98. *Molecular Complexes exhibiting Polarization Bonding. Part III.*[1] *A Structural Survey of Some Aromatic Complexes.*

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The molecular orientations and intermolecular separations in the crystal structures of a number of aromatic complexes are discussed. It is concluded that polarization bonding in such complexes results in a characteristic plane-to-plane packing of the components and that, where charge-transfer forces might be significant in determining the structure, the relative dispositions of the components are such as to allow the maximum degree of overlap between their molecular π-orbitals.

THE term "polarization bonding" was first used by McKeown, Ubbelohde, and Woodward[2] to describe what was thought to be a close intermolecular approach in a structure suggested[3] for *p*-nitroaniline. Although it is now known that this structure is incorrect[4] and that there is no such close approach in the correct structure, it is convenient

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[1] Part II, Harding and Wallwork, *Acta Cryst.*, 1955, **8**, 787.

[2] McKeown, Ubbelohde, and Woodward, *Acta Cryst.*, 1951, **4**, 391.

[3] Abrahams and Robertson, *Acta Cryst.*, 1948, **1**, 252.

[4] Donohue and Trueblood, *Acta Cryst.*, 1956, **9**, 960.

to retain the term " polarization bonding " to describe the intermolecular attraction found in certain molecular complexes. The class of molecular complexes is exemplified by the complexes formed by *s*-trinitrobenzene with aromatic hydrocarbons, by the quinhydrones, and by the iodine–aromatic hydrocarbon complexes. " Polarization bonding " is intended to include both charge-transfer bonding described by Mulliken[5] and the weaker interaction, between polar groups on one component and a polarizable second component, described by Briegleb.[6] It therefore leaves open the question of the precise nature of the interaction in any particular case.

Preliminary structural data are now presented for a number of polarization-bonded complexes. The crystal structures of the phenol–*p*-benzoquinone[7] and the chloranil–hexamethylbenzene[1] complexes have already been reported in some detail * and full accounts of the crystal structures of most of the other complexes mentioned will be presented later. Most of these structures are awaiting further refinement on the basis of better *X*-ray data from low-temperature photographs. Meanwhile a preliminary report may be of value since some reliable information can be given about the arrangement of the molecules in the crystal lattices.

Before discussing the experimental data, the structural effects to be expected from polarization bonding will be considered. For weak bonding, arising from the interaction of polarizing groups and polarizable molecules, the main feature to be expected is the juxtaposition of the polarizing groups of one component and the most polarizable regions of the other component. To be certain that such a juxtaposition does not arise merely because this represents the most efficient way of packing together particular shapes of molecules, it would be necessary to observe similar tendencies in related complexes containing molecules of shapes varying as widely as possible. Besides causing particular orientations of molecules, such weak polarization bonding might be expected to result in a slight decrease in the van der Waals separation of the mutually attracting molecular regions.

For charge-transfer complexes the question of the relative orientation of the two components has been discussed by Mulliken.[5] The stabilization of the complex depends upon overlap between the highest filled molecular orbital of the donor molecule and the lowest unfilled molecular orbital of the acceptor molecule. The extent of this overlap depends upon the symmetries of these two orbitals and the relative orientations of the molecules. For complexes where both the donor and the acceptor molecules are aromatic Mulliken's theory predicts that they will be superimposed plane to plane and, in the case of mononuclear aromatic molecules, probably will lie in the same orientation with the centres of the rings directly over each other. Packing considerations and polarizations of the type considered above might distort this arrangement in some cases, however. Again, an intermolecular separation less than normal is to be expected, the decrease being greater for larger charge-transfer stabilization of the ground state of the complex.

Small reductions in van der Waals separations are very difficult to establish. In the first place a " normal " van der Waals separation is probably better represented by a range than by a definite value. This is because it represents the balance between repulsive forces and weak attractive forces which depend upon the particular crystal structure. Secondly, the range of values to be accepted as " normal " is not well established. Thirdly, from a consideration of the shapes of the electron charge-clouds, one should probably not expect the van der Waals radii to be the same for plane-to-plane molecular packing as for the edge-to-plane packing which is common in the crystal structures of small aromatic molecules. Fourthly, although the van der Waals separation should strictly be measured

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* The unusual standard deviations[1] to which attention has been drawn[4] are incorrect. The recalculated values (in Å) are: for carbon $\sigma_x = 0{\cdot}085$, $\sigma_y = \sigma_z = 0{\cdot}023$; for oxygen $\sigma_x = 0{\cdot}044$, $\sigma_y = \sigma_z = 0{\cdot}016$; for chlorine $\sigma_x = 0{\cdot}022$, $\sigma_y = \sigma_z = 0{\cdot}008$. These values suggest that the reported distortions of the molecules are probably not significant.

[5] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

[6] Briegleb, " Zwischenmolekulare Kräfte und Molekülstruktur," Enke, Stuttgart, 1937.

[7] Wallwork and Harding, *Acta Cryst.*, 1953, **6**, 791.

between atomic centres, the perpendicular separation between molecular planes, irrespective of the precise positions of the atoms, is a quantity much more conveniently measured and discussed in structures with plane-to-plane packing. The best guide that one has for structures of the latter type is that both in graphite and in crystals of large polynuclear aromatic molecules [8] the perpendicular distance between the layers is about 3·4 Å.

EXPERIMENTAL RESULTS

A common feature in all the structures now described is a plane-to-plane stacking of the components. In every case but one the stoicheiometric ratio of the components in the complexes is 1 : 1, and the two types of molecule are arranged alternately in an infinite stack. The exception is the complex between phenol and benzoquinone where the ratio of 2 : 1 seems to be determined by hydrogen-bonding requirements,[7] and the molecules are arranged in groups of three with each quinone molecule sandwiched between two phenol molecules. This plane-to-plane arrangement is consistent with the inference that each of the complexes described is of the charge-transfer type. It is not essential that this inference should be made in every case, however, since a plane-to-plane arrangement is the typical mode of crystallization of large polynuclear aromatic molecules [8] and even of hexamethylbenzene.[9] The problem may be considered further, however, in the light of the relative positions of the component molecules and their intermolecular separations. Although the positions of the atoms are known with varying degrees of accuracy in the structures described in this paper, there is no doubt about the overall positions of the molecules, and their orientations are known fairly accurately in many cases. If the axis along which the molecules are stacked is known, division of the length of the repeat unit of this axis by the number of molecules in the unit gives the average separation of molecules along the stack. If also the orientation of the molecules relative to this stacking axis is known with reasonable certainty the average perpendicular separation between molecules can be calculated. In the Table both these values are quoted for the molecular compounds investigated. Where the orientation of molecules is uncertain the value for the perpendicular separation is given in parentheses. For convenience, the compounds have been classified in terms of donor and acceptor molecules irrespective of whether or not the charge-transfer character which this classification implies is justified. The acceptors for all groups except the first are *p*-benzoquinones. According to Mulliken's theory of charge-transfer complexes,[5] the stabilisation energies of a series of complexes formed by the same acceptor would be expected to increase with decreasing ionization potentials of the respective donors. If the acceptor molecules in the series are similar in type and contain atoms of similar van der Waals radii it is

Donor	Ionisation potential (ev)	Separation along stack (Å)	Perpendicular separation (Å)
Acceptor: s-*trinitrobenzene*			
Benzene	9·245 [10]	3·68	?
Naphthalene	8·12 [10]	3·49	3·45
Anthracene	7·4 [11]	3·31	3·28
Benzidine	—	3·54	(3·32)
Acceptor: *benzoquinone* (*Redox potential* 0·71 v)			
Phenol	8·50 [10]	3·87	3·33
Quinol	—	3·84	3·16 [12]
Acceptor: *chloranil* (*Redox potential* 0·742 v)			
Hexamethylbenzene	8·0 [11]	3·65	3·51
Dimethylaniline	7·3 [11]	3·40	(3·40)
Tetramethyl-*p*-phenylenediamine ...	6·6 [11]	3·26	3·26
Acceptor: *bromanil* (*Redox potential* 0·746 v)			
Tetramethyl-*p*-phenylenediamine ...	6·6 [11]	3·31	3·31

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[8] Robertson and White, *J.*, 1945, 607; White, *ibid.*, 1948, 1398; Donaldson and Robertson, *Proc. Roy. Soc.*, 1953, *A*, **220**, 157; Donaldson, Robertson, and White, *ibid.*, 1953, *A*, **220**, 311.

[9] Brockway and Robertson, *J.*, 1939, 1324.

[10] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

[11] Briegleb and Czekalla, *Z. Elektrochem.*, 1959, **63**, 6.

[12] Matsuda, Osaki, and Nitta, *Bull. Chem. Soc. Japan*, 1958, **31**, 611.

to be expected that the complexes with higher stabilization energy will have smaller average perpendicular separations between the molecules. In the Table the ionization potentials of the donors are given where these are available, and it may be seen that in each of the series for which the relevant information is available the perpendicular separations follow the expected trend.

The above limitations being borne in mind, it would seem that the average perpendicular separations of the components in nearly all the complexes shown in the Table are less than the expected van der Waals separations. This is particularly true of the complexes of *NNN'N'*-tetramethyl-*p*-phenylenediamine with chloranil and bromanil where the separations are 3·26 and 3·31 Å, respectively. It is interesting that these are among the complexes for which paramagnetism has been reported.[13] The paramagnetism was sought for in these complexes because it was considered that they might be largely ionic in the ground state (*i.e.*, consisting of molecular ions D^+A^-, where D and A represent donor and acceptor respectively); a largely ionic structure should result in molecular separations smaller than those observed. (It might be argued that the close approaches need not be along the stack of molecules but could occur in a sideways direction if the charge were appropriately localized. However, all the sideways contacts appear to be normal van der Waals separations.)

FIG. 1. *The relative orientations of the molecules in the complexes of* s-*trinitrobenzene with naphthalene and benzidine.*

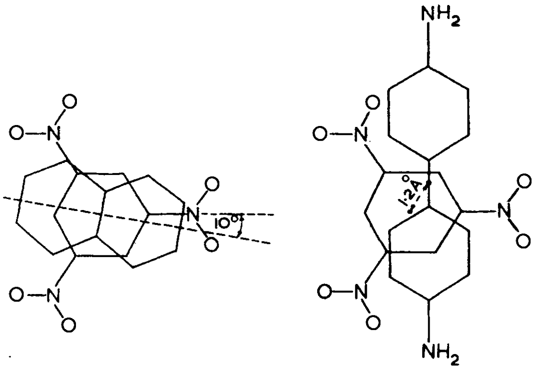
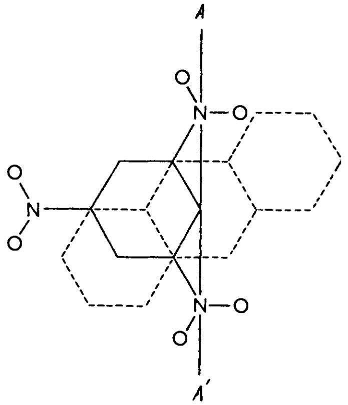


FIG. 2. *Two of the four molecules in a repeat unit of a column of the* s-*trinitrobenzene and anthracene complex. The two further molecules which are superimposed on them are seen in projection by reflecting the first two about the line AA'.*



The other structural feature of interest is the relative orientations of the component molecules. In the trinitrobenzene series this has not been determined for the benzene complex, but the results for the complexes with naphthalene, benzidine, and anthracene are illustrated in Figs. 1 and 2. It can be seen that the aromatic rings of the two components have similar orientations in the anthracene complex but not in the naphthalene and benzidine complexes. This might imply charge-transfer interaction in the anthracene complex and, in fact, a model having an anthracene–trinitrobenzene pair with the same relative orientations and with central nuclei exactly superimposed has recently been suggested[14] on the grounds of symmetry necessary for charge-transfer interaction, and has been used to interpret successfully the absorption and luminescence spectra of this complex. However, in the crystalline complex the central nuclei in adjacent molecules are shifted sideways through approximately 1·4 Å from the position where they would be directly under each other. The interpretation of this shift is not possible until more detailed information is available about this and similar structures. However, this effect in the anthracene complex and the lack of parallel orientation in the naphthalene

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[13] Kainer, Bijl, and Rose-Innes, *Naturwiss.*, 1954, **41**, 303; Kainer and Überle, *Chem. Ber.*, 1955, **8**, 1147; Bijl, Kainer, and Rose-Innes, *J. Chem. Phys.*, 1959, **30**, 765.

[14] McGlynn and Boggus, *J. Amer. Chem. Soc.*, 1958, **80**, 5096.

and benzidine complexes suggest that if there are charge transfer forces operating in the crystal lattices of any of these trinitrobenzene complexes they must be weak. This conclusion may seem rather surprising in view of the calculations by Briegleb and Czeckalla [15] based on the spectra of trinitrobenzene complexes in solution. These authors deduce that charge transfer accounts for about half the energy of stabilisation of the ground state of such complexes. However, in the crystalline state, other lattice forces may be more important and may have the determining influence on the molecular orientation.

The two members of the quinhydrone series show similar orientations of the two components, but again the centres of the aromatic nuclei are not directly over each other. The relative orientations and shifts found for phenoquinone are shown in Fig. 3. By comparison of cell dimensions a similar structural arrangement for quinhydrone was postulated [16] and has more recently been confirmed.[12] From the detailed structure determination the shift of the centre of each quinol molecule relative to that of the adjacent quinone molecule is known to be about 2·1 Å in the direction of the C=O group. In these two structures the shifts can be attributed to the compromise with hydrogen-bonding requirements, and the parallel orientations and short perpendicular separation can be taken as being indicative of charge-transfer stabilisation by overlap of molecular π-orbitals. This indication is supported by the remarkable pleochroism of quinhydrones [17] with the maximum absorption of light when its electric vector is parallel to a molecular stack.

FIG. 3. *A group of two phenol molecules and one quinone molecule in phenoquinone, showing the sideways shifts of the molecular centres.*

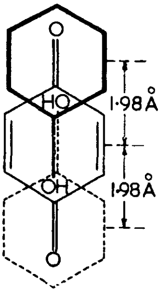
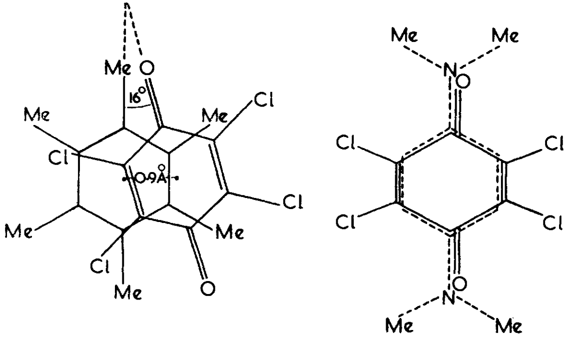


FIG. 4. *Complexes of choranil with hexamethylbenzene and with* NNN′N′-*tetramethyl*-p-*phenylenediamine.*



The chloranil complexes give more definite indications of the orientating effect of the forces acting between the molecules in each stack. In the complex with hexamethylbenzene the rather large substituents cause the aromatic nuclei of adjacent molecules to differ in orientation by about 16°, and their centres are also shifted through about 0·9 Å relative to each other (see Fig. 4). No detailed information is yet available for the complex with dimethylaniline, but that formed with the more basic *NNN′N′*-tetramethyl-*p*-phenylenediamine is the most interesting. In this case the two component molecules lie directly over one another in the stack and have the same orientation (within the limits of experimental error). It is probably significant that this most suitable orientation for overlap of molecular π-orbitals is associated with one of the shortest perpendicular separations in the Table. There seems to be no doubt that charge-transfer by overlap of π-orbitals is the determining feature of this structure. The complex formed by the same base with bromanil as acceptor is very similar to that just described. There is again the direct superposition of components in the stack but they are separated by 3·31 Å in this case. The increase over the corresponding value for the chloranil complex can be attributed to the larger bromine atoms, and there is other evidence [13] that the charge-transfer forces are larger for the bromanil than for the chloranil complex.

The general conclusions that can be drawn from this work are: (*a*) polarization bonding in complexes between aromatic molecules results in a characteristic plane-to-plane structure in the crystal lattice; (*b*) where charge transfer forces might be expected to be more significant

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[15] Briegleb and Czeckalla, *Z. Elektrochem.*, 1955, **59**, 184.

[16] Wallwork and Harding, *Nature*, 1953, **171**, 40.

[17] Nakamoto, *J. Amer. Chem. Soc.*, 1952, **74**, 1739.

in determining the structure (*e.g.*, from low ionization potential of the donor) the relative orientation and positions of the components are found to be such as to allow the maximum degree of overlap between their molecular π-orbitals. These conclusions are in agreement with the views expressed by Briegleb [6] and Mulliken [5] on the interactions in such molecules.

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