Oxidative Coupling of Phenols. Part 8.[1] A Theoretical Study of the Coupling of Phenoxyl Radicals

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A theoretical study is described of the stereochemistry of mutual approach of two phenoxyl radicals. Both the CNDO and MINDO/3 methods are used and Morse curves are calculated for each reaction where the reaction co-ordinate is the interplanar distance. From a number of possible stereochemistries the most favoured involves an initial coaxial sandwich geometry, which undergoes conformational changes as bond formation between the two radical species occurs. The most energetically favoured path, which is given by the staggered form of the rings, leads to *ortho-para*- and *ortho-ortho*-coupled products. Of lesser importance is a head-to-tail approach which can lead to either *ortho-ortho*-carbon coupling or *para*-oxygen coupling. The *para-para*- and *ortho-para*-couplings obtained from the eclipsed form are of still smaller significance.

Part 7[1] dealt with the calculation of the spin densities at various positions in the phenoxyl radical. A variety of calculations was made and a number of geometries investigated. It was concluded that geometry is probably more important a factor than is basis-set size in arriving at a satisfactory theoretical description of the spin-density distribution in this radical. This paper takes the problem further and we here present the results of a study of the mechanism of the coupling of two phenoxyl radicals to yield the various coupled products.

Although intermolecular interactions have been extensively investigated on a number of theoretical levels and for a range of systems,[2-5] the dimerisation of phenoxyl radicals has never been subjected to a theoretical investigation. The case of the isoelectronic benzyl radical has, however, been studied and the results showed that, at large separation, the most favourable approach of radicals leading to dimerisation was one in which a sandwich-type configuration was adopted.[6] Indeed, at 2.9 Å separation this geometry was shown to be 22 kcal mol^{-1} more stable than two isolated benzyl radicals.[6] It has been suggested[7] that a similar attractive force between two phenoxyl radicals may account for the very low (frequently negative)[8,9] energy of activation observed in the dimerisations of aryloxyl radicals and may be indicative of some sort of complex formation, possible charge-transfer in nature. If such a metastable complex exists, however, its lifetime must be shorter than 10^{-7} s, since no contribution to line-widths from such a complex was observed in an n.m.r. study of aryloxyl dimerisations.[9]

The following sections describe the results and conclusions drawn from a semi-empirical SCF MO study of the dimerisation of the phenoxyl radical.

Method

The number of two-electron integrals in an n-orbital system is proportional to the fourth power of n. Hence, single-zeta UHF *ab initio* calculations on the dimeric species are just possible for single unperturbed systems. Double-zeta calculations would, however, be preferred, since a better representation of the spin-density distribution in the phenoxyl radical is obtained with these calculations[1] but are impossible due to restrictions on the size of the basis set. In consequence, semi-empirical techniques rather than *ab initio* MO methods were used to study the dimerisations of phenols. The CNDO and MINDO/3 semi-empirical methods employed in the present work have been fully described previously[10,11] and the standard parameterisation process[12,13] was adopted. In the CNDO approach Dewar's half-electron method[14] was employed to obtain a pseudo-closed-shell electronic configuration for the radical.

Results and Discussion

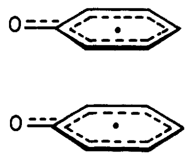
The spin-density distribution in the phenoxyl radical using the INDO optimised geometry[15] in the CNDO and MINDO/3 formalisms is given in Table 1. From the CNDO method, spin densities are obtained by simply squaring the coefficients of the p-orbital in the singly occupied molecular orbital (SOMO). Hence, negative spin densities are not predicted. The results are, however, in reasonable agreement with experiment.[16,17] The spin-density distribution obtained from the UHF MINDO-3 technique is that obtained before annihilation of the major contaminating multiplet and closely resembles the corresponding spin-density distribution obtained from the *ab initio* calculations[1] before such a single annihilation was performed. The overestimation of the hyperfine splitting constants by the MINDO/3 method, as seen from Table 1, is not as serious a fault as it first seems. In the dimerisation process only energy changes are important and since the energy minimisation of the molecular orbitals is carried out prior to spin annihilation (as with the *ab initio* calculations), then the total energy does not change on the annihilation. We expect that the results for these radicals would be improved if spin-extended MO methods were employed, where energy minimisation is performed after the single annihilation.

In any theoretical investigation of chemical reactions, the energy of interaction of the reacting species must be calculated over a wide range of separation distances. Quantum mechanical methods based on the Hartree–Fock approximation, especially the semi-empirical MO methods, are less reliable in different distance ranges of application, partly

Table 1. Spin density and proton hyperfine interactions in the phenoxyl radical from CNDO and MINDO/3 calculations

	CNDO	MINDO/3	Observed[a]
a_2 (G)	5.20	−10.64	−6.6
a_3 (G)	0.10	7.56	1.96
a_4 (G)	10.25	−16.66	−10.4
ρ_O	0.25	0.32	
$\langle S^2 \rangle_{BA}$		0.96	0.75

[a] Refs. 16 and 17.



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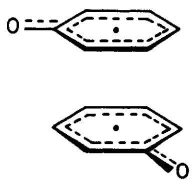

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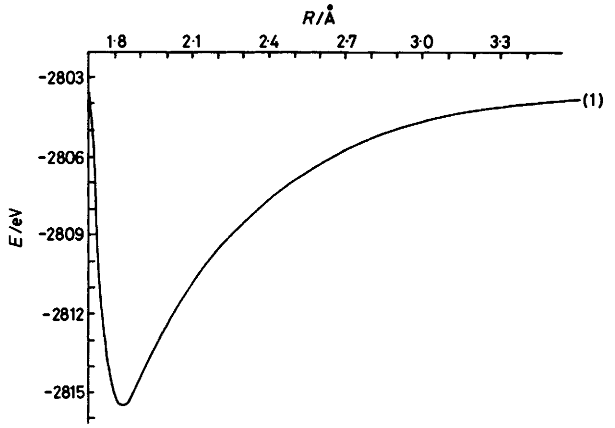
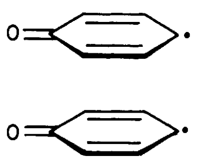


Figure 1. Variation in energy with interplanar separation, *R*, for the sandwich-type complex (1) from CNDO calculations

because the methods were originally parametrised with respect to experimental observations on molecules, containing ' normal ' interatomic distances, *e.g.*, the MINDO-3 method does not reproduce well the heat of formation of the initially formed cyclohexadienone dimers[8] obtained by coupling of two aryloxyl radicals. In the initial parametrisation of MINDO/3, the two-electron integrals were calculated by the method of Ohno[18] and Klopman.[19,20] Use of other recipes, such as that due to Mataga and Nishimoto,[21] brings about no improvement in the heat of formation. Because of these difficulties we have constructed a new representation of the two-electron two-centre integral $\gamma_{\mu\nu}$ for use with MINDO/3. This method for evaluating this type of integral was originally devised for solid-state calculations[22] where long-range interactions are also very important. A full description of the above expression for $\gamma_{\mu\nu}$ is given in ref. 22. The use of this expression for the integral $\gamma_{\mu\nu}$ yields much better results for the heat of formation of the cyclohexadienone dimers than does any previous method of integral evaluation. A full re-parametrisation of MINDO/3 was however not effected.

The Dimerisation of Phenoxyl Radicals.—There are three possible modes of coupling in the oxidation of phenol to form a new C–C bond, *i.e.*, *para-para-*, *ortho-para-*, and *ortho-ortho-*coupling. Two sandwich-type complexes (1) and (2) can adequately account for these The mechanism of bond formation between the two rings at the required positions is more obvious by drawing the canonical forms as shown below. Thus, (3) and (4) lead to *para-para-* and *ortho-ortho-*coupling, whilst (5) gives rise to *ortho-para-*coupling. *ortho-ortho-*Coupling can clearly also arise from (2) schematically through two *ortho-* canonical forms (6). A Morse curve which corresponds to the mutual approach of two phenoxyl radicals and having geometry based on (1) was calculated from the CNDO method. The curve is shown in Figure 1. Since the dimeric species, with all spins paired, is a singlet state, the expectation value of S^2 is 0. No spin contamination thus occurs. The Morse curve



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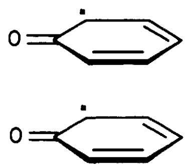

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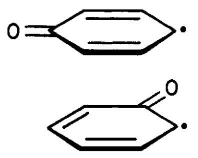

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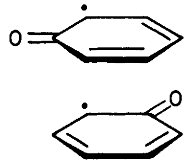

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shows a minimum in energy when the interplanar separation is 1.85 Å. Within this distance the repulsive forces rapidly predominate and the curve rises sharply. The bottom of the well, in fact, corresponds to the formation of a new single bond between the two *para-*carbons of the phenoxyl radicals and this result is clearly shown by an analysis of the density matrix. Two unpaired electrons have become localised between the two *para-*carbon atoms of the radicals. In terms of electronic states one could have here either singlet or triplet: which was the preferred state would then depend on their mutual splitting. A triplet–singlet crossover might then result.

The onset of bond formation is precipitated mainly by the π-type MOs governed by the symmetry of the situation. This interaction becomes strong in the well and results in energy-level crossings between the pseudo-bonding intermolecular orbital formed from one pair of MOs and the pseudo-antibonding intermolecular orbital of another. Close to the minimum in the Morse curve, the mixing involves other orbitals from each radical.

The canonical form (4) which illustrates an *ortho-ortho-*coupling of two phenoxyl radicals by the eclipsed stereochemistry of approach, appears to be a relatively unimportant pathway, as evidenced by the density matrix for this composite system; this reveals only very weak interactions between the two *ortho-*positions. It is not at this stage suggested that the dimer in the well represents the *final* conformation of the dimeric cyclohexadienone intermediate for *para-para-*coupling of phenoxyl radicals. The conformational changes will be discussed later. It should be noted that close scrutiny of the Morse curve reveals no evidence for the formation of an intermediate metastable complex at any separation, in contrast to that reported for the dimerisation of benzyl radicals.[6] Any such complex would have to involve charge-transfer between the two identical reacting species and in valence bond terms, this ionic contribution could only be a minor part of the total wave function. A *full* consideration of the reaction path, however, would indeed require a multi-configuration treatment in which such charge transfer excited states would undoubtedly play a part. We believe, however, that the present calculations embody the essentials of the reaction path and that no metastable complex occurs.

The Morse curve for *ortho-para-* (and *ortho-ortho-*) coupling illustrated by (2) is exactly analogous to that for (1). Again, no evidence for the existence of an intermediate sandwich complex was found. Examination of the density matrix for the dimeric system (2) indicates that the strongest interactions arise between the *ortho-* and *para-*positions which lie in direct

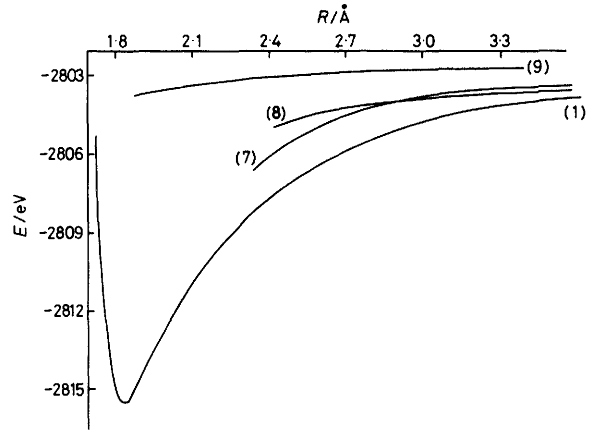
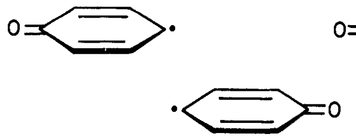


Figure 2. Variation in energy with distance between coupling atoms, R, for alternative modes of approach for complexes (7)—(9) and for comparison sandwich-type complex (1), from CNDO calculations



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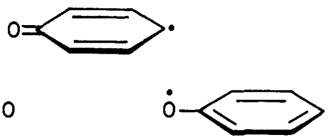

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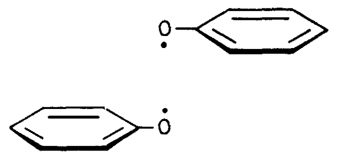


(9)

alignment with one another. There are two identical pairs of these interactions. In addition to this, however, there is also a significant interaction between the remaining two *ortho*-positions, which are also in direct alignment. This latter force is much stronger than the corresponding one between adjacent *ortho*-positions in (4), but weaker than the interaction between the adjacent *ortho*- and *para*-positions in (5). Hence, all the coupled biphenyls could conceivably arise from the modes of coupling described above.

Despite the absence of evidence from these calculations for the formation of an intermediate complex prior to ' final ' bond formation, the coaxial sandwich-type modes of approach are shown to be preferred to stereochemical configurations not involving a sandwich system. For example, an alternative mode of approach leading to *para-para* coupling (7) is shown. Alternative conformations for *para*-oxygen and oxygen–oxygen coupling are (8) and (9), respectively. The Morse curves appropriate to these modes of approach are given in Figure 2. Included for comparison is the Morse curve for *para-para*-coupling with the radicals in a coaxial configuration. In addition to these alternative modes of approach, we investigated a number of other configurations. For brevity we do not detail the results here but none proved to be more favourable than the sandwich arrangement. In these isomeric systems, the rings are rotated with respect to one another or tilted with respect to one another or both effects were combined; the overlap between the $p\pi$ type orbitals is smaller than in the cases of parallel planes depicted in (7)—(9). These modes of approach therefore, represent the most favourable non-coaxial approaches for each type of coupling (C–C, C–O, and O–O) which have been studied to date.

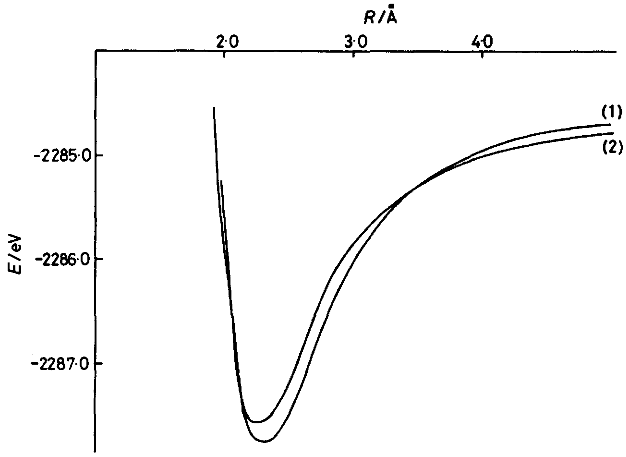


Figure 3. Variation in energy with interplanar separation, R, for the sandwich-type complex in eclipsed (1) and staggered (2) conformations from MINDO/3 calculations

In summary, therefore, we found no evidence for a ' transition-state complex ', although this has been postulated by various workers.[23] Instead, we found a chosen stereochemistry of approach, the radicals preferring to unite in a sandwich-type configuration prior to final bonding. Such a conformation [as in (1) or (2)] maximises the HOMO–SOMO–LUMO interactions. Opposing this is the increased nuclear repulsion energy of the coaxial conformations relative to the non-coaxial modes of approach. We would expect, therefore, that as bonding proceeds further, this balance may well change and further conformational changes take place which rotate the rings. This will be discussed in context later.

We thus have a view of the coupling reaction as one which ' runs downhill ' from reactants to products. There is a large class of reactions of this type which do not possess an activation energy and it is not difficult to envisage that thermodynamic factors rather than kinetic effects will dominate the course of the reaction. In processes of this kind, however, it is difficult to obtain the precise location of the ' transition state ' along the reaction co-ordinate. If the activation enthalpy is indeed zero, then it is only the activation entropy which can aid in locating the form and dimensions of the ' transition state '. Till now, the problem has remained one of some difficulty.

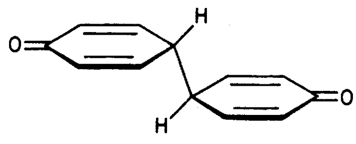
Since the CNDO technique does not, in general, yield reliable total energies, the less approximate and better parametrised MINDO/3 method was next used in order to reinvestigate and confirm which of the two coaxial sandwich modes of approach, (1) where the two phenoxyl radicals are in an eclipsed conformation or (2) where a staggered conformation is present, is preferred. Figure 3 shows the superposition of the two Morse curves obtained by the MINDO/3 method for the approach of the radicals given by (1) and (2). The results indicate that, in the initial stages of dimerisation, there is a distinct preference for the radicals to approach each other in such a manner as to give rise to *ortho-para-* or *ortho-ortho-*coupling. This can be rationalised in terms of the charge distribution of the phenoxyl radical (Table 2). There is an expected polarisation of charge towards the oxygen atom leaving C(1) with a large positive charge. The *ortho-* and

Table 2. Charge distribution in the phenoxyl radical

C(1)	+0.40
C(2)	+0.03
C(3)	−0.03
C(4)	+0.03
O	−0.45
H(2)	+0.01
H(3)	+0.01
H(4)	+0.01

para-carbon atoms carry a small positive charge while the *meta*-carbon atoms possess a small negative charge. Therefore, when the two phenoxyl radicals approach each other the initial dominant long-range repulsions between the oxygens and between the pair of carbon atoms will tend to favour *ortho-para*- and *ortho-ortho*-couplings (2). The major interactions between the rings, as in the CNDO calculations, are those between adjacent *ortho*- and *para*-positions, with the *ortho-ortho*-interaction being weaker but still significant. An identical orbital mixing pattern to that of the CNDO calculations was also apparent. As the radicals fall further down into the well, they reach a minimum at *ca.* 2.2 Å in each case (*cf.* 1.9 Å in the CNDO calculations) which reflects the greater extent to which MINDO/3 takes account of electron-repulsion terms. However, the dimer never reaches the bottom of the well and new, important, configurational changes assert themselves. Increasing nuclear-repulsion energy effectively offsets the bonding and causes the two rings to rotate away from each other and adopt an alternative conformational change once the contribution from new bond formation is constant. This conformational change begins to occur at an inter-ring separation of *ca.* 2.5 Å and involves concomitant rotation of one ring with respect to the other, with collapse of the new bond to its equilibrium bond length. This proceeds until the conformation for the *para-para*-coupled cyclohexadienone intermediate (10) is as shown. Final determination of the optimum geometry of this intermediate (10) is, unfortunately, precluded by the considerable number of intrinsic geometrical variables. However, it is suggested that it probably represents a reasonable estimate of the actual structure of the cyclohexadienone. Conformational analysis indicates that the *ortho-para*- and *ortho-ortho*-coupled cyclohexadienone intermediates have structures similar to (11) and (12), respectively.

Another mode of approach of the two phenoxyl radicals must now be considered. This envisages the mutual approach of radicals (13) in such a manner as to give rise to either *ortho-ortho*- or *para*-oxygen coupling (a head-to-tail approach). The MINDO/3 Morse curve for this mode of approach is given in Figure 4 and is very similar to those curves obtained for (1) and (2) but differs in fine detail. The first point is that the nuclear repulsion energy for (13) is reduced relative to (1) or (2). However, the mutual SOMO–SOMO orbital interactions between the two radicals are also reduced, at least in the initial stages of dimerisation. The major interactions between the two radical species in (13) are between the adjacent *ortho*-positions. *para*-Oxygen coupling is also feasible, since a smaller (relative to the *ortho-ortho*-interactions) but still significant, interaction between the *para*-positions and the oxygen atoms exists. As the radicals approach each other more closely, the strength of the interaction is such that the depth of the well in Figure 4 is greater than either of those for (1) or (2).



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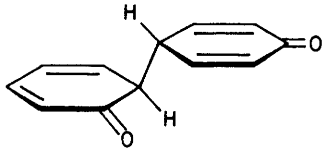

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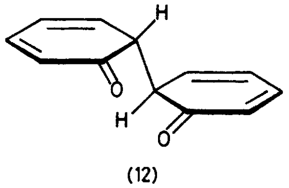

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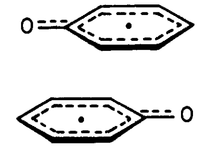

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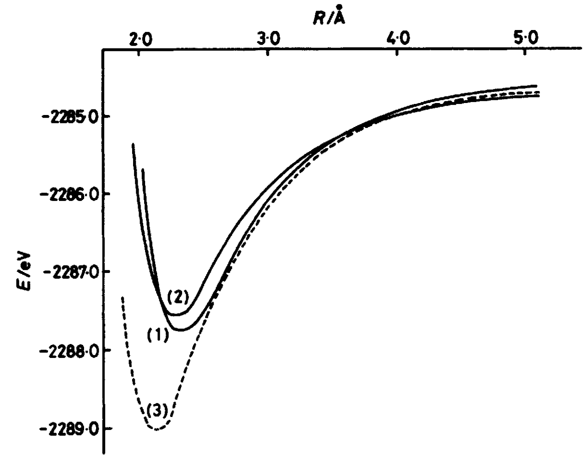

Figure 4. Variation in energy with interplanar separation, *R*, for the sandwich-type complex with a head-to-tail arrangement (13) and for comparison sandwich-type complexes (1) and (2)

In fact, the energy of this minimum is lower than the corresponding energy minima for any of the cyclohexadienones (10)—(12). Thus, these conformations cannot represent exactly (and nor were they intended to) the true shape of these molecules but rather act as a guide to the changes which occur in the molecule as bond formation proceeds. Computational restrictions prevent us from investigation of such effects as non-coplanarity of rings, ring-puckering, and distortion of bonds which would undoubtedly play a role in any conformational changes.

However, the calculations do indicate that, in the initial stages of dimerisation, the head-to-tail approach (13) is more favourable than the eclipsed form (1) but less so than the staggered mode (2). Thus, calculations indicate that (13) must play some role in determining the final product distribution although experimental observations[24] suggest that this is small.

In conclusion, these theoretical calculations indicate that the most favourable direction of approach of two phenoxyl radicals is given by (2), which can lead to *ortho-para*- and *ortho-ortho*-coupled products. These results substantiate the experimental study[24] which showed that these, in fact, were the major C–C coupled products and that very little of the *para-para*-coupled product was formed.

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