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The Geometries of Molecular Complexes: An Extended Hückel Approach*

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The extended Hückel scheme of Hoffmann is approximated to allow relatively easy energy calculations as a function of relative intermolecular geometry for a variety of planar charge transfer and charge resonance molecular complex pairs. The Hoffmann scheme is briefly discussed and the pertinent features of the method are illustrated with particular reference to weakly interacting molecular pairs. A dominant experimental structural feature is noted for all the complexes studied, in which a π-bond of one molecule is centered over and parallel to two edges of a hexagonal ring of the second molecule; it is basically a bonds-over-bonds arrangement. The calculated structures show good agreement with those observed for systems containing TCNE-like fragments and fair agreement for those in which this dominant structural feature occurs through the projection of two six-membered rings. In general no absolute binding is predicted. However, the agreement of relative minima between calculated and observed geometries coupled with the ease of calculation indicate the simple method may be useful in predicting relative geometries and further elucidating the more complicated structural features which must be involved.

Das erweiterte Hückelschema von Hoffmann wird angenähert und erlaubt damit eine relativ leichte Berechnung der Energie als Funktion der relativen intramolekularen Geometrie einer Anzahl von Molekülpaarkomplexen mit ebener Ladungsübertragung und Ladungsresonanz. Das Hoffmann-Schema wird kurz erörtert und die wesentlichen Züge der Methode beleuchtet mit besonderer Berücksichtigung von Molekülpaaren mit schwacher Wechselwirkung. Ein hervorstechender, experimentell beobachteter, struktureller Grundzug wird für alle untersuchten Komplexe, in denen eine π-Bindung eines Moleküls der einen Sorte oberhalb und parallel zweier Seiten eines hexagonalen Ringes liegt, der aus Molekülen der anderen Sorte aufgebaut ist, festgestellt; es ist hauptsächlich eine Bindungen-über-Bindungen-Anordnung. Die berechneten Strukturen zeigen gute Übereinstimmung mit denjenigen, die bei Systemen mit TCNE-artigen Fragmenten beobachtet wurden, und befriedigende Übereinstimmung mit solchen Strukturen, bei denen dieser dominierende Charakter durch die Projektion von zwei sechsgliedrigen Ringen hervorgerufen wird. Allgemein wird keine absolute Bindung vorhergesagt. Die Übereinstimmung der relativen Minima zwischen errechneten und beobachteten Geometrien verbunden mit der Einfachheit der Rechnung deutet jedoch an, daß die einfache Methode nützlich sein kann bei der Vorhersage relativer Geometrien und weiterer Aufklärung komplizierter struktureller Grundzüge, die in Betracht gezogen werden müssen.

Le schéma de la méthode de Hückel étendue d'Hoffmann est utilisé d'une manière approchée pour permettre des calculs relativement faciles de l'énergie en fonction de la géometrie intermoléculaire pour des complexes moléculaires plans de type transfert de charge et résonance de charge. Le schéma d'Hoffmann est brièvement discuté et les traits pertinents de la méthode sont illustrés avec référence particulière à des paires moléculaires en interaction faible. Les complexes étudiés présentent une caractéristique structurale dominante: une liaison π d'une des molécules se trouve parallèlement au dessus de deux côtes d'un cycle hexagonal de l'autre molécule; c'est fondamentalement une disposition liaisons sur liaisons. Les structures calculées sont en bon accord avec celles observées pour des systèmes contenant des fragments du type TCNE et en accord satisfaisant pour des systèmes où cette carac-

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téristique structurale dominante intervient par projection de deux cycles hexagonaux. En général on ne prédit pas de liaison absolue. Cependant, l'accord entre les minima relatifs des géométries calculées et observées joint à la facilité du calcul montre que cette méthode simple peut être utile pour prédire des géométries relatives et éclaircir des caractères structuraux plus complexes.

Introduction

The problem of the geometry of molecular solids is a difficult and as yet unsolved one. The greater part of the problem – beyond the computational enormity of the problem – is the related and equally complex problem of molecular geometry itself. Only the simplest of molecules have been treated with any degree of rigor. There has been considerable interest in simplified self-consistant field methods in which simplifying assumptions regarding certain integrals make application of the SCF-LCAO method practical on reasonably large molecules [1]. A simpler and certainly less rigorous procedure has been put forth by Hoffmann [2] in which the simple one-electron molecular orbital method may be applied to a system of any geometry; resonance integrals are related to an average of valence state ionization potentials and the corresponding orbital overlap and in this way distance effects and relative geometry enter in. The Hoffmann method gives quite reasonable results and has the very decided advantage that it is simple and simple to use.

The present study deals with the application of a partially-extended Hückel theory to the problem of the relative geometry of charge transfer and charge resonance complexes. In dealing with organic solids, present computer programming still limits the size of a problem in terms of the number of orbitals involved; for example, our present program can handle up to 90 orbitals. Furthermore, such calculations are still lengthy and expensive. For these reasons we have tried to simplify the method appropriate to our present interests while still maintaining the basic ideas of the method. As is discussed in a later section the Hoffmann method appears to work due to the presence of non-motonically varying overlap integrals as a function of internuclear separation; in particular, such is the case for $2p\sigma$-type overlap. Our premis is that in parallel, planar, conjugated complex pairs at distances of 3 to 4 Å the basic intermolecular interactions may be mimicked by treating only the π-system of each molecule of the interacting pair. This idea and a careful inspection of both the full and the present "π-only" Hoffmann methods are detailed in a later section.

The physical problem of interest arose initially in questions concerning why certain complexes of TCNQ exhibiting unusual electrical and magnetic properties have the particular intermolecular geometry they do [3, 4]. This problem is readily generalized to donor-acceptor pairs forming charge-transfer complexes in the solid state. Such materials as well as the TCNQ ion radical salts (charge resonance complexes) exhibit generally a type of intermolecular arrangement where the molecular planes are essentially parallel; it is generally felt that interactions involving the π-systems are dominant in determining the relative geometry. It is not understood why the molecules lie over each other as they do although, as we point out, an inspection of the relative geometries does reveal a structural feature common to most of those complexes whose geometries are known.

We don't expect to really "understand" such complicated systems when the nature of the simple chemical bond is still not easily comprehended. What has been done is to investigate the predictions of a relatively simple calculation which shows fair to very good agreement with those relative geometries that are exhibited experimentally. To the extent that the simple theoretical approach is understood and to the extent that calculated and observed structures agree can we offer some insight into the general problem of intermolecular interactions.

Calculations

Calculations were performed using the Hoffmann Production Program prepared by Sumru Inal and Lee A. Stone of the Engineering Department of the E.I. duPont Nemours and Company, Inc. The program was modified so that it could be run in H-level Fortran on an IBM 360/75 computer at the Triangle Universities Computation Center, Research Triangle Park, North Carolina.

Input parameters to the program consist of atomic parameters and atomic coordinates. The parameters used were as follows:

Atom	Z	IP (eV)
C	1.625	−11.4
F	2.60	−18.1
N	1.95	−13.9
O	2.275	−17.26

Z is the Slater exponent and IP is the appropriate valance state ionization potential for the $2p$ electron of a given atom and are the values of Skinner and Pritchard [5]. An additional program modification enabled all geometries of a complex to be run with only one loading of atomic coordinates. A typical thirty orbital calculation required seven seconds of computer time.

The Hoffmann Scheme and the π-Only Approximation

A. Basic Interactions

Hoffmann's extension of the simple Hückel method is defined by expressing the matrix elements of an effective one-electron Hamiltonian:

$$H_{ij}=0.5K(H_{ii}+H_{jj})S_{ij}, \tag{1}$$

where S_{ij} is the overlap integral of the two orbitals i and j, and H_{ii}, the diagonal elements, are chosen as valence state ionization potentials. K is a parameter, taken by Hoffmann as 1.75; the particular value used is that chosen by Hoffmann to give a reasonable compromise between working in a region of K where atomic populations are stable and matching the barrier to internal rotation in ethane.

The purpose of this section is to look at the molecular orbital behaviour that Eq. (1) gives for some very simple 2- and 4-orbital cases in order to see why it is that the method leads to energy minima as a function of interatomic separation (R) and why we expect the use of π-systems only to be a reasonable approximation

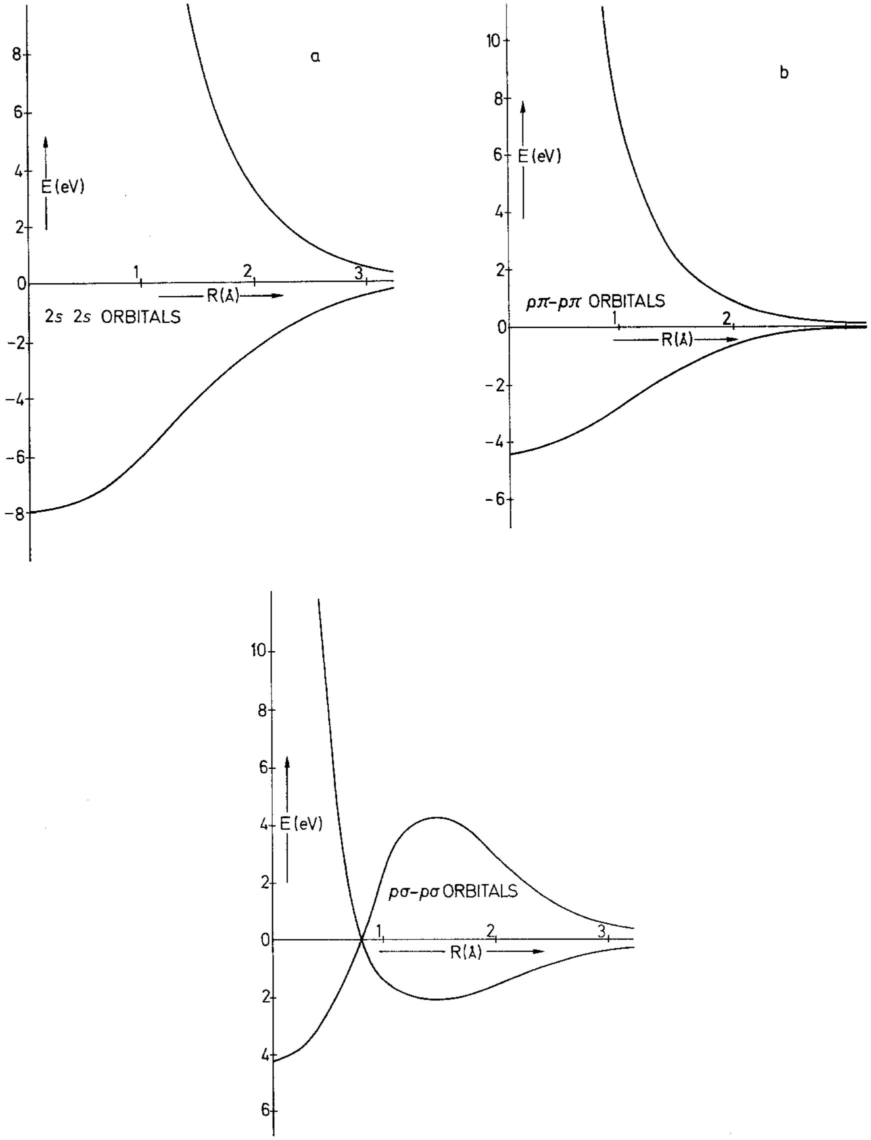


Fig. 1. Energy levels of 2*s*, 2*p*π, and 2*p*σ two-orbital diatomics as a function of the distance between the orbital centers

of the method for our present purposes. We use in all our calculations Slater atomic orbitals with exponents following the usual simple rules (e.g., carbon exponent = 1.625); as mentioned previously, the valence state ionization potentials are those of Skinner and Pritchard.

Consider first Fig. 1 in which the energy levels of three two-orbital model diatomic problems are given. In each case a single orbital is used on each center so that two molecular orbitals result; we imagine that our model diatomic or model bond has two electrons to be accommodated so that the energy of the system will be given by simply twice the energy of the lowest molecular orbital (MO). For the case of the $2s$- and $2p\pi$-orbitals no minima are exhibited and, other influences aside, the bond would like to shorten as much as possible. In the $2p\sigma$-case, however, a minimum is indicated at about 1.5 Å although the system energy is still lower at $R=0$. These three results follow very simply from the behaviour of the overlap of the orbitals involved; only when the overlap integral varies non-monotonically will a minimum be exhibited.

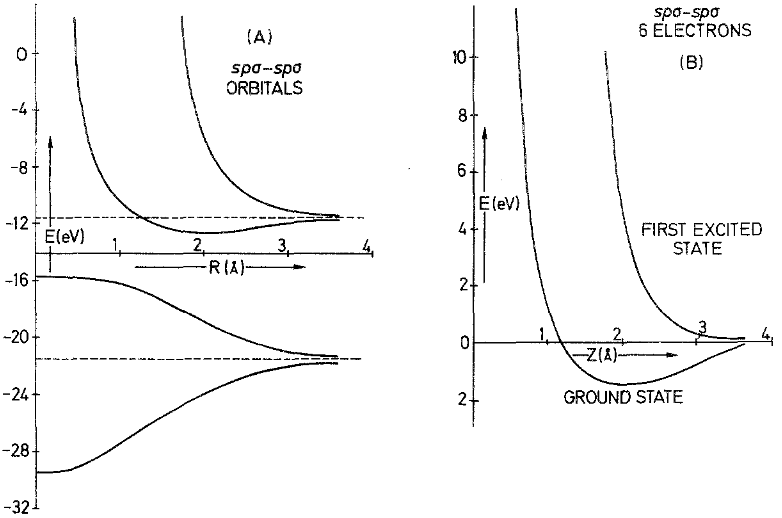


Fig. 2. a Energy levels of a four-orbital diatomic as a function of the distance between the orbital centers. A $2s$ and a $2p\sigma$-orbital are located on each center. b Relative energies of the ground and first excited states when six electrons are placed in the orbitals of Fig. 2a. Energies are relative to that with the orbital centers at infinite separation

Consider next the four orbital problem of Fig. 2a. Here we allow one $2s$- and one $2p\sigma$-orbital per center. The $2s$- and $2p\sigma$-orbitals on different centers mix with the result that the upper two curves resemble very much potential energy curves for a simple diatomic. One might then argue that the effects of repulsion which prevent real bonds from tending to zero length might be mimicked by considering the model system to exist as atoms with configurations $(2s)^2(2p\sigma)$ so that upon interaction, the lower three orbitals are doubly occupied yielding the ground state energy curve shown in Fig. 2b. The first excited state shown in Fig. 2b is that corresponding to a one-electron excitation from the highest occupied orbital of the ground state to the otherwise unoccupied anti-bonding MO. Neglecting the effect of the $1s$ inner-shell electrons the model case here could be taken as a crude presentation of B_2. Cade *et al.* [6] list an equilibrium internuclear distance of 1.59 Å while our model distance is 2.2 Å.

Inclusion of the $p\pi$-orbitals for the six electron case would not remove the minima but would cause an effect similar to that of Fig. 1c in which a minima exists but where $R=0$ is lower in energy. The addition of two more electrons (to give a total of eight) would generally restore the picture to that of Fig. 2b. In the full Hoffmann scheme all 2*s* and 2*p* orbitals as well as hydrogen 1*s* orbitals are used.

Basically it appears that it is the effects arising from interpenetrating 2*p*-orbitals which cause energy minima to appear in the calculations. For two coplanar conjugated systems one above the other these *p*-penetration effects will, in one-electron theory, be dominated by contributions from the individual-molecule π-systems. This is the basis of our choice of using only the π-orbitals of each separate molecule in looking at the intermolecular interactions.

One flaw in the method is clear from the behaviour of Fig. 1c; at small R the pair of molecules will want to collapse. By including doubly filled 2*s* shells one might avoid this difficulty as indicated from the results of Fig. 2. However this means a greater computational effort since our program time varies roughly as the cube of the number of orbitals. Furthermore, molecular complexes have intermolecular distances which are well outside this region; therefore, as long as the calculations are restricted to distances greater than, say, 2 Å, this particular region of instability will be avoided.

The π-only contraction of Hoffmann's method is then to use an orbital basis consisting of the $2p\pi$-orbitals of each molecule; *intra*molecular geometries are held fixed (experimental geometries) and the relative intermolecular geometry varied in such a way as to keep the molecular planes parallel. Because the basic interaction of the Hoffmann scheme and the dominant intermolecular interaction in these molecular complexes are both felt to be due to the $2p\sigma$-type penetration, at reasonable intermolecular distances we would expect this approach to mimic the true interactions. The approach is clearly approximate; however, the basic ideas appear sound and the results obtained indicate the method may be useful.

B. Comparisons of Full and π-Only Approximations

In order to see the effects of the π-only approximation on the full Hoffmann method we compare here the results of the two approaches on a system of two benzene molecules. The system consists of two benzene molecules superimposed over each other (atoms over atoms) at various intermolecular separations; part of the data has previously been reported [7]. Fig. 3 exhibits the system total energies as a function of the intermolecular separation for the ground states of the neutral and dinegative bi-molecular systems. The di-benzene dianion is shown because the full calculations exhibit a minimum versus Z (intermolecular separation) while the neutral system is repulsive. So far as we know, such di-positive or di-negative systems exhibiting minima have not been demonstrated experimentally. The purpose here, however, is not so much to compare experiment and theory but to compare two different kinds of calculation: one in which a minimum is shown and one where the energy curve is repulsive.

Three effects are observed in comparing the results shown in Fig. 3. At small Z the π-only calculations show energies that are moving too rapidly either toward positive or negative energies. This effect is readily understood from our previous considerations of the simple two-$p\sigma$-orbital case. Those considerations showed that the diatomic system wanted to collapse to $Z = 0$ at sufficiently small Z for the two-electron two-orbital case; if one adds an extra electron the system is strongly repulsive at small Z. Thus, for two superimposed benzene rings, as Z is reduced the problem effectively becomes 6 diatomic fragments. The second effect to note is the appearance of "structure" at intermediate distances (0.5 Å to 2.0 Å). As is indicated in the drawing by the cusps in the curves, this structure is due to level crossing with the levels involved behaving much as the $2p\sigma$-case at the same distances.

These two comments above serve to confirm our decision to avoid application of the π-only approximation at close distances. The third and more positive observation is that at expected and reasonable intermolecular distances ($Z > 2.5$ Å), the full and π-only methods have a similar behaviour. The π-only approximation seems to lower energies; that is, in the π-only approximation the neutral ground state curve is less repulsive at a given distance while the corresponding minimum in the dianion curve is shifted to small Z and is deeper.

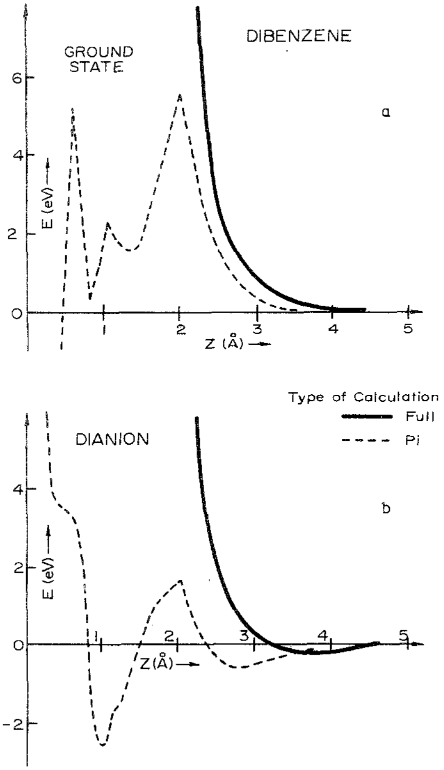


Fig. 3. Relative energies for full and π-only calculations of the neutral and dianion ground states of two superimposable benzene molecules as a function of interplanar distance

We conclude that using reasonable intermolecular separations the qualitative features of the calculation are relatively unaffected by truncating the Hoffmann procedure to the π-only approximation. Of course, the Hoffmann procedure itself is still open to criticism.

Presentation and Discussion of Results

A. Presentation

Figures 4 thru 10 exhibit the basic results of the present set of calculations; excepting the TCNQide figures each figure is composed of two parts. The projected structure observed experimentally is indicated by a line drawing and within the framework of the upper molecule which was translated (and rotated) is indicated a solid circle; knowledge of the location of this point and the structure of that molecule then allows one to denote the projected geometry of the aggregation by drawing the lower molecule and the location of the solid circle. Recall that only geometries translated from the experimental geometry have been calculated in general. This notation then is used for the contour part of each figure which shows the necessary section of the framework of the lower molecule (held fixed) and contours whose values represent the system energy when the denoted point of the translated molecule is at the specific point on the contour map. The triangle on the contour map indicates the *experimental* structure point while the square represents the calculated local minimum energy of the map. Generally points for the contour maps were taken on a rectangular grid of 0.5 to 1.0 Å separation. The contour lines thus represent interpolation to this degree of fineness. We do not show in these figures energies as a function of rotation about the calculated minima.

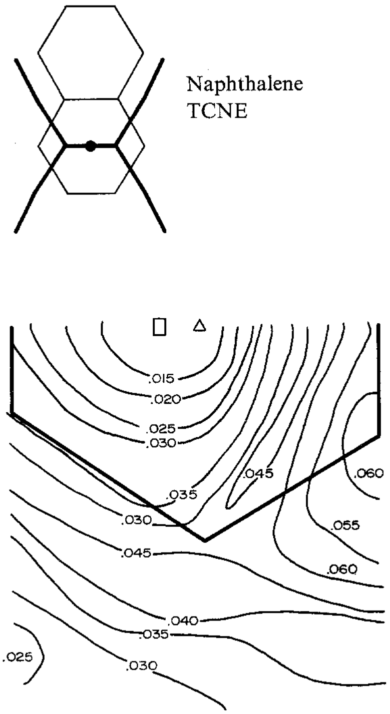


Fig. 4. Energy contour map for the Naphthalene-TCNE complex

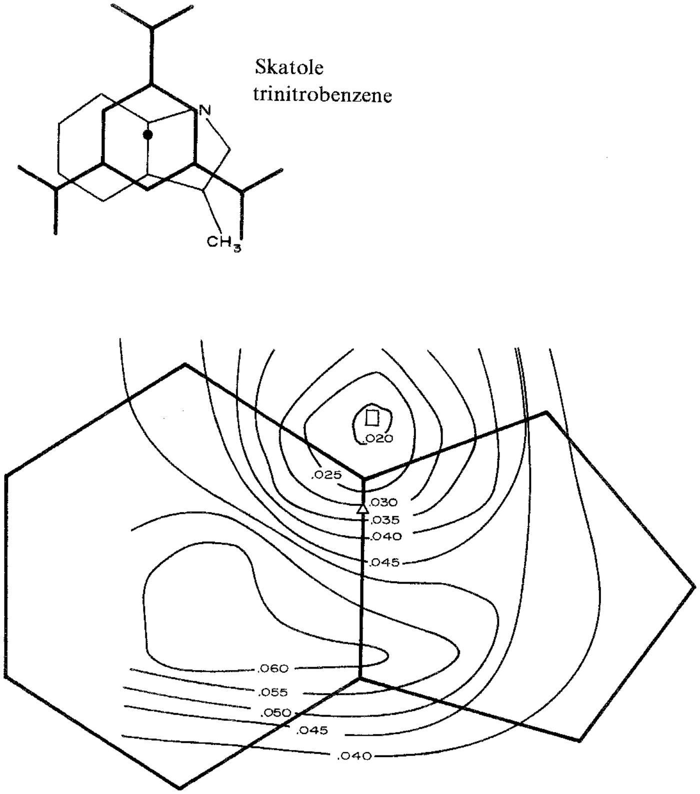


Fig. 5. Energy contour map for the Skatole-Trinitrobenzene complex

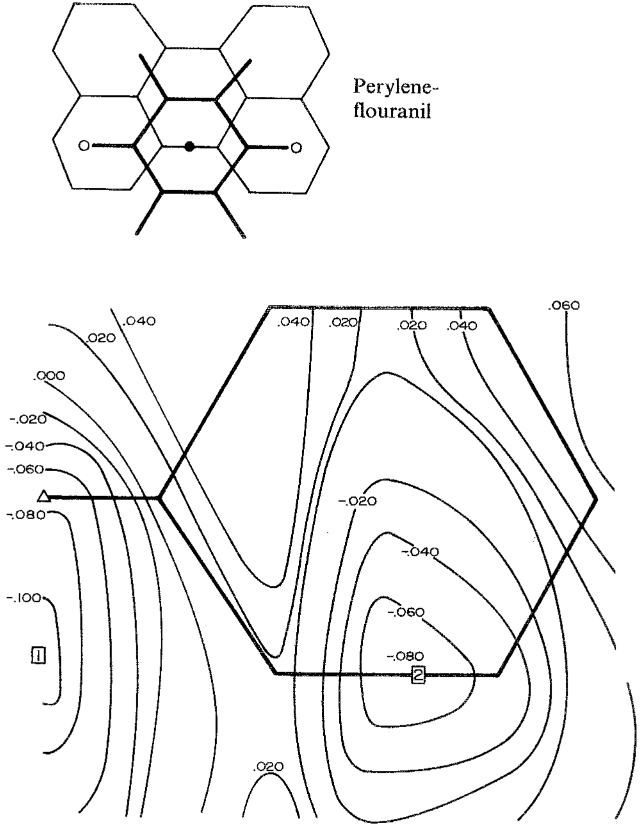


Fig. 6. Energy contour map for the Perylene-Fluoranil complex

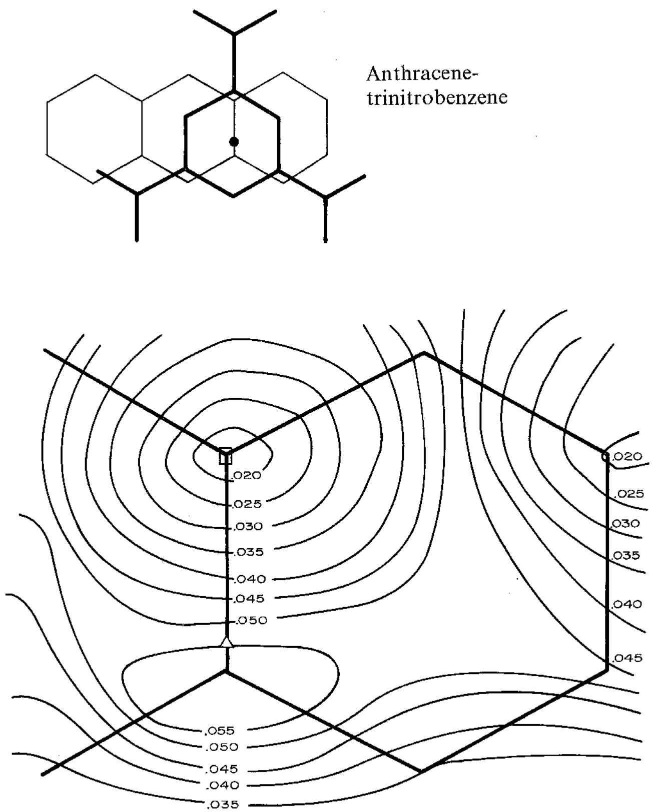


Fig. 7. Energy contour map for the Anthracene-Trinitrobenzene complex

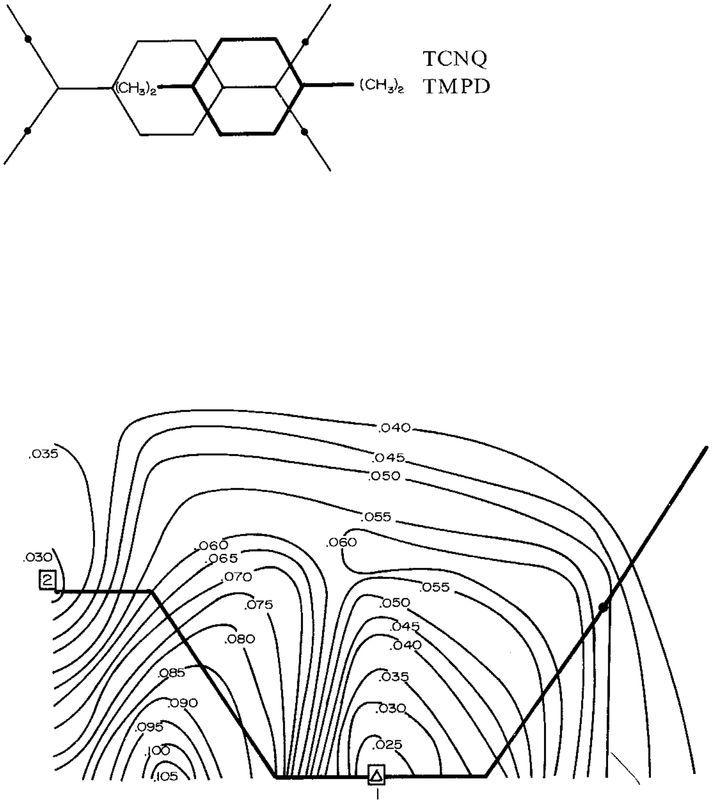


Fig. 8. Energy contour map for the TCNQ-TMPD complex

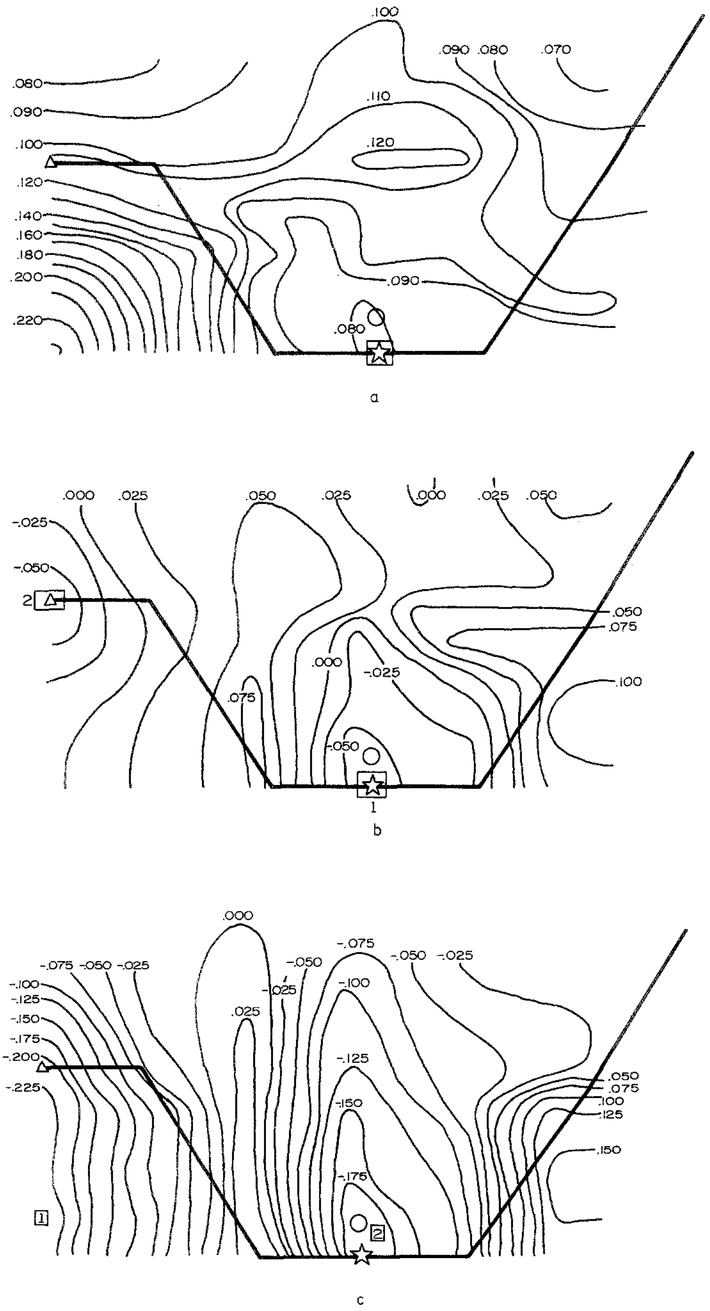


Fig. 9. Energy contour maps for the uncharged species (a), the anion (b) and the dianion (c) of $(TNCQ)_2$. The experimental projections found in $(Cesium)_2(TCNQ)_3$ are denoted by a triangle (noncentric-noncentric case) and by a circle (centric-noncentric case). That found in (N-methylphenazinium) (TCNQ) is denoted by a star. Calculated minima are shown by numbered squares

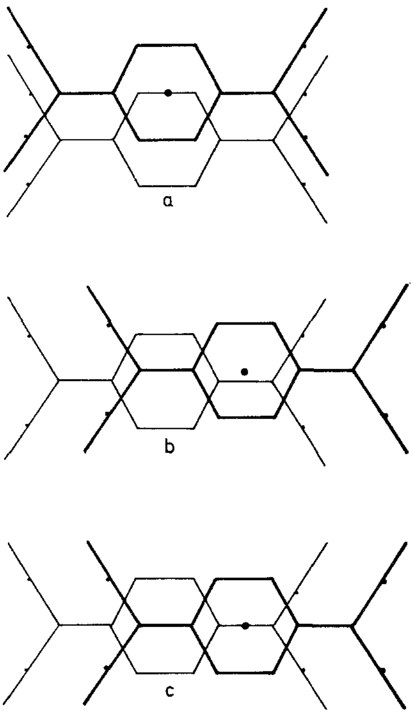


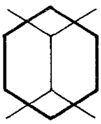
Fig. 10. Line drawings are given showing the experimentally observed projections for (a) centric-centric(cesium)$_2$(TCN$_2$)$_3$, (b) centric-noncentric(cesium)$_2$(TCNQ)$_3$, and (c) (N-methylphenazinium) (TCNQ)

These, however, were done and *all* were found to be stable to rotation with the exception of the neutral TCNQ system which is discussed later. The structures studied, their references, and other data of interest are tabulated in the Table.

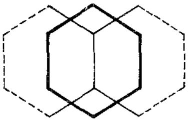
B. Discussion: Charge Transfer Complexes

We discuss here charge transfer complexes by which we mean a pair of neutral donor-acceptor molecules forming the pair complex; the TCNQ ion radical salts are referred to under the separate category of charge resonance complexes.

Study of the experimental projected geometries of the five charge transfer complexes (as shown in Figs. 4 thru 8) reveals a feature common to all: the presence of a π-bond of one molecule is approximately centered over and parallel to two edges of a hexagonal ring of the second molecule. The N-TCNQ structure reveals this feature most clearly. The dominant structural fragment in that case and for the TMPD-TCNQ complex has the appearance



For the three remaining complexes this feature presents itself in the form of projecting six-atom rings such as the fragment



The configurations are basically ones which may be described as a bonds-over-bonds arrangement.

Deviations from a completely symmetrical projection are apparent in the S-TNB case with a five-membered ring and for the A-TNB case with "external" (and slightly rotated) nitro groups. Basically, however, the presence of this dominant structural feature characterizes all the complex pairs. In all cases but N-TCNE where the situation does not allow it, other projected fragments also occur in which conjugated ring substituents or other rings are involved. The P-F case most readily reveals this feature. Thus, with relatively little error, by orienting the molecular pairs so that these fragments appear in projection the experimental projections are obtained. This structural feature also reveals itself in the TCNQ charge resonance salts as is discussed in a subsequent section.

In those cases in which the dicyanomethane group is present (N-TCNE, TMPD-TCNQ) agreement between calculated local minima and the experimental structure is very good. Agreement for the three remaining cases is only fair.

With the exception of the charged TCNQ systems to be discussed separately and the perylene-fluoronil complex none of the charge transfer complexes studied indicated binding (i.e., relative negative energy) as a function of varying intermolecular separation (Z) in the experimentally observed projected configuration, a behaviour found also by Wold [8] in his study of the TCNE-benzene complex. The curves are repulsive well into the shorter Z regions where the calculations – as discussed previously – lose significance. This fact is clearly one flaw of the model calculations. Accordingly, the Z distance was fixed in each case as that observed experimentally and energy calculations carried out for various translations from the observed configuration. Examples of this behaviour are shown in Fig. 11.

We find that local minima exist which are close to the experimental structure. The comparison of the experimental projected structure and the location of the calculated minimum can be made by comparing the denoted points on the contour maps. The Table also contains further pertinent data. We don't believe much significance can be put on the magnitudes of the energy differences calculated but these are noted for completeness; one could certainly *force* more reasonable values by rescaling the calculations. However, the important aspects are qualitative and concern the relative geometries.

In the three cases for which only fair agreement is obtained, the calculated minima occurs shifted away from the experimental point in a direction perpendicular to the long axis of one (or both) of the molecular pairs. A second local minima is calculated for a bonds-over-bonds arrangement in the P-F case (also TMPD-TCNQ) but it is not the lowest minima.

Several points should be made. First, although we believe the reasoning used to justify the π-only approximation to be sound, it is clearly an approximation

Table

Structure	Abbreviation	Z (Å) experimental	Energy (eV) Calc. minima	Minima depth (eV) relative to surroundings	Charge transfer (e) at experimental Z	
					Charge	Donor
Naphthalene-TCNE[a,h]	N-TCNE	3.30	0.01	0.02	0.04	N
N,N-dimethylparaphenylene diamine-TCNQ[b]	TMPD-TCNQ	3.27	0.02	0.03	0.06	TMPD
Perylene-fluoranil[c]	P-F	3.23	−0.11	0.11	0.36	P
			−0.08	0.08		
Anthracene-trinitrobenzene[d]	A-TNB	3.35	0.01	0.02	0.03	A
Skatole-trinitrobenzene[e]	S-TNB	3.30	0.02	0.01	0.04	S
$(Cs^+)_2(TCNQ)_3^=$[f,i]	Cs-TCNQ	3.22[j,l]	−0.24	0.24	0.0[m]	—
		3.26	−0.22 dianion	0.27		
(N-methylphenazinium$^+$) (TCNQ$^-$)[g]	NMP-TCNQ	3.26[j,k,l]	−0.05	0.05	0.0[m]	—
			−0.06 monoanion	0.06		

[a] Williams, R. M., and S. C. Wallwork: Acta crystallogr. **22**, 899 (1961).

[b] Hanson, A. W.: Acta crystallogr. **19**, 610 (1965).

[c] Hanson, A. W.: Acta crystallogr. **16**, 1147 (1963).

[d] Brown, D. S., S. C. Wallwork, and A. Wilson: Acta crystallogr. **17**, 168 (1964).

[e] Hanson, A. W.: Acta crystallogr. **17**, 559 (1964).

[f] Fritchie, C. J., and P. Arthur, Jr.: Acta crystallogr. **21**, 139 (1966).

[g] Fritchie, C. J.: Acta crystallogr. **20**, 892 (1966).

[h] TCNE = tetracyanoethylene.

[i] TCNQ = tetracyanoquinodimethane.

[j] Distances are between TCNQ molecules.

[k] NMP molecular separation is 3.36 Å.

[l] TCNQ plane separation in neutral TCNQ (Ref. [9]) is 3.45 Å.

[m] Charge transfer is zero by symmetry.

to an approximate method and may well contain flaws which particular structures accentuate. The general inability to calculate absolute binding is one of these. Van der Waals interactions are thought to be very important for the general stability of charge transfer complexes [9] so formal neglect of two-body interactions may account for this result. The largest shift between calculated and observed structures occurs for the A-TNB and P-F structures and is about 1 Å; we would expect the method to be better than this but not an order of magnitude better. On the other hand the calculations are carried out for isolated pairs of molecules whereas the experimental geometries are those for species in crystals surrounded by a molecular environment. Furthermore, this molecular environment is more than just a "background"; all the structures studied exist as *chains* of molecules in which donors and acceptors alternate. The intermolecular distances are very similar if not essentially the same. Thus, a given donor most likely interacts with two adjacent acceptors; perhaps our calculations should be done on two, three, four, or more pairs instead of just one. Such calculations are feasible but time-consuming and expensive, but should receive serious consideration in further refinement of calculations of this type.

The inability to obtain binding (negative relative energies) probably causes a distortion on the position of the minima that a more rigorous or exact calculation would show. The general swelling upward (positive energies) of the energy surface as the molecules approach instead of exhibiting a concave appearance (negative, binding energies) would tend to push the calculated minima "outward" from their true positions, as is observed in our calculations.

Finally, in principle *all* of the geometric configuration space should be studied. The use of the observed intramolecular geometries and intermolecular separations does not imply that the results will be improved since one is not absolutely sure that the calculation is properly scaled. However, this should be more of a quantitative rather than a qualitative effect and we stress here the qualitative features of the method.

C. Discussion: TCNQ Salts

Data on neutral, singly and doubly charged TCNQ dimers are shown in Figs. 9 and 10. Note in Fig. 10 the *three* types of projected structure that are known. The TCNQ ion radical salts differ from the usual charge transfer complex in that the main source of molecular packing stability appears to come from aggregation of the negatively charged and/or formally neutral TCNQ molecules. The original papers [10, 4] on these two structures represent the best source for a detailed picture and discussion of the relative geometries and possible aggregation effects.

In both structures the same structural fragment is present as was noted for the five charge transfer complexes studied. This dominant fragment projection is shifted slightly in the Cs-TCNQ structure and, due to non-equivalent crystal symmetry sites, a second type of projection is also observed in which one TCNQ undergoes a sideways shift from a completely superimposed projection, i.e., a shift in a direction perpendicular to the long axes of the molecules. Note that the NMP-TCNQ complex is a 1:1 complex in which all TCNQ molecules are *formally* ion radicals whereas the Cs-TCNQ is a 2:3 complex containing some *formally* neutral TCNQ molecules as well as the formally charged species. We stress the *formal* nature of the charge of the various species since intermolecular charge and spin delocalization are thought to be quite important in these materials [4].

Fig. 11 contains the Z-dependence of the energy of the molecular pairs in several projections to illustrate that bonding *is* predicted for these charged species

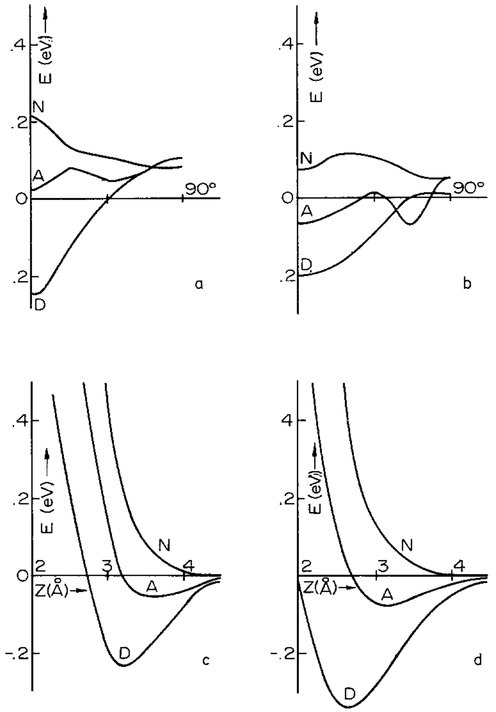


Fig. 11. (a) and (b) show the relative energy of N (neutral), A (anion), and D (dianion) of $(TCNQ)_2$ as the top molecule is rotated about its center. (c) and (d) show energy as a function of interplanar distance. Data for (a) and (c) were obtained using the superimposable configuration while that for (b) and (d) was obtained with the upper molecule centered over the quinoid double bond of the lower molecule

for certain orientations. In the main they illustrate what seems to be a fairly general result: singly charged species (that is, each species with a singly occupied orbital) tend to want to bond in the Hoffmann procedure. For example, the di-benzene di-anion is predicted to be bonding in the full Hoffmann approximation. The result is explainable, we believe, in the approximation used. Consider two identical molecules at distances where the intermolecular interaction are weak. The one-electron levels are degenerate at $Z = \infty$ and this degeneracy is removed and the levels split as Z is decreased. If the levels are doubly occupied initially, the splitting lowers the energy of one level about as much as it raises the energy of the other level. However, if the levels were singly occupied initially, both electrons will want to be in the lower level of the split pair and the energy of the system will want to be reduced. There are, of course, other factors which shift the center of the split levels so that absolute binding cannot be rigorously predicted. However, it is clear that pairs of molecules each with a singly occupied orbital will tend more toward binding – at least initially – than their doubly-occupied analogues. Finally, it is interesting that the observed minima in Z for the TCNQ salts is very close to that observed experimentally. We must conclude, however, that it is most likely a property of $p\sigma$-type interactions in the Hoffmann procedure and not a special property of the molecular systems in general.

The significant aspects of the TCNQ calculations presented here are the local energy minima found for the translated structures and the fact that the calculations show that only for the charged systems (mono- and di-negative molecule pairs) is stability predicted for a parallel plate-like stacking such as is observed experimentally.

In all three cases a local minimum is calculated for the TCNQ pairs in which the center of one TCNQ is over the quinoid double bond (the dominant structural fragment). For the neutral system, this structure, however, is *not* stable with respect to rotation, the calculation showing that the long axes of the molecules prefer to be at right angles with respect to one another. This is consistant with the known type of structure for neutral TCNQ in the sense that the molecules in this structure assume the general type of herring-bone pattern of many ordinary planar organic molecules [11]. The mono-negative system is weakly stable to rotation about this point whereas the di-negative pair is strongly stable to rotation and conforms very closely to the experimentally determined configurations. Actually, while the mono-anion system has its lowest energy when one TCNQ is centered over the quinoid double bond and a higher minima for the sideways shifted position mentioned earlier approximately the opposite is true for the dianion case. Here the lower of the two minima is that of the partially sideways translated configuration. For the dianion both minima configurations are stable with respect to rotation. The presence of several minima both from the calculation and experiment is an interesting result. One might advance the argument that *if* one considered the extra coulombic repulsive energy of the charged system the molecules would tend to take up a configuration in which they are further removed from each other so that one minima might really be more strongly favored. However, it is not known if this formally unaccounted for coulombic repulsion is *not* somehow accounted for in the Hoffmann procedure, or, if it is not, that perhaps it is *over*-compensated for. Although there do appear to be some difficulties in the method as applied to net charged systems as mentioned earlier, our present ignorance forces us to discuss our results in *just* the one-electron framework of the method.

The situation is complicated from several points of view. First, the charge resonance TCNQ systems in which plate-like stacking of TCNQs exists are not simple systems. Intermolecular coupling is known to occur and its effects may well be long range. Second, we have not accounted for the electrostatic energy of the total system – anions *and* cations – in our calculations. Certainly this electrostatic lattice energy will have an influence of the relative geometry of the anionic portion of the system. Third, we have calculated only the energy of a pair of TCNQ's; it would be more meaningful and certainly interesting to treat a system of three or four TCNQ molecules to examine some of the effects of the crystal environment of the molecules, particularly since aggregates of these sizes may tend to exist in the crystals.

D. Degree of Transfer of Charge

For each structure in its experimental projection we calculated the degree of transfer of charge as a function of Z. These figures (in units of the electronic charge) for the experimental Z are given in the Table. In each case the direction of charge transfer is correct in terms of our chemical ideas of electron donors and acceptors. In no case is their charge transfer at infinite separation, which, of course, is possible in one-electron theories of this type. There is, of course, no net charge transfer for the TCNQ molecular pairs because of the molecular symmetry. Charges were calculated as gross atomic charges [12] by the computer program; the charge transferred is then the sum of the gross charges for the acceptor in the complex less the similar sum for the isolated acceptor (simply its number of (π, in this case) electrons).

No especially unusual behaviour of charge transferred is observed as a function of Z. The calculations were carried no further than $Z = 2.0$ Å and generally showed a monotonic increase in amount of charge transferred as Z decreased. There is some hint that the charge transfer may level off or become smaller at lower Z; the P-F complex actually exhibits a maximum at about 2.2 Å. However, due to the misbehaviour of the method at small distances only the general trends at larger Z are meaningful.

Summary

We have discussed the one-electron Hoffmann procedure with particular reference to what we feel to be the important interactions at intermediate distances. A simple, relatively easy method of calculations has been carried out on interacting molecular pairs involved in complex formation. In general the method is unable to predict binding although local energy minima are found which exhibit agreement with the experimental structures which ranges from fair to very good. Study of the experimentally known crystal structures reveals a dominant bonds-over-bonds structural feature common to *all* the structures.

The truncated basis method employed in the Hoffmann procedure is lacking in several respects. Our results possibly can be viewed as a critique of the general Hoffmann method; however, since we believe the general ideas are qualitatively correct, we also feel some of the inadequacies of the calculations reflect flaws any *one-electron* method may not remove, as well as general complexities involved in studying molecular interactions of isolated pairs when longer range crystal effects are probably important. We believe that the simplicity of the method coupled with the fairly good agreement with experiment obtained makes it a useful first approach to the very complicated problem of the geometry of molecular solids.

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Note Added in Revision. Not all complexes whose structures are known have been considered in this work. In particular, a number of structures have appeared within the last year which bear comment with respect to the dominant structural fragment discussed previously in the paper. The pyrene-TCNE [13], TCNQ-bis-(8-hydroxy-quinolato) copper (II) [14], and the 1:1 and 2:1 complexes of para-halogenated phenols with p-benzoquinone [15] do exhibit this structural fragment, whereas the para-phenylenediamine-chloranil [16] and TCNQ-anthracene [17] complexes do not. Although cases exist where the predicted structural arrangement is not found, it does seem to be present on the majority of the known structures.

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