, and hence there is no evidence that the non-planarity of the rings involves any loss of resonance.

The same effect occurs in centrosymmetric di-*m*-xylylene also the subject of a three-dimensional analysis (Brown, *J.*, 1953, 3278), which reveals a similar bending of the benzene rings due to repulsion between the two carbon atoms, one in each ring, *ortho* to the substituted positions. These carbon atoms are only 2·69 Å apart, and each is displaced by 0·143 Å from the mean plane of ring atoms 2, 3, 5, and 6 (the overcrowded atom being numbered 1). Atom 4 is also displaced from this plane, by 0·042 Å, so that the deformation of the ring may be regarded as consisting in part of a folding about the diagonal 1—4. If chemically-equivalent bond lengths are averaged, those of all the benzene bonds are found

to lie between 1·38 and 1·39 Å. It is likely that correction for overlap of adjacent peaks and series-termination would result in a slightly higher estimate for these bond lengths, but the very close equality of all aromatic bonds seems to be established. The bond angles within the ring, when averaged in accordance with an assumed molecular mirror plane through atoms 1 and 4, range from 117° to 122°.

A common feature of the compounds in Groups I, II, and III is the planarity of their conventional models in which overcrowding forces are neglected. Consequently, any deviation from planarity in the observed structures is *prima facie* evidence of the effect of intramolecular compression on molecular shape. Although in these compounds and the two in Group IV discussed above the situation is thus fairly clear cut, further complications are presented by such borderline structures as diphenyl and *trans*-stilbene. Here the chemical forces tending to maintain a planar configuration appear to be of the same order of magnitude as the lattice forces responsible for crystal formation. Accordingly, the latter cannot be ignored in any discussion of the equilibrium between intramolecular compression and chemical bonding forces. On the assumption that coplanarity of the two rings in diphenyl leads to maximum resonance and hence to the lowest molecular-energy state, one arrives at a model in which the distance between carbon atoms 1 and 1′ is about 2·9 Å. In fact, while diphenyl in the solid state is centrosymmetric and thus planar (*e.g.*, Hengstenberg and Mark, *Z. Krist.*, 1929, **70**, 283), electron diffraction by the vapour (Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408) indicates that the two rings are inclined to one another at an angle of about 45°. The obscure situation discussed above with regard to hexachlorobenzene demands caution in interpretation of any apparent discrepancy between crystallographic and electron-diffraction data as implying a real difference between the molecular configurations in the solid and in the gaseous phase. Nevertheless, it seems reasonable to assume, in accordance with Bastiansen's suggestion (*loc. cit.*), that the energy of repulsion between the overcrowded atoms in diphenyl exceeds the gain in resonance energy achieved by the planar configuration but that this difference is insufficient, in the solid state, to offset the gain in lattice energy that results from the easier packing of the planar molecules.

In *trans*-stilbene, as in diphenyl, the structure with maximum resonance energy is, presumably, the planar configuration, in which the separation between carbon atoms 1 and α′ would be under 2·9 Å if all bond angles were 120°. This overcrowding could be relieved either by a twist of the benzene rings out of the plane of the central ethylenic system or by an increase of the C–C=C angle. A crystallographic analysis (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568), based on only one projection, reveals two types of stilbene molecule in the crystal. In one, the angle of twist is given as 10·4° and the C–C=C angle as 128°, while for the other the corresponding values are 2·8° and 133°. The two mechanisms for the relief of overcrowding thus appear to be complementary, each predominating in one of the two molecular species. The difference between the two molecules, if real, must be attributed to their different environments in the crystal.

Clearly, compounds in which steric repulsion leads to rotation about a bond of intermediate bond order present greater difficulties in interpretation than compounds whose conventional bond structures are unambiguously planar. The work to be described in this series of papers has therefore been confined to molecules of the latter type.

The evidence summarised above indicates that repulsion between non-bonded atoms may result in a wide variety of observable deviations from the conventional molecular configurations. Such deviations are often expressed in non-planarity of aromatic systems, involving distortions in the planar valency distribution of the trigonal carbon atoms, as well as abnormal bond angles at both aromatic and aliphatic carbon atoms. One useful generalisation that seems to be warranted by these data is that repulsion between non-bonded carbon atoms at a distance of 3·0 Å or less is sufficient, in many compounds, to produce appreciable deformations. But even this conclusion, while it may serve at this stage to provide an empirical criterion for overcrowding between carbon atoms, must be regarded as questionable in view of the structure reported for difluorenylidene and also in view of the as yet unexplained intermolecular approach distance of 2·58 Å found in crystals of triphenylene (Klug, *Acta Cryst.*, 1950, **3**, 165).

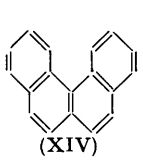
The first step in the present experimental study of the problems outlined here was a

crystallographic survey of several aromatic structures in which the forces due to overcrowding may be expected to lead to conspicuous deviations from the hypothetical planar configuration. Because of the complexity of many of these molecules and the uncertainty as to their shapes it was considered advisable to begin this investigation with a preliminary

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*β*	Space-group	*d* calc.	*d* exp.	*n*	Mol. sym.	
3 : 4-Benzophenanthrene (XIV)	14·69	14·19	5·76	—	$P2_12_12_1$	1·261	1·265	4	—	See Part III
5 : 4′-Dimethyl-3 : 4-benzophenanthrene (XV)	15·53	12·44	7·25	—	*Pbna*	1·214	—	4	2	
3 : 4-5 : 6-Dibenzophenanthrene (III)										
α-form	25·96	8·88	19·46	104°	*A*2/*a*	1·27	1·27	12	2	By sublimation (cf. McIntosh, Robertson, and Vand, *Nature*, 1952, **169**, 322)
β-form	17·46	14·24	5·83	94°	$P2_1/a$	1·27	1·26	4	—	From acetic acid
9 : 10-Dihydro-3 : 4-5 : 6-dibenzophenanthrene	20·0	20·0	7·43	—	$P4_22_1$	1·26	1·271	8	—	
Tetrabenzonaphthalene (IV)	20·45	7·74	12·18	119° 33′	$P2_1/a$	1·275	1·292	4	—	See Part IV
Dianthronylidene (VI)	10·20	8·45	12·67	119° 48′	$P2_1/c$	1·345	1·35	2	$\bar{1}$	See Part II
1 : 1′-Dibromodianthronylidene	10·31	27·76	7·66	102° 30′	$P2_1/n$	1·675	1·695	4	—	
1 : 1′-Dimethyldianthronylidene	9·99	27·35	7·66	92° 22′	$P2_1/n$	1·307	1·320	4	—	
3 : 4-3′ : 4′-Dibenzodianthronylidene (XVI)	14·7	11·5	7·6	α = 101° β = 92° γ = 103°	P1 or $P\bar{1}$	1·326	1·33	2	—	
Dixanthylidene (XVII)										
α-form	15·19	6·26	18·93	93° 9′	*Aa* or *A*2/*a*	1·32	—	4	possibly $\bar{1}$ or 2	Blue plates, obtained only once. Decompose to yellow powder
β-form	14·87	12·90	9·41	95° 15′	*Cc* or *C*2/*c*	1·314	1·326	4	$\bar{1}$ or 2	Wilson test indicates *C*2/*c*. Both blue and yellow needles found
9-Xanthylidene-anthrone (XVIII)	25·02	8·75	12·63	98° 30′	$P2_1/a$	1·35	1·35	6	($\bar{1}$) 2	Molecules have statistical centres of symmetry
10 : 10′-Dimethyldiacridylidene (XIX)	13·21	12·40	12·55	91° 30′	$P2_1/c$	1·27	1·31	4	—	
Dithioxanthylidene (as XVII)	5·73	17·98	18·11	—	*Pbc* or *Pbcm*	1·395	1·390	4	$\bar{1}$ or 2	Wilson test indicates *Pbcm*
Difluorenylidene (V)										
α-form	17·2	36·9	8·23	—	*Pcan*	1·28	1·26	12	$\bar{1}$ (or 2)	Cf. Fénimore, *Acta Cryst.*, 1948, **1**, 295
β-form	19·43	9·02	9·75	—	$P2_12_12_1$	1·276	1·283	4	—	Cf. Groth, Vol. V, 431
Bis-1 : 2-3 : 4-dibenzofluorenylidene (XX)	47·0	21·9	7·45	—	*Pnca*	1·37	1·38	12	$\bar{1}$ or 2	
Bisdibenzosuberenylidene (XXI)	11·3	16·6	11·6	107° 30′	$P2_1/n$	1·22	1·25	4	—	

study of as many compounds of this type as were available to us in the hope that some information regarding molecular shape could be derived from the cell dimensions and space-groups even before complete crystallographic analyses of the more promising structures were undertaken. The Table summarises the results of this survey. All cell dimensions were determined from Weissenberg photographs with nickel-filtered copper radiation and are accurate to 1% or better.

Little information on molecular shape of the compounds in Group II can be deduced from the preliminary data. Comparison of the series 3 : 4-benzophenanthrene, 5 : 4′-dimethyl-3 : 4-benzophenanthrene, β-3 : 4-5 : 6-dibenzophenanthrene, suggests that the lattice arrangements of these hydrocarbons, and hence their molecular shapes, must be closely related, a conclusion that is borne out by the correspondence in relative intensities of the low-order *hk*0 reflections of the three crystal structures. Since both 5 : 4′-dimethyl-3 : 4-benzophenanthrene and 3 : 4-5 : 6-dibenzophenanthrene (in the α-modification) crystallise with exact molecular twofold axes of symmetry, one may assume that 3 : 4-benzophenanthrene at least approximates to twofold symmetry.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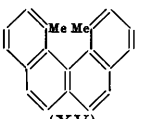

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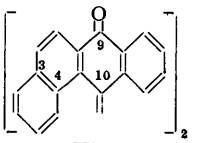

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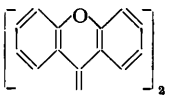

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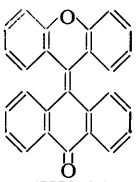

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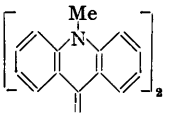

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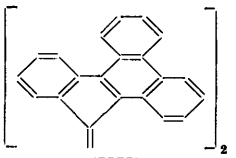
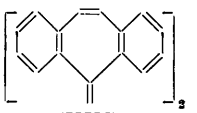


(XX)



(XXI)

In the dianthronylidene series (Group III) a number of compounds crystallise with centres of symmetry. Thus, dianthronylidene occurs in space-group $P2_1/c$ with two molecules in the unit cell; it follows unambiguously that it possesses a molecular centre of symmetry. In β-dixanthylidene the systematic absences alone do not allow of a choice between space-groups Cc and $C2/c$; however, the Wilson test (*Acta Cryst.*, 1949, **2**, 318) shows that the crystals are centric and that their space-group must therefore be $C2/c$ (Harnik, Herbstein, and Schmidt, *loc. cit.*). As there are four molecules in the unit cell they must have either a molecular centre or a twofold axis of symmetry. The latter being unlikely for reasons of space requirement, one may conclude that dixanthylidene, like dianthronylidene, is centrosymmetric. The asymmetrical xanthylideneanthrone crystallised in space-group $P2_1/a$ with six molecules in the cell; two molecules therefore possess pseudo-centres of symmetry, which can only be explained by the random packing of their long axes in the crystal lattice. Of the substituted dianthronylidenes only the isomorphous pair, 1 : 1′-dimethyl- and 1 : 1′-dibromo-dianthronylidene, have been studied. Here the crystallographic situation imposes no symmetry requirements on the molecules; nevertheless, the similarities in cell dimensions with the parent compound (after allowance for the interchange of the *b* and *c* axes and for the larger number of molecules per cell in the substituted derivatives) suggest that the shapes and space requirements of these compounds are essentially similar.

A second modification of difluorenylidene has the space group $P2_12_12_1$. Since centrosymmetric molecules rarely crystallise in non-centric space groups, it is possible that the molecule here, unlike the modification analysed by Fenimore (*loc. cit.*), has either no symmetry or else a (non-crystallographic) twofold axis.

These conclusions with regard to molecular symmetry in the various classes of compounds provide no detailed information on the nature or extent of the deformations present in these molecules, which can be determined only by complete structure analyses; these will accordingly be the subjects of later papers in this series.

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