62. *Electron Distribution in Conjugated Free Radicals.*

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In the two systems $CH_{3-x}Ph_x$ and $CH_{3-x}(C_6H_4Ph)_x$ the free-valence numbers are deduced from an investigation of bond orders as defined in the molecular-orbital theory. The corresponding quantities arising in certain *p*-benzoquinone dimethides are also reported. On the basis of these data, changes in aromatic character of the hexagons under increasing phenylation are observed and the diradical behaviour of certain meriquinones is discussed. The results are correlated with predictions of reactivity ascribed to the presence of free electrons.

SYSTEMS with one unpaired electron are usually free radicals. Two types of radicals may be distinguished by the degree of mobility of their unpaired electron: (i) if the electron is more or less localised, the reactivity is mostly concentrated at one centre, as in alkyl radicals; (ii) if the electron is free to move over part or all of the molecule the reactivity will be correspondingly spread out. We are concerned only with conjugated hydrocarbon radicals in which the odd electron moves in a π-type orbital extending over the whole carbon framework. In so far as reactivity is governed by properties of the conjugation electrons, all electrons in such π-type orbitals must evidently be taken into consideration.

It seems desirable to introduce some differentiation between the several meanings attached to the word reactivity. Indeed it may be necessary to distinguish between the various reactivities of an atom, expressed by its readiness to participate in reactions, relative to other centres in the same molecule, or to corresponding centres in related molecules. Again the reaction rates may refer to a specific reagent, a single group or a conjugating system, to homolytic or heterolytic substitutions. In no way can it be claimed that the present methods of calculation are adequate to deal with these several reactivities; but the two theoretical quantities, free-bonding power and electron density, may be correlated with two different aspects of reactivity.

To some extent the reactivity of an atom in a molecule is governed by the number and type of bonds in which this atom participates. In the theory of molecular orbitals (M.O.) this has been measured by a free-valence number defined as the potential bonding power not already engaged in bond formation. We may therefore expect that the free valence at an atom is an indicator of its readiness to undergo homolytic reactions. Likewise the electron density at an atom, as defined in the molecular-orbital theory, may be expected to serve as a rough index of the ability of an atom to take part in heterolytic reactions.

Using the molecular-orbital technique we have investigated the dependence of free-valence values on the environment within a particular compound, and have applied our considerations to the phenyl-, $CH_{3-x}Ph_x$, and diphenylyl-methyls, $CH_{3-x}(C_6H_4Ph)_x$. As the two series of compounds are closely allied, changes in free valence may be observed not only from atom to atom within one molecule, but also between corresponding atoms of the two groups. The other quantity that has a bearing on reactivity is the odd-electron density, for which we have established values at all carbon atoms. This seemed worthwhile not only to discover variations in the availability for ionic reactions, but also for the sake of a comparison with predictions made on the basis of the valence-bond (V.B.) theory. For these molecules, results of valence-bond calculations are available (Pullman, *Discuss. Faraday Soc.*, 1947, **2**), some of which are reproduced below. All these radicals have one non-bonding orbital with zero orbital energy which is occupied in the ground state by just one unpaired electron. (The value of the Coulomb integral for a $2pz$-electron is taken as zero on this scale.) This electron of zero orbital energy is not concerned with bonding and may therefore be associated with the "free" electron of the conventional bond diagrams. In the molecular-orbital theory this electron is not confined to one single carbon centre but has a distribution over the whole framework; this distribution is recorded below as the odd-electron density.

A comparison of molecular-orbital (M.O.) and valence-bond (V.B.) results has been given for some radicals (Moffitt and Coulson, *Trans. Faraday Soc.*, 1948, **44**, 81). In their work, Pauling, Brockway, and Beach's (*J. Amer. Chem. Soc.*, 1935, **57**, 2705) formula for bond orders was used, which is unsatisfactory as the free-bonding power depends on the initial choice of canonical structures (Daudel, Jacques, Jean, Sandorfy, and Vroelant, *J. Chim. phys.*, 1949, **46**, 249). It is, however, more readily adapted to include unpaired electrons than the more consistent Penney–Dirac (*Proc. Roy. Soc.*, 1937, *A*, **158**, 306) formula for bond orders. By means of the latter substantial agreement with calculations by the molecular-orbital method is reached for bond orders in conjugated hydrocarbons.

It is also the purpose of these calculations to follow the effect of increasing phenylation on the electron density at the methyl carbon; the latter being the site of the free electron in the conventional bond diagram for these radicals. Our numerical results will make more precise the correlation that exists between the conventional structural diagrams and theoretical predictions.

METHOD AND RESULTS

The molecular-orbital method was applied in its simplest form with neglect of all overlap integrals and with equality of all resonance integrals, approximations which are insignificant in a discussion of free valence (Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265). The bond orders of all bonds were then determined by the standard technique (see *e.g.*, Coulson, *Quart. Reviews*, 1947, **1**, 44). In molecular-orbital theory the total bonding of an atom r is denoted by:

$$N_r = \sum_s p_{rs} + C_r$$

where C_r = number of σ-bonds concurrent at atom r, s = a neighbouring carbon atom, and p_{rs} = mobile order of the bond r–s. The free valence at atom r is then defined in terms of the maximum potential bonding power as:

$$\text{free valence} = N_{\text{max.}} - N_r = 4{\cdot}732 - N_r$$

The value of the constant $N_{\text{max.}}$ has been given by Coulson as 4·680 for the condensed polynuclear hydrocarbons. Recently Moffitt (*Trans. Faraday Soc.*, 1949, **45**, 373) has obtained the value $3 + \sqrt{3} = 4{\cdot}732$ for the hypothetical radical $C(CH_2)_3$, which value we adopt for our discussion. It has been found (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 533) that for certain purposes it is better to use different values of $N_{\text{max.}}$ according as the relevant carbon atom is a primary, secondary, or tertiary one. In the present discussion, however, we have used the tertiary value $N_{\text{max.}} = 3 + \sqrt{3}$ throughout both for simplicity and for convenience; for it seemed desirable to include CH_3 in the comparison and this would not fit immediately into the above authors' scheme.

The diagrams (Figs. 1 and 2) show values of bond orders along bonds, free valences on arrows, and odd-electron densities at atoms. Values at positions not marked follow from symmetry. Hydrogen atoms are omitted altogether. In Fig. 3 fractional orders of bonds are represented schematically. Only portions of molecules are shown; values at the remaining portions again follow from symmetry. The diagrams of Fig. 4 allow a comparison of V.B. and M.O. results for free valence at the methyl carbon. These V.B. results were published by Pullman (*loc. cit.*) (P.B.B. denotes that Pauling, Brockway, and Beach's definitions of bond orders were used to determine free valences).

Extension to Diradicals.—The determination of free valence from calculated bond orders has also been carried out for certain meriquinones. Some of these compounds may exist as diradicals but at low temperatures they exist in a singlet diamagnetic state.

Fig. 5 shows *p*-benzoquinone dimethide (I) and its diradical (II) which have been discussed by Coulson, Craig, Maccoll, and Pullman (*Discuss. Faraday Soc.*, 1947, **2**). For (I) they find the free valences of the ring nuclei are much the same as in benzyl or diphenylyl; but the values of free valence at the end carbon nuclei are unusually high, as for a free radical. If the molecule were originally formed as the diradical (II) it would be in a triplet state, the two free electrons having unpaired spins. For this form of the molecule the above authors report free valences differing little from those of (I). They conclude therefore that the triplet is not much more reactive than the singlet ground state.

We extend our considerations to the more complex compounds of meriquinone type, *G*, *H*, *J*, *K*, in order to investigate how far we are justified in describing them as diradicals. The

FIG. 1.

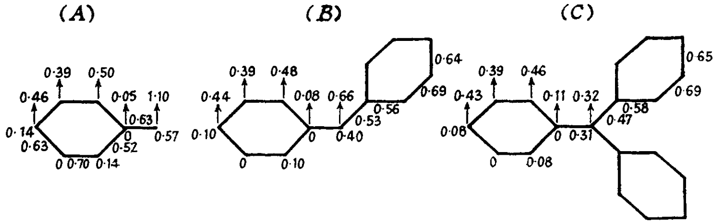


FIG. 2.

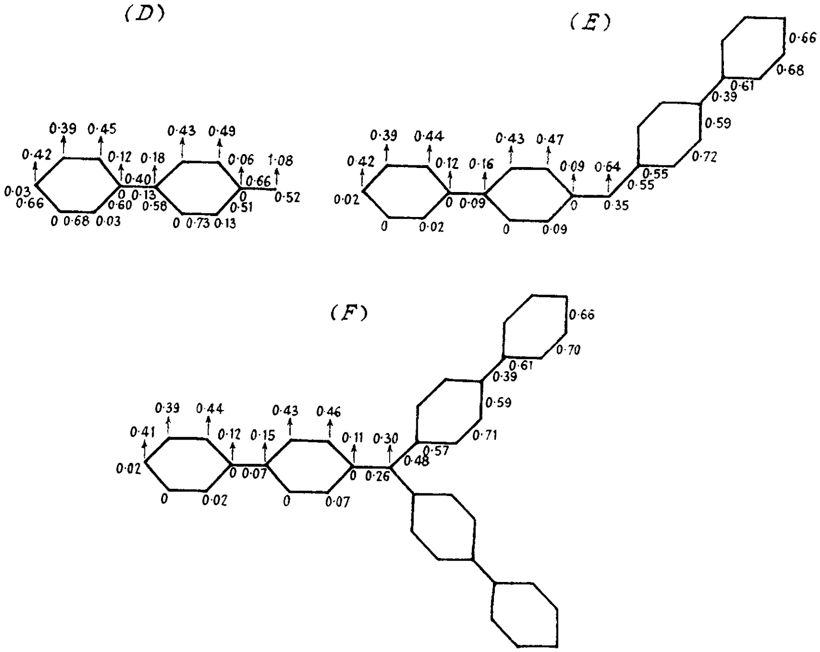
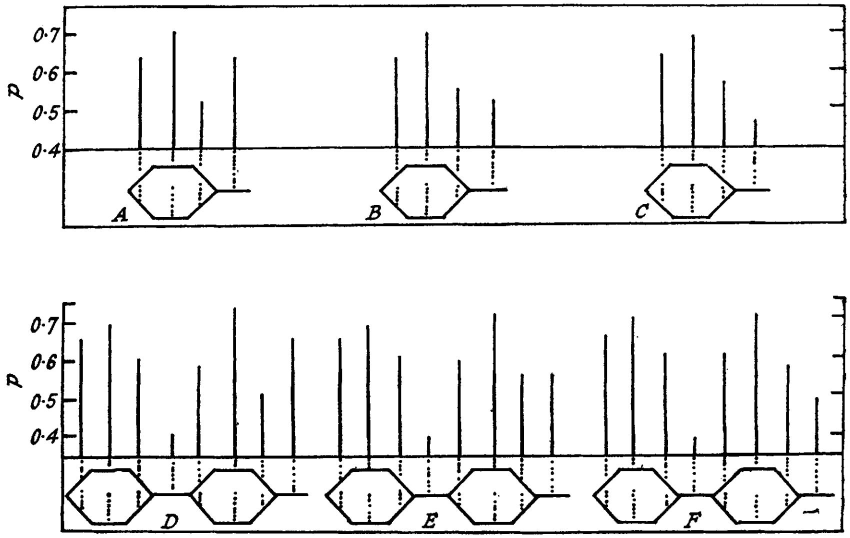


FIG. 3.



calculated bond orders will decide whether the hexagons should be of quinonoid or benzenoid type. The nature of these rings will in turn determine whether the structural diagram requires an odd electron on the methyl carbon; for if the central ring has an aromatic bond diagram, a free electron is required as in (II), which does not arise from a quinonoid ring as in (I). The greater reactivity at the methyl carbon atom may be due to a pair of loosely bound electrons, in the sense in which it depends on the odd electron in a free radical. However, in terms of the M.O. treatment, the odd electron in a free radical is clearly distinguished from other conjugation electrons by having an orbital energy value $\varepsilon = 0$, which cannot arise in these compounds. Each of the molecules G to K contains an even number of mobile electrons, the energy value $\varepsilon = 0$ does not occur, in the ground state all bonding orbitals are doubly filled, and all anti-bonding orbitals are empty. Nevertheless, a level with a small ε value exists in all four compounds; this means they each have a pair of electrons whose spins are paired but whose binding energy is approximately zero. These electrons do not actively participate in bonding but behave rather like isolated electrons. To this extent they can be associated with the odd electron pair shown in (II) (Fig. 5). We have therefore calculated the probability distribution of the pair of π-electrons with small orbital energy.

FIG. 4.

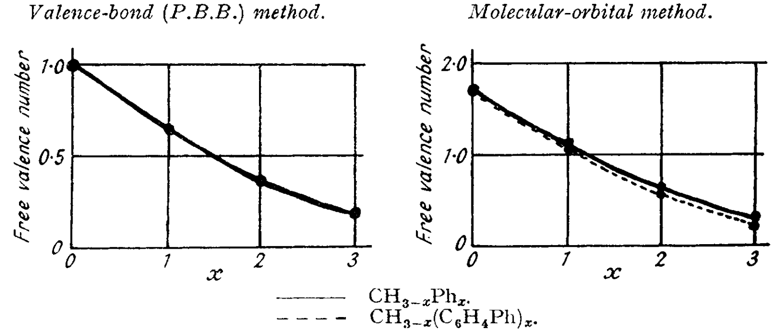
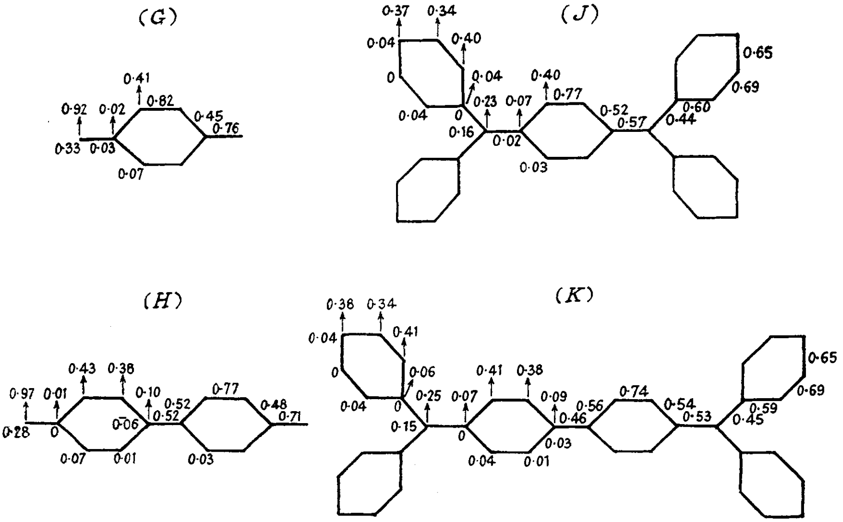

Valence-bond (P.B.B.) method. *Molecular-orbital method.*

FIG. 5.

FIG. 6.



For compounds G and H similar results for bond orders and free valence according to the

M.O. method have already been published by Pullman and Pullman (*J. Chim. phys.*, 1949, **46**, 212). These authors demonstrated also how, with increasing conjugation, *i.e.*, increasing the number of double bonds through a series of similar compounds, the maximum value of free valence may increase or decrease according to the particular way in which hexagons are added to the simpler radicals.

The compounds investigated are shown schematically in Fig. 6, the positions of carbon atoms only being indicated. Again the bond orders are shown along bonds, free valences on arrows, and electron densities of the nearly non-bonding electrons at atoms.

In these calculations the molecules have been assumed planar, although steric hindrance to planarity certainly exists. Consequently our calculated values must not be given an absolute significance, but should be considered as giving relative values only among these compounds.

DISCUSSION

(a) *Substituted Methyl Radicals.*—The older theory of reaction ascribed the reactivity of a radical to the presence of an odd electron at a specific centre. This is clearly inadequate, for it is a characteristic property of the radicals under discussion that their reactivity is not localised at one particular atom. According to the M.O. theory, no π-electron is thus confined, but rather all conjugation electrons are treated as moving in orbitals extending over the whole molecule, *i.e.*, they are given a certain probability density at all atoms. In alternant hydrocarbons (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193), the electron density in the ground state is uniformly unity and therefore can give no indication of a varying reactivity. We may associate the " free " electron with the non-bonding one found in M.O. theory. It is the density distribution of this electron which would be expected to give a better estimate of the reactivity than is derived from the picture of a free electron confined to a single site. This zero-energy electron has assumed further significance since Longuet-Higgins (*loc. cit.*) has recently predicted that a close parallelism must exist between charge distributions due to unpaired electrons of zero orbital energy and those obtained from a consideration of only the principal resonance structures. He pointed out, however, that usually calculations of odd-electron density will be more effective for predicting reactivities.

Our calculations of odd-electron density show that its alternating character, observed in chain molecules with an odd number of carbon atoms, persists in these radicals. Starting from the methyl carbon the odd electron is to be found only on alternate nuclei, but the uniformity of its distribution over these centres is destroyed. The odd-electron density shows a maximum at the methyl carbon atom, and the probability of finding this electron on alternate nuclei decreases as we recede from this atom. The odd-electron density at the methyl carbon atom also decreases with increase in x, *i.e.*, with increasing phenylation. Furthermore, there is a slight reduction in this electron density with the transition from phenylmethyls to diphenylylmethyls.

No exact parallelism exists between variations in odd-electron density and free valence. However, throughout both systems of radicals there is a comparatively high free valence and odd-electron density at the methyl carbon atom with relatively low values at all its neighbours. The decrease in odd-electron density at the methyl carbon is accompanied by a simultaneous reduction in free valence there. Thus in the simpler structures, $x = 1$, the free valence has a maximum value for the whole molecule there, but its value is diminished rapidly with the passage to the more complex molecules in the group.

The loss in free valence at the methyl nucleus in passing through both the phenyl and the diphenylyl series from $x = 1$ to $x = 3$ is to some extent compensated by a slight increase in free valence at atoms which are its nearest neighbours, where the free valence is consistently low. In the near rings of A, B, and C the free valences have closely similar values with a minimum at the *meta*-positions. A similar minimum occurs at the carbons in the *meta*-positions in the outer rings of D, E, and F; however, the total variations in free valence in these rings are small, both within each hexagon and within the whole group of diphenylyl compounds. Approaching the rings from the methyl carbon atom we find an extremely low free valence on the first ring nuclei. In D, E, and F the free valences decrease considerably in passing along each hexagon away from the methyl carbon, and the values again lie close to one another in all three compounds.

The overall picture is the close similarity of the variations in free valence within the phenyl- and the diphenylyl-methyls. In both groups the initially outstanding value of free valence at the methyl carbon atom is decreased rapidly through approximately the same sequence of numerical values, as phenylation is increased.

The calculated bond-order distribution may be related to the classical structural diagrams for these compounds by following the changes in fractional bond order around the rings. If the variations in bond-order values around a conjugated ring are small, we have a situation rather as in benzene, where, according to the M.O. theory, all bonds have a fractional mobile order $p = 2/3$. The conventional way is, however, to show a benzene ring with three double and three single bonds alternating with one another. A quinonoid hexagon is suggested by a bond order which for the central bonds is nearly double and greatly exceeds the orders of the end bonds of the ring.

The actual values as well as the variations in bond order within the near rings are very similar in the phenyl and diphenylyl compounds (Fig. 3). In each group for $x = 1$ the changes of bond order inside a ring are large, suggesting four single and two double central bonds; for $x = 3$ the values in the near rings have become more nearly uniform and are, numerically also, close to the corresponding bond orders in benzene. Increased phenylation modifies therefore the quinonoid nature of the first rings to a benzenoid one. The quinonoid quality of the near rings, characterised by greater differentiation in bond orders, is more marked throughout in the diphenylyl compounds than in their analogues of the phenyl group. In the diphenylylmethyls the outer rings remain aromatic under successive addition of phenyl groups from $x = 1$ to $x = 3$.

The differences in bond order between corresponding bonds of the phenyl molecules or the diphenylyl ones are small, with the exception of the methyl bonds. Together with the trend towards aromatic character of the inner rings this bond changes its order considerably, from a double-bond value to a much smaller single-bond value.

Finally, the graphs (Fig. 4) show that essentially similar results are obtained from calculations by the valence-bond technique as reported by Pullman for the group *A*, *B*, and *C*. While the actual values differ somewhat from our calculated free valences, both methods obtain equivalent sequences of decreasing free valence. Similar curves were published by Coulson and Jacobs (*Dicuss. Faraday Soc.*, 1947, 2), but the present values include the results for the diphenylyl radicals *D*, *E*, and *F* and have also been corrected for the more recently established value of $N_{\text{max.}}$ $(3 + \sqrt{3})$.

(b) *Diradicals.*—Our approach to the investigation of the diradical nature of the meri-quinones falls into three separate aspects which are, nevertheless, closely interconnected. First, we have determined the bond orders of all links in the ground state. Of particular interest are the orders of the ring bonds, for they decide whether the diagrams are of type (I) or (II). The calculated bond-order differences in the central hexagons of *G* and *H* are considerable, and their actual numerical values also warrant a quinonoid structural diagram. As phenyl groups are added to give compounds *J* and *K*, these differences in bond order are smoothed out; all ring orders approach the benzene value, giving a more aromatic character to these rings. The outer phenyl groups of *J* and *K* show only small deviations of bond order from the benzene value and so may be assigned an aromatic bond diagram.

Secondly, we have calculated the probability distributions of the pair of electrons whose orbital energy is small; their energy value justifies the treatment of them as little concerned in bonding, *i.e.*, as almost free electrons. This pair is mostly concentrated at the methyl carbon atoms but on increasing phenylation (transition from *G* to *J* and *H* to *K*) this concentration is reduced to almost half its original value. Substitution of a phenyl group therefore tends to destroy the apparent existence of the free electrons on the end carbons.

A glance at Fig. 6 shows that these almost free electrons also give rise to an alternating distribution going outwards from the methyl carbon atoms in *J* and *K*. This alternation of high and low electron density becomes more pronounced also on passing inwards from the methyl nucleus in changing from *G* to *H*, and from *J* to *K*.

The third and last aspect which has been examined concerns the free valences, in particular at the methyl carbon atoms. In molecules G and H the free valence has clearly a maximum value there. This marked favouring with free bonding power of the methyl carbon nuclei is considerably diminished on substitution of a phenyl ring, indeed the free valence does not remain a maximum there for the whole molecule. We conclude that a large free valence in itself need not adequately describe the reactivity of a particular site in the molecule. The reactive centres of the molecules under investigation are known to be the methyl carbon atoms, even for homolytic reactions. A distinguishing feature is that these atoms are throughout surrounded by very low free valence numbers and have also a high non-bonding electron density compared with their nearest neighbours.

A discussion of the radical nature of these compounds has also been given by Schwab and Agliardi (*Ber.*, 1940, *B*, **73**, 95) who have examined Tschitschibabin's hydrocarbon (K above) and a number of similar molecules. Magnetic measurements had demonstrated that the molecule as a whole is diamagnetic, *i.e.*, that two independent electron spins do not occur. From their measurements of para-hydrogen conversion, however, the above authors concluded that the compound K does show some paramagnetic behaviour. Indeed they find it is as much as 10% diradical in nature.

There certainly exist other factors, however, that influence reactivity, which are not embraced either by the free valence or the non-bonding electron density concept. Indeed a knowledge of the free valence alone may be misleading if used as a guide for predicting reactivity. An example is afforded by the investigation of acenaphthylene due to Coulson and Crawford (*J.*, 1948, 1990). These authors discussed the dimerisation which takes place across the 7 : 8-bond. The large free valence at $C_{(7)}$ and $C_{(8)}$ was considered as theoretical evidence for the greater readiness to form new bonds. A high calculated free valence does, however, also occur at $C_{(3)}$ and $C_{(4)}$, where dimerisation almost certainly does not take place. For if it did, the resulting complex would involve only quinonoid rings, destroying the aromatic nature of the initial naphthalene rings. Thus there is less resonance possible in such an end product which would therefore be of higher energy, *i.e.*, less stable. Free valence alone, they concluded, is an inadequate criterion of reactivity.

Some interest centres on the possibility of a rotation being imposed on a bond that is normally double in these molecules. In the case of compound K, a rotation about the central bond leads to two triphenylmethyl radicals. For the latter the odd-electron density and free valence are evaluated in the earlier part of this paper. Now Longuet-Higgins (*loc. cit.*) has shown that if a diamagnetic alternant hydrocarbon is twisted through a right angle from a planar configuration about a C–C bond that is double in all principal resonance structures, the ground state of the twisted configuration is a triplet.

Seel ("F.I.A.T. Reviews of German Science," Vol. I, p. 89) has investigated the possible radical nature of compounds J and K. He finds that in a planar configuration K is not a true diradical; but in the tetrachloro-derivative the molecule has become twisted through a right angle so that two triphenylmethyls in mutually perpendicular configurations arise. The compound then exists as a mesomeric system of a true diradical. This means that no quinonoid valence structures are required in the ground state, and the compound has two independent radical centres. He further demonstrated (*Z. Elektrochem.*, 1948, **52**, 182) that the fact that the molecule behaves in part like a diradical is not due to some form of equilibrium between quinonoid and diradical forms. Rather it is a question of the de-coupling energy of part of the π-electron system required for a change from a quinonoid to a benzenoid structure.

A further theoretical investigation by the M.O. method of this problem has been given by Diatkina and Sirkin (*Acta Physicochem. U.R.S.S.*, 1946, **21**, 23).

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