Tetrahedron Vol. 38, No. 6, pp. 765 to 775, 1982
Printed in Great Britain.

0040-4020/82/060765-11$03.00/0
Pergamon Press Ltd.

RADICAL PAIRS IN CRYSTALLINE DIBENZOYL PEROXIDE EVIDENCE FOR TRIPLET GROUND STATES

J. MICHAEL MCBRIDE* and MICHAEL W. VARY
Department of Chemistry, Yale University, New Haven, CT 06511, U.S.A.

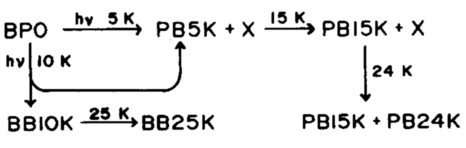
(*Received in U.S.A.* 31 *March* 1981)

Abstract—Zero-field splitting (zfs) tensors and g tensors are reported for two phenyl-benzoyloxyl radical pairs (PB5K and PB15K) and two benzoyloxyl–benzoyloxyl pairs (BB10K and BB25K) in photolyzed single crystals of dibenzoyl peroxide. The g tensors show that in three of the pairs a benzoyloxyl radical has undergone in-plane rotation by about 40°. In PB15K this motion relieves steric repulsion from a CO_2 molecule, and it is suggested that motion in the BB pairs relieves repulsion between radical oxygens in a ground-state triplet radical pair. Spin-orbit coupling is necessary to explain the zfs of PB5K. This explanation requires that the triplet of the electronically excited radical pair lie below the corresponding singlet by an amount which is significant in comparison to the excitation energy. The source of singlet–triplet splitting is discussed briefly and simple VB calculations are shown not to support the above interpretation, although the STO3G and 4-31G basis sets employed are very likely inadequate. Atomic coordinates are reported for crystalline dibenzoyl peroxide.

We previously reported observing a number of radical-pair species in single crystals of dibenzoyl peroxide (BPO) after low-temperature photolysis in an EPR spectrometer and after subsequent warming.[1,2] Among others these included three differently arranged pairs of phenyl with benzoyloxyl (PB) and two differently arranged pairs of benzoyloxyl with benzoyloxyl (BB). The observations are summarized in Scheme 1, where the name of each radical pair includes the temperature at which it appeared. Thus, PB15K denotes a phenyl–benzoyloxyl radical pair which appeared at 15 K.

We noted four peculiarities in this system.[2] (1) Although one would anticipate that BB should represent a more primitive stage of decomposition than PB, its spectrum appears only after photolysis at a higher temperature. (2) While the persistence of the PB pairs may be attributed to interposition of a CO_2 molecule between them, there is no obvious reason why the BB pairs should not easily recombine, even at very low temperature. (3) During the growth of the PB24K spectrum, there is no decrease in the intensity of the PB15K signal, even when this is the only signal present. This suggests that X, which must be a radical pair to yield PB24K thermally at such a low temperature, has no EPR spectrum. (4) The zero-field splitting (zfs) tensor of PB5K is unusual for a radical pair in showing very large departure from the axial symmetry expected for localized radicals separated by a substantial distance.

Because at that time we were unsure of the electronic structure of ground state benzoyloxyl radical, we attempted no detailed interpretation of the structural information present in the g and zfs tensors of these radical pairs. Subsequent analysis of ^{17}O hyperfine splitting has shown the ground state to be a delocalized sigma radical of $^2B_2$ symmetry.[3] In this paper we report accurate g and zfs tensors for PB5K, PB15K, BB10K and BB25K, and our attempt to interpret them.



Scheme 1.

Although our interpretation remains incomplete, it suggests that all of the peculiarities mentioned above may be explained in terms of varying ground- and excited-state spin multiplicities of the radical pairs. Spin multiplicity is one of the most important properties of molecular biradicals and of radical pairs. While a number of conjugated and non-conjugated molecular biradicals are known to have triplet ground states,[4] it is commonly assumed that radical pairs have singlet ground states, if their separation is small enough for the singlet–triplet designation to be appropriate.[5] At greater separation the singlet and triplet are so nearly degenerate that they mix, and the resulting pair-of-doublet states provide a more appropriate description of the system.[1,6] Most CIDNP observations have been consistent with singlet ground states, at least for the time-average interaction within a pair of mobile radicals.[7]

Even if radical pairs are ground state singlets, the splitting may not be large on the scale of bond energies, because the radical-pair and biradical mechanisms of CIDNP require singlet–triplet mixing by weak magnetic interactions. The observability of radical-pair EPR spectra at very low temperature confirms that the singlet does not lie far below the triplet in many static pairs, and it raises the possibility that the triplet may sometimes be the ground state.[8] Indeed Flossman, Westhof, and Mueller used a fortuitous degeneracy between S and T_{+1} at the field for 9 GHz EPR absorption in an elegant demonstration that the triplet lies $0.31\ cm^{-1}$ (0.9 cal/mole) below the singlet for a pair of radicals separated by about 6Å in x-irradiated 1-methyluracil at 95 K.[9] This seems the strongest evidence for existence of a radical pair with a triplet ground state. Other workers have found systems in which the singlet is favored by a similarly small margin.[10]

Since we will propose that singlet–triplet splittings in some of our radical pairs are substantially larger than this, we should review briefly the quantum mechanical basis for singlet–triplet splittings.[11] The most important sources of electronic energy in atoms or molecules are the kinetic energy and the coulombic energies from electron-nuclear attraction and from electron–electron repulsion. The first two of these are one-electron properties, while the third obviously depends on correlation in pairs of electron positions.

In a one-electron system only the first two sources are relevant, and the ground state electronic wave function assumes a shape which minimizes the energy by balancing electron-nuclear attraction (which is improved by contracting the wave function toward the nucleus in an atom, or toward the nuclei and into the overlap region in a molecule) against electron kinetic energy (which is lowered by spreading out the wave function, so as to reduce its curvature).

When there are several electrons in a system, coulombic repulsion keeps them apart. It thus reinforces kinetic energy in tending to spread the wave function away from the nucleus in an atom or away from the nuclei and the overlap region in a molecule. Two electrons cannot stay apart from one another if they are both concentrated near the same point.

In systems with closed-shell ground states the one-electron energies for various electronic wave functions are so different that the Pauli principle must be satisfied by coupling spins into an antisymmetric singlet state so that all electrons may profit from this difference. When the one-electron energy differences do not strongly favor the singlet state, however, the spins may couple into a spin-symmetric triplet state. The resulting spatial antisymmetry of the two-electron wave function reduces electron–electron repulsion. When, as in atoms, the spatial orbitals which contain one electron are orthogonal, spatial antisymmetry can reduce this repulsion without affecting either the kinetic energy or the electron-nuclear attraction (but see the discussion of second-order effects below). This is the source of the increased stability of high-spin states, which is expressed in Hund's Rule.

The preceding time-honored rationale for Hund's empirical Rule has recently been brought into question by recognition of an apparent paradox.[11b,c] Good atomic wave functions, such as those for excited helium atoms, show that electron–electron repulsion is in fact *greater* in the triplet than in the singlet state for a particular electronic configuration. This observation is, however, easily reconciled with the truth that the fundamental source of greater stability for triplets is the tendency of electrons to stay apart in an antisymmetric two-electron function. The reconciliation can be based on qualitative consideration of the physical model or, equivalently, on perturbation theory and the Virial Theorem, as we show in the following two paragraphs.

Since spatial antisymmetry tends to keep electrons apart in the triplet state, electron repulsion is less influential than in the singlet in spreading the wave function away from the region of favorable nuclear attraction. Thus to achieve balance among the three sources of electronic energy, the triplet wave function must be more compact than that of the corresponding singlet. The triplet must have higher kinetic energy and more electron-nuclear attraction. It is easy to imagine, if difficult to predict, that in achieving balance the triplet may shrink to the point that repulsion is greater than it would be in the expanded singlet. Still, the reason the shrinkage takes place at all is that the triplet's electrons tend to stay apart, other things being equal.

The standard rationale for Hund's Rule considers only first-order perturbation and assigns the singlet and triplet different repulsion but the same kinetic and nuclear attraction energies. This cannot be correct since the Virial Theorem links average kinetic energy with average potential energy, so that two states cannot have the same kinetic energy and different potential energies. When, in second order, the form of the triplet wave function is allowed to change, the kinetic energy increases and the first-order stabilization from reduced repulsion is transformed into increased nuclear attraction. The first-order stabilization is very close to the true singlet-triplet difference, and its ultimate appearance in an unusual guise should not cloud the fact that the fundamental difference between the singlet and the triplet is the spatial antisymmetry of the latter, which keeps electrons apart, other things being equal.

When electrons are confined to different regions of space, their mutual repulsion is already small, so that the triplet can gain little over the singlet by reducing the repulsion further. This is so in molecular systems, like cyclobutadiene, where the degenerate molecular orbitals share no atoms,[4b,12] and also in radical pairs, where in the important valence-bond wave functions the two odd electrons are on different radicals.

The singlet–triplet splitting in a radical pair depends on the exchange integral.[11] The one-electron contribution comes from kinetic and nuclear attraction energies in the overlap region and is scaled by the overlap integral. The two-electron contribution comes from repulsion between electrons in the overlap region. Although the nuclear attraction term usually dominates, both the one-electron integrals and the scaling factor approach zero as the radical orbitals approach orthogonality, while many repulsion integrals persist. Thus for appropriate radical orientations it is usually possible to have a triplet ground state, although the splitting may be small, and the orientations narrowly circumscribed.

RESULTS

The X-ray and single crystal methods used in this work were described in our previous report,[2] but detailed results were omitted because the structure was not discussed. The space group of BPO is $P2_12_12_1$, $a = 8.992(2)$, $b = 14.322(3)$, $c = 9.446(2)$ Å. Fractional coordinates for the atoms of one molecule (the asymmetric unit) are given in Table 1, with the previous numbering scheme.[13]

ZFS and g tensors for PB5K, PB15K, BB10K and BB25K were determined by least-squares fitting of from 85 to 193 observations made by rotating two crystals mounted in different general orientations. The mounting angles were refined on the basis of agreement among the zfs tensors of four symmetry-related BB pairs in the orthorhombic crystal.[2] ZFS splittings were weighted both for error in measurement and for sensitivity of the splitting to mounting errors, while g shifts (from DPPH) were weighted only for measurement error. The data were fit by the Hamiltonian $\mathbf{H} = \beta H\cdot\mathbf{g}\cdot S + S\cdot\mathbf{D}\cdot S$, using an iterative technique described previously.[6] Errors in eigenvalues and in eigenvector directions for each tensor were estimated by refinement in a coordinate system in which the tensor is diagonal, according to a procedure devised by Walter.[14]

The observed zfs tensors are presented in Table 2, and the observed g tensors in Table 3. The cartesian coordinate system is based on the *a*, *b* and *c* crystallographic axes. For interpretation it is useful to separate the experimental g tensor into contributions from the individual radicals. This is possible because the g tensor of a radical pair is simply the average of the individual g

Table 1. Fractional crystal coordinates ($\times 10^4$) for BPO[a]

Atom	X	Y	Z
C1	1243(4)	-2741(2)	3748(4)
C2	2164(5)	-2328(2)	4715(5)
C3	2272(4)	-1345(2)	4741(4)
C4	1473(4)	-0827(2)	3774(3)
C5	0561(4)	-1261(2)	2815(4)
C6	0454(4)	-2236(2)	2814(4)
C7	1540(4)	0225(2)	3689(4)
C8	3572(4)	1887(2)	3915(4)
C9	4524(5)	4334(2)	2925(5)
C10	4492(5)	3369(3)	2982(5)
C11	3567(4)	2917(2)	3932(4)
C12	2689(4)	3445(3)	4827(4)
C13	2745(4)	4405(2)	4763(5)
C14	3650(4)	4836(2)	3825(5)
O15	2445(3)	0550(1)	4770(3)
O16	0946(3)	0705(1)	2856(3)
O17	2453(3)	1551(2)	4745(3)
O18	4397(3)	1385(2)	3274(3)

[a] Estimated standard deviation of the final digit given in parentheses. R(wtd) = 5.4% for 801 3σ reflections and 163 parameters. See References 2 and 13.

tensors.[1,6] In the PB pairs separation is easy, because the g tensor of the phenyl radical is known and nearly isotropic,[15] and its approximate orientation is known from hydrogen hyperfine splitting in PB5K.[2] The first two entries of Table 4 give the g tensor eigenvectors for the benzoyloxyl radicals of the PB pairs. The benzoyloxyl eigenvalues for PB5K and PB15K are closely similar (although the difference is beyond our estimated error), and the isotropic values (2.0109 and 2.0122) bracket those of BB10K (2.0116) and BB25K (2.0115).

Separating the g tensors of BB is more difficult because both constituents are strongly anisotropic and neither has a known orientation. The similarity in isotropic g values suggests strongly that both BB pairs consist of radicals with the same g tensor found for benzoyloxyl in PB5K and PB15K. In principle one could adjust six parameters (three eulerian angles describing the orientation of each radical in the crystal frame) to make two g tensors, of known magnitude, combine to give an average tensor with the observed magnitude and orientation. In practice it is much simpler to adjust the three angles which orient one radical relative to the other, average their g tensors, and diagonalize, until the eigenvalues match those observed. It is then possible to find four rotations of the rigid pair which give agreement between calculated and observed eigenvectors. One is left with the problem of identifying which rotation is appropriate for the system at hand.

When this approach was applied to BB10K and BB25K (assuming benzoyloxyl eigenvalues of 2.0238, 2.0080 and 2.0030, the average of PB5K and PB15K), mutual radical orientations were found which fit the observed eigenvectors with r.m.s. errors of less than 0.0001. The correct rotation was readily identified as the only one which did not require one or both of the 2.0080 eigenvectors (normals to the carboxyl planes) to lie closer than 56 degrees to the crystallographic *b* axis. The true 2.0080 eigenvectors should be about perpendicular to the *b* axis, since *b* is very close to the local C2 axis of each radical in the BPO precursor. With the correct choice of rotation the angles to *b* were 72 and 89 degrees for BB10K and 70 and 86 degrees for BB25K.[16]

The correctly chosen g eigenvectors for the individual radicals in BB10K and BB25K are entered in Table 4. For most departures from these arrangements the r.m.s. deviation between calculated and observed BB eigenvectors more than doubles with a rotation of 4 degrees or less. However the deviation is less sensitive to one type of rotation: namely, the one which changes the direction of the 2.0030 and 2.0080 eigenvectors of the first radical in the BB10K and BB25K entries in Table 3 without appreciably redirecting its 2.0238 eigenvector or any of the eigenvectors of the other radical in either pair. For the eigenvectors indicated by an asterix in Table 4, a rotation of some 15 degrees about the 2.0238 eigenvector is required to double the r.m.s. deviation.

Table 2. Radical pair zerofield splittings

Pair	No. Obs.[a]	RMS Err.[b]	Trace[c]	Value [d]	Eigenvector [e]		
					a	b	c
PB5K	85	1.5	0.6	-156.8(2)	.3385	.9409	-.0069
				36.8(2)	.7826	-.2775	.5572
				120.6(1)	-.5224	.1941	.8303
PB15K	134	1.9	0.1	-109.8(2)	.5338	.8113	.2386
				52.0(1)	.2333	-.4125	.8806
				57.9(2)	.8128	-.4144	-.4094
BB10K	193	2.1	-3.4	-440.7(3)	.7542	.5522	.3554
				96.6(8)	-.6180	.4136	.6686
				341.7(4)	.2222	-.7238	.6532
BB25K	181	2.9	-2.8	-421.4(5)	.7679	.4736	.4316
				103.1(5)	-.6353	.4754	.6086
				315.4(7)	.0831	-.7414	.6659

[a] Number of observed splittings included in fit.

[b] Root mean square difference between calculated and observed splitting constants in gauss.

[c] Trace of the zfs tensor in gauss. Since the trace should vanish, this value is an independent measure of eigenvalue error.

[d] Eigenvalues of the splitting constant in gauss with estimated standard deviation of the final digit given parenthetically. The spectral line separation is three times the splitting constant.

[e] Direction cosines. All angular errors were estimated as <1° except for the nearly degenerate eigenvectors for PB15K, which had 3° estimated error.

DISCUSSION

The PB pairs. Studies of the g and ^{17}O hfs tensors of the methyl–benzoyloxyl radical pair in acetyl benzoyl peroxide have shown that the 2.024 eigenvector of the benzoyloxyl radical connects its two oxygens.[3] The 2.008 eigenvector is normal to the carboxyl plane, and the 2.003 eigenvector is the radical's long axis. The g tensors of the PB pairs thus reveal the orientation of their benzoyloxyl radicals.

If we assume provisionally that the center of the phenyl group of benzoyloxyl coincides with its center in intact BPO, and that the bond distances and angles within the radical are normal,[17] we may deduce the oxygen locations relative to the precursor molecule which are shown in Fig. 1 and Table 5. In PB5K the benzoyloxyl radical has undergone in-plane rotation by 8° in the direction which would relieve the CO$_2$–benzoyloxyl repulsion between the oxygens which initially constituted the peroxide group. At 15 K the radical rotates by 41° in the opposite direction. It seems to push past the CO$_2$, leaving behind a space in which that molecule can more comfortably lodge. During this rotation the direction of the normal to the carboxyl group changes by only 7°. The methyl-benzoyloxyl pair from acetyl benzoyl peroxide shows this same type of in-plane rotation.[1,3]

The well known magnetic dipolar interaction between the spins of two radicals gives rise to zfs, which can be used to infer the distance and direction between them.[1,6] The zfs tensor of PB15K is closer to axial symmetry than one might expect for a pair including a benzoyloxyl radical in which most of the spin density resides on two oxygens separated by about 2.1 Å. By chance the O–O vector of benzoyloxyl lies only 31° from the unique (negative) axis of the zfs tensor (Fig. 1). Since the three spin centers of the radical pair are near a common line, delocalization does not disturb the axial symmetry appreciably.

In PB5K however the O–O vector is 85° from the negative zfs axis, and the zfs tensor is far from axially symmetric. In fact it is *too* far. This may be appreciated by considering a simple model in which the phenyl spin is placed at the base of a T and the benzoyloxyl spin is evenly divided between the tips of the cross. To match the observed zfs the T must be 3.73 Å high and the O–O distance must be 4.01 Å, about twice what would be realistic. Changing the shape of the T or distributing spin unevenly between the oxygens only increases the

Table 3. Radical pair g tensor eigenvectors

Pair	No. Obs.[a]	RMS Err.[b]	g Value[c]	Direction Cosines a	Direction Cosines b	Direction Cosines c	Angular Error[d]
PB5K	85	0.5	2.0135(1)	.7299	-.1467	.6677	<1
			2.0042(1)	-.6818	-.0849	.7266	2
			2.0022(1)	.0500	.9855	.1620	2
PB15K	134	1.0	2.0135(2)	.5610	.4967	.7722	1
			2.0053(2)	-.7226	-.0964	.6845	3
			2.0031(2)	-.4038	.8625	-.3049	3
PB10K	193	1.3	2.0173(5)	-.1412	.3072	.9411	5
			2.0129(2)	.8952	.4455	-.0111	5
			2.0047(3)	-.4227	.8409	-.3379	3
BB25K	181	1.0	2.0165(2)	-.0884	.3714	.9242	5
			2.0134(1)	.9126	.4020	-.0742	5
			2.0046(2)	-.3991	.8369	-.3745	2

[a] Number of observations included in fitting.

[b] Root mean square difference between calculated and observed g shift from DPPH signal in gauss.

[c] Estimated standard deviation of the final digit is given parenthetically.

[d] Estimated error in degrees in the direction of the eigenvector.

Table 4. Benzoyloxyl g tensor eigenvectors[a]

Pair	g Value	Direction Cosines a	Direction Cosines b	Direction Cosines c
PB5K	2.0236	.7210	-.1537	.6756
	2.0070	-.6864	-.0248	.7268
	2.0022	.0949	.9878	.1234
PB15K	2.0240	.5294	.5154	.6738
	2.0090	-.7405	-.1069	.6635
	2.0037	-.4140	.8503	-.3251
BB10K	2.0238	-.5272	.0521	.8481
	2.0080*	.7967	-.3170	.5147
	2.0030*	-.2957	-.9470	-.1257
	2.0238	.5270	.6340	.5661
	2.0080	-.6706	-.0989	.7351
	2.0030	-.5221	.7670	-.3730
BB25K	2.0238	-.4497	.1632	.8781
	2.0080*	.8091	-.3418	.4779
	2.0030*	-.3782	-.9254	-.0217
	2.0238	.6657	.6341	.3933
	2.0080	-.5562	.0704	.8279
	2.0030	-.4974	.7700	-.3996

[a] Derived from the pair tensors as described in the text. The benzoyloxyl g values in the BB pairs were assumed to be the average of those in the PB pairs. Entries indicated by an asterisk have greater uncertainty in direction (10-15°) than the others (4°), and they correspond to the remote radical in Figure 3b.

Table 5. Atomic coordinates for models[a]

Pair	Atom [b]	a	b	c
PB5K	C7	1.495	0.264	3.913
	O16	0.775	1.051	3.259
	O15	2.332	0.719	4.721
	C11	2.128	5.500	3.984
PB15K	C7	0.040	-0.130	2.630
	O16	-0.794	-0.152	1.695
	O15	0.352	0.964	3.154
	C11	2.812	5.438	3.935
BB10K	C7	-0.270	-0.368	2.493
	O16	-1.169	-0.573	1.645
	O15	-0.028	0.801	2.871
	C8	2.401	2.854	3.304
	O18	2.786	2.201	2.308
	O17	1.645	2.314	4.144
BB25K	C7	-0.199	-0.359	2.416
	O16	-1.233	-0.561	1.739
	O15	0.209	0.812	2.590
	C8	2.165	2.916	3.602
	O18	2.413	2.155	2.637
	O17	1.441	2.509	4.539

[a] In cartesian coordinates based on the crystallographic axes.
[b] Using the numbering of Sax and McMullan.[2] C7 is the carboxyl carbon near the viewer in Figs. 1(b) and 3(b). C8 is the remote carboxyl carbon. O15 and O17 are near and remote peroxy oxygens in BPO. C11 is the substituted carbon of the remote phenyl ring.

required O–O separation. Increasing both oxygen spin densities and compensating with negative spin density on the carboxyl C (positioned above the T, 0.65 Å from the crossing) decreases the O–O separation. But even with an unrealistically large carbon spin density of − 1.0, the O–O separation is 3.35 Å, which would require C–O bonds 1.93 Å long. Dividing the spin of each oxygen into halves centered in the lobes of its p orbitals does not help the model. A spin density map for HCO_2, based on a 4-31G unrestricted open-shell SCF calculation,[18] shows very similar amounts of spin in the p-lobes of each oxygen.

We have reluctantly concluded that it is not possible that the zfs of PB15K is due solely to the spin–spin magnetic dipolar interaction between phenyl and benzoyloxyl.

Spin-orbit ZFS in radical pairs. Spin–orbit coupling can also give rise to zfs.[19] But it is less commonly invoked in organic systems than spin–spin coupling, and, as we shall show, there would appear to be a good reason to neglect it in the case of radical pairs. The scalar coupling between spin and orbital angular momentum operators can be approximated as a sum of scalar products of the corresponding local operators at each atom with an appreciable spin–orbit coupling constant.[20]

The orbital angular momentum operator of a radical mixes its ground state with particular excited states, and the spin angular momentum operator of one radical in a pair mixes the triplet spin functions with one another and with the singlet spin function. The effect of the scalar product of these operators can be understood with reference to the example of the PB5K pair shown in Fig. 2.

The energies of S_0 and T_0, the singlet and triplet states for the PB5K pair with benzoyloxyl in its ground electronic state (σ,$^2B_2$), and of S_1 and T_1 for the pair with benzoyloxyl in its lowest excited state (π, $^2A_2$) are shown schematically at the left of Fig. 2. We have neglected zfs and assumed provisionally that triplets lie below singlets. Even though the excitation energy of the benzoyloxyl radical is small (perhaps 10 kcal/mole)[3], we have assumed that it is much larger than the singlet–triplet splitting, as indicated by the break in the vertical scale.

The spin–spin splitting of the triplet levels is shown at the right of Fig. 2. Since the largest component of the spin–spin distance is along the interradical vector, which we label z, T_z is raised in energy while T_x and T_y are lowered. Because there is a larger component of spin–spin distance in the direction (x) of the O–O vector of benzoyloxyl than in the direction (y) perpendicular to its plane, T_x lies at slightly higher energy than T_y. As mentioned above, the difference in spin–spin energy between T_x and T_y should not be very large for the PB5K pair, whereas experiment shows that T_x lies almost midway between T_y and T_z.

The vertical arrows in Fig. 2 connect levels which are mixed by spin–orbit coupling. Only the x component of orbital angular momentum can mix the $\sigma(^2B_2)$ with the $\pi(^2A_2)$ state, so in the scalar product L·S we need consider only L_xS_x. S_x mixes T_y with T_z, and T_x with the singlet. The spin–orbit coupling can be treated as a second-order perturbation which lowers the energy of the T_0 and S_0 states. The matrix elements are of identical magnitude for all four pairs of levels being mixed. Thus the only source of a *selective* lowering of certain T_0 sublevels would be a difference in the energy gap for the states being mixed.

Since the observed difference in energy between T_{0z} and T_{0y} is less than 0.03 cal/mole, and the difference between T_{1z} and T_{1y} should be similar, the energy gaps should differ by only about 1 part in 10^5, and spin–orbit perturbation should lower T_{0z} and T_{0y} by virtually identical amounts. If the splitting between S_1 and T_1 were also small, one would expect that the x sublevel of T_0 would be lowered by about the same amount, so that spin–orbit coupling would not contribute to the zfs of T_0. Small S–T splittings are the reason that in general one would expect negligible spin–orbit conbributions to radical-pair zfs.

The fact that experiment places T_{0x} about midway between T_{0z} and T_{0y} suggests that singlet–triplet splitting in the PB5K* pair (with a π benzoyloxyl radical) must be significant in comparison to the σ–π energy difference and that the triplet lies below the singlet. Only in this way can the energy gap between T_{0x} and S_1 be large enough that T_{0x} should be lowered less than T_{0z} and T_{0y}.

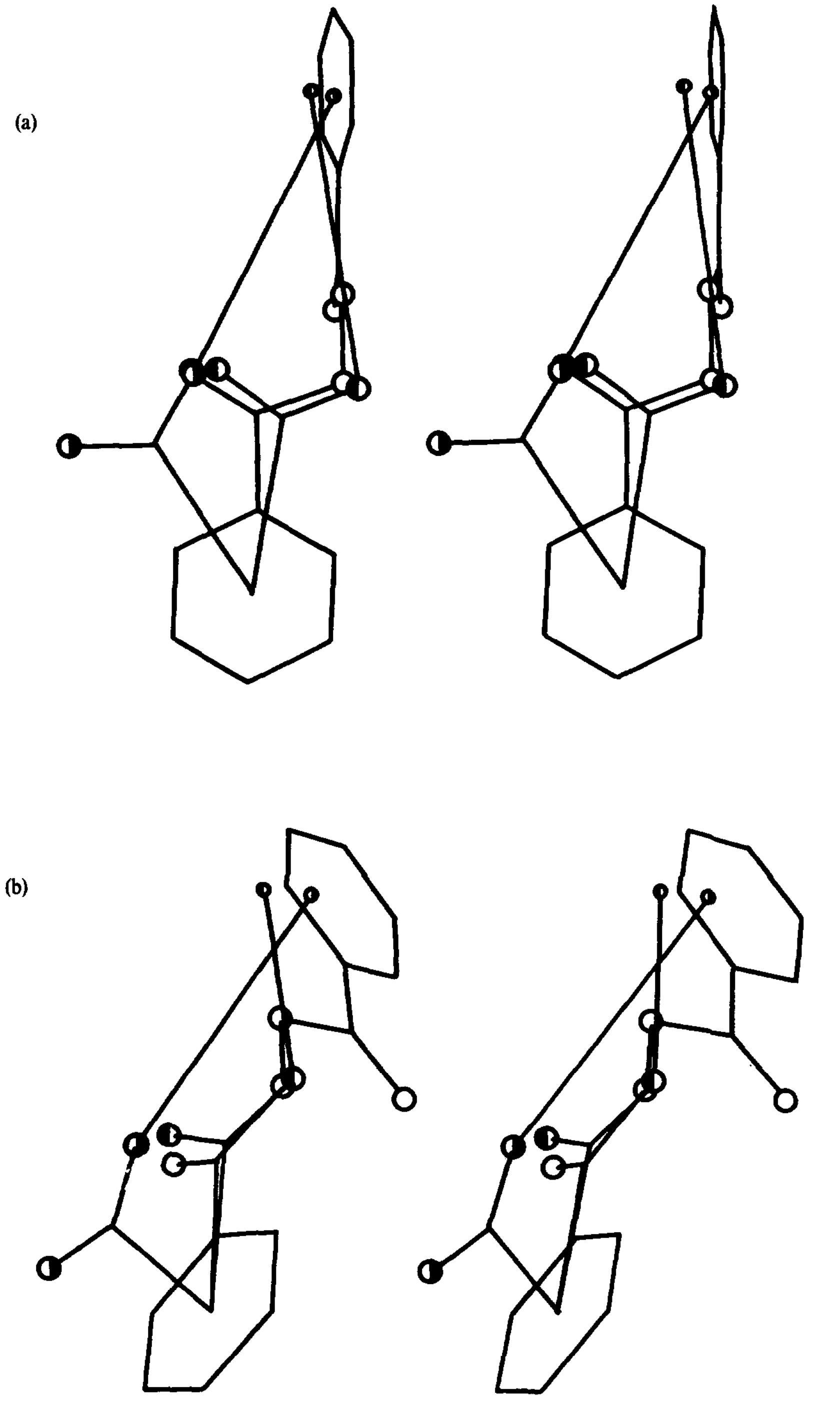


Fig. 1. Stereo pair views of the PB models superimposed on the framework of their BPO precursor. Large half-filled circles denote oxygens of the benzoyloxyl radical, and small ones denote the phenyl carbon with a free valence. PB5K circles are darkened on the left; PB15K circles, on the right. Orientations have absolute significance, but translations have only relative significance. In the upper view the crystallographic *b* axis lies in the plane of the page and points up, while the *c* axis is inclined by 50° to the right from pointing toward the viewer. In the lower view the *z* axis lies in the page and points to the right, while the *c* axis is inclined by 45° toward the page top from pointing toward the viewer.

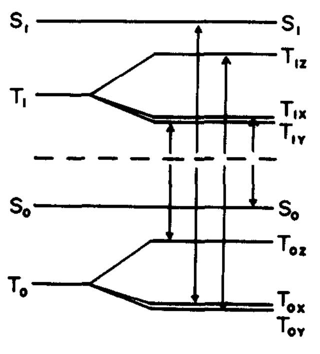


Fig. 2. Schematic energy levels for PB radical pairs in a "T" geometry. The energies of pairs with ground (σ, $^2B_2$) and with excited (π, $^2A_2$) benzoyloxyl radicals, but without zfs, are shown at the left as S_0-T_0 and S_1-T_1, respectively. At the right is shown the effect of spin-spin zfs, where z is the interradical axis, and x is the O-O direction within benzoyloxyl. Vertical arrows connect states which are mixed by the L_xS_x spin-orbit interaction.

Interpretation of the PB ZFS tensors. A zfs tensor has five independent elements. We have adjusted the following four-parameter model to give least-squares agreement between calculated and observed zfs tensors for PB5K and PB15K.

The phenyl radical was approximated by two point-spins positioned to represent an sp^8-hybridized Slater orbital on the radical carbon pointing along the b axis toward the benzoyloxyl radical.[21] These were 0.771 spin in the larger lobe at 0.572 Å from the carbon and 0.229 spin in the smaller lobe 0.642 Å from carbon.[22] The benzoyloxyl radical was approximated by five point-spins on a framework oriented by the g tensor. The carboxyl C was assigned −0.24 spin,[23] and the balance was distributed evenly among four points representing the p lobes of the O atoms, each 0.49 Å from O in the direction indicated by ^{17}O hfs of the radical.[3]

The spin-spin portion of the zfs was varied by adjusting the a, b and c components of translation between the phenyl and benzoyloxyl radicals. The spin-orbit portion of the zfs was assumed to be axially symmetric about the direction of the O-O vector and was adjusted with a single scaling parameter.

Refining this model for PB5K gave a weighted r.m.s. deviation between observed and calculated tensor elements of 6.3 G. Table 6 presents the observed and calculated zfs elements and the spin-spin and spin-orbit contributions to the latter. When spin-orbit is ignored the r.m.s. deviation rises to 18.7 G. Diagonalizing the spin-orbit portion shows a maximum contribution of 64.6 G.

For PB15K the maximum spin-orbit contribution is only 12.8 G, and the change in r.m.s. deviation is only from 0.85 without spin-orbit to 0.03 G including it. This is not surprising, because in this case the singlet-triplet splitting may well be smaller, so that spin-orbit zfs is reduced and the spin-spin model alone suffices.

The calculated positions of the radical C of phenyl relative to benzoyloxyl for PB5K and PB15K appear in Table 5 and are shown by the small circles in Fig. 1. These points are 1.73 and 1.34 Å, respectively, from the position of the corresponding atom in intact BPO, but they are only 0.69 Å from one another. This shows that the phenyl radical and the center of benzoyloxyl are further apart in the radical pairs than in BPO, but that the relative displacements are similar in the two radical pairs. We emphasize that the phenyl displacements are relative to benzoyloxyl, and could be achieved through absolute motion of phenyl, or of benzoyloxyl, or, most probably, of both. Examining Fig. 1 shows that the sense of the relative motion of the radicals is what one might reasonably expect from cramming a non-bonded CO_2 molecule between them. Our earlier, provisional assumption that the center of benzoyloxyl's phenyl group retains the position it had in intact BPO is probably not strictly correct, but not far wrong.

By assuming that the triplet PB5K* pair lies well below the singlet we can explain the unusual shape of the PB5K zfs tensor, the fourth peculiarity mentioned at the beginning of this paper. There is nothing special about the fact that PB5K* happens to be electronically excited, the triplet would also have lain below singlet had $\pi(^2A_2)$ been the ground state of benzoyloxyl.

The apparently large gap between singlet and triplet is as striking as the ordering of these states. If triplet can

Table 6. ZFS tensor elements for PB5K[a]

Element	Obs.	Calc.	Spin-Spin	Spin-Orbit
aa	37.5	46.6	58.7	-12.1
bb	-131.4	-127.4	-147.4	20.0
cc	94.6	80.8	88.7	-8.0
ab	-70.2	-74.8	-82.0	7.2
ac	-35.9	-37.1	-5.6	-31.5
bc	14.8	14.7	8.0	6.7

[a] In gauss. When the tensor is transformed to a coordinate system in which $\underline{z}$ is the high-field direction, the observed epr line separation is three times the $\underline{zz}$ element. The final two columns give the spin-spin and spin-orbit contributions to the element which is calculated from the model described in the text.

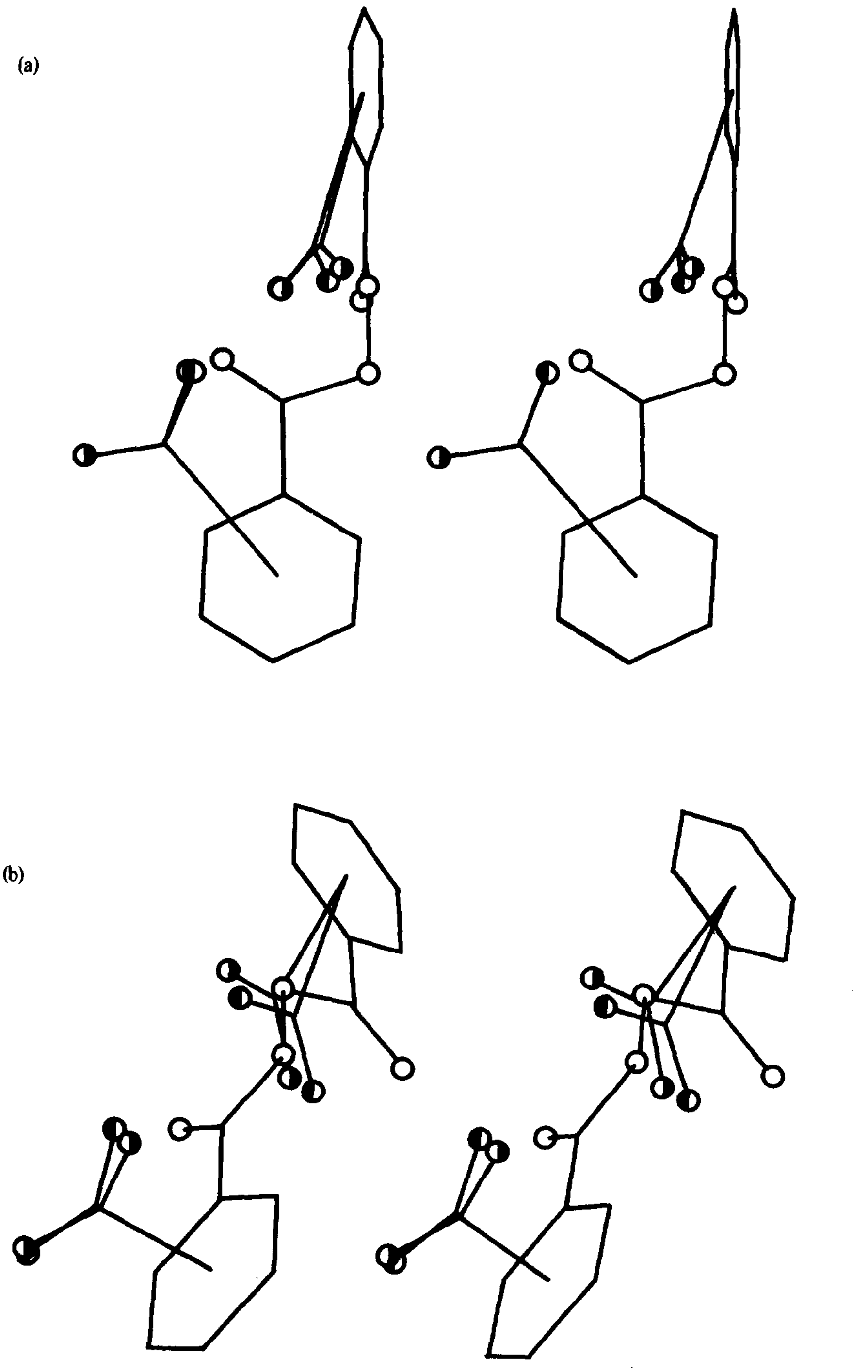


Fig. 3. Stereo pair views of the BB models analogous to Fig. 1. BB10K circles are darkened on the left; BB15K circles, on the right. Only the radical orientations are significant, and in radicals nearer the top of either view only the directions of the O–O vectors are experimentally well determined.

lie well below singlet, then the converse should be possible, and there should be molecule-separated radical pairs with singlet ground states, where the triplet is not thermally accessible at cryogenic temperature. This suggests an explanation of the third peculiarity. X, the precursor of PB24K, may be such a ground state singlet PB pair, which undergoes a motion at 24 K that alters the exchange integral to give a ground state triplet.

The BB pairs. Figure 3 and Table 5 present models of the benzoyloxyl orientations in the BB10K and BB25K pairs, which were constructed from the g tensor information in the same way as for the PB pairs. The most notable features of these models are that one of the radicals is oriented very similarly to the benzoyloxyl of PB15K and that the other radical has rotated toward its partner. We believe that the first feature is quite reliable, but the second is probably an artifact from unscrambling the averaged g tensors. As mentioned above, the O–O vector of the second radical is well defined experimentally, but the direction of its two-fold axis may be in error by 10–15°. We suspect that in fact the remote radicals in Fig. 3(b) have only undergone small rotations about their long axes, which themselves retain the direction they had in the molecular precursor.

The models suggest a simple explanation of the first peculiarity, that BB pairs appear only after photolysis above 10 K, while PB pairs appear at lower temperature. PB5K pairs are made persistent by the intervening CO_2, even though the radicals have not moved much from their original positions. Unmoved BB pairs, however, recombine quickly unless one of the radicals can rotate into the more stable position which PB pairs achieve at 15 K. Only above 10 K is there enough thermal energy to allow benzoyloxyl rotation to compete with recombination.[24]

The only remaining peculiarity is that rotation can make the BB pairs persistent. We suggest that the radicals are held apart by non-bonded repulsion between their O atoms. At first this seems unlikely, since the O atoms are the centers of radical reactivity. But if BB pairs in this arrangement are ground state triplets, their interaction should indeed be repulsive. Only when the singlet state becomes thermally populated, or when the pair shifts to a new arrangement with a singlet ground state, would recombination be possible.

We had hoped to use the zfs tensors of the BB pairs to derive information about relative translation of the radicals. However in these pairs there are two different excited states which should contribute to zfs by mixing with the ground state. The only difference between them involves which of the benzoyloxyl radicals is excited to the π state. Because no symmetry relates the radicals, the singlet–triplet gap could be quite different in these two states. It would not be surprising if the triplet were lower for one excited state and the singlet for the other.

A model for calculating the zfs tensors needs at least five parameters (three translations and two spin–orbit scaling factors) to fit five experimental observations. In practice we have found that least squares refinement of these models can exhibit instabilities. Further definition of the BB geometries will require more experimental evidence.

Reservations. Although the hypothesis of large singlet–triplet splittings of variable sign in radical pairs can explain the four peculiarities mentioned at the beginning of this paper, we advocate it reluctantly. There is a disconcerting *ad hoc* flavor to the explanations for the persistence of the BB pairs and the epr invisibility of X. If radical pairs can hide as singlets and subsequently become observable as triplets, it is surprising that this behavior has not been found in many previous epr studies of radical pairs in organic solids.

In a naive theoretical attempt to estimate the plausibility of large splittings and of triplet ground states we have performed simple valence–bond calculations using the overlap, one-electron, and two-electron integrals between 2p orbitals on oxygen atoms separated by 2.5–3.25 Å. We tried integrals from both STO3G and 4-31G orbitals of the GAUSSIAN76 program.[25] In the 4-31G case we fixed the ratio of the outer and inner contributions to the p orbital at the value for SCF solution of the triplet O atom. Over this range of distances the integrals for both orbital types decrease by one to two orders of magnitude, and the STO3G integrals are an order of magnitude smaller that those for 4-31G. In all cases the exchange contribution from one-electron potential energy is about an order of magnitude larger than that either from one-electron kinetic energy or from the most important two-electron integrals.

Using the 4-31G results with the geometries for BB10K and BB25K shown in Fig. 3, we estimate singlet–triplet gaps of 13 and 10 kcal/mole, respectively, favoring the singlet. This would suggest that the splittings can be large, but, as mentioned above, we suspect that the radicals are too close together in Fig. 3. Because the one-electron contributions can be so large relative to the two-electron contributions, triplet ground states are predicted only when the radical orbitals are very nearly orthogonal. This would make it unlikely that the two different BB arrangements should both have triplet ground states.

The orbitals used in our calculations are surely far from optimum, and we look forward to more reliable calculations on these systems.

In closing we reemphasize that our strongest evidence for a triplet ground state is our inability to reconcile the experimental zfs of PB5K with spin–spin zfs calculated for any reasonable model of spin distribution in the phenyl and benzoyloxyl radicals. This requires invoking spin-orbit zfs, and thus singlet–triplet splitting significant on the scale of the electronic excitation energy of the benzoyloxyl radical. The sign of the necessary correction to the spin–spin zfs tensor requires that the triplet of PB5K* lie below its singlet.

If through-space coupling is unlikely to be so large for these radicals, it may be that they communicate through the CO_2 molecule between them.

Acknowledgements—This work was supported by the National Science Foundation through grants DMR 76-01996 and 78-25002, by a Camille and Henry Dreyfus Teacher-Scholar grant to J. M. M., and by a Dox Fellowship to M. W. V. The epr spectrometer, the X-ray diffractometer, and data handling facilities were obtained with the aid of NSF instrument grants. We are grateful to Dr. Marshall D. Newton and Profs. E. R. Davidson, S. I. Weissman, and K. B. Wiberg for helpful discussions.

REFERENCES

[1] J. M. McBride, M. W. Vary and B. L. Whitsel, *ACS Symp. Ser.* **69** (*Organic Free Radicals*) 208 (1978).

[2] M. W. Vary and J. M. McBride, *Mol. Cryst. Liq. Cryst.* **52**, 133 (1979).

[3] J. M. McBride and R. A. Merrill, *J. Am. Chem. Soc.* **102**, 1723 (1980).

[4] See for example [a] P. Dowd, *Acc. Chem. Res.* **5**, 2587 (1972); [b] E. Wasserman and R. S. Hutton, *Ibid.* **10**, 27 (1977); [c] J. A. Berson, *Ibid.* **11**, 446 (1978); [d] S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.* **101**, 4688 (1979); [e] M. Iwasaki, K. Toriyama, H. Muto and K. Nunome, *J. Chem. Phys.* **65**, 596 (1976).

[5] R. G. Lawler, *Acc. Chem. Res.* **5**, 25 (1972). For more theoretical background see R. Kaptein, *J. Am. Chem. Soc.* **94**, 6251 (1972); and J. N. Murrell and J. J. C. Teixeira-Dias, *Mol. Phys.* **19**, 521 (1970).

[6] N. J. Karch, E. T. Koh, B. L. Whitsel and J. M. McBride, *J. Am. Chem. Soc.* **97**, 6729 (1975).

[7] But see H. Shindo, K. Maruyama, T. Otsuki and T. Maruyama, *Bull. Chem. Soc. Jpn.* **44**, 2789 (1971).

[8] I. M. Brown and S. I. Weissman, *J. Am. Chem. Soc.* **85**, 2528 (1963). Brown and Sloop interpreted the temperature dependence of the rapid spin–lattice relaxation of a triplet complex between zinc and two radical anions in terms of spin–orbit mixing with a singlet state 15 cm^{-1} higher in energy. I. M. Brown and D. J. Sloop, *J. Chem. Phys.* **47**, 2659 (1967). We thank the referee who brought this work to our attention.

[9] W. Flossman, E. Westhof, and A. Mueller, *Phys. Rev. Lett.* **34**, 959 (1975).

[10] For example S. H. Glarum and J. H. Marshall, *J. Chem. Phys.* **47**, 1374 (1967); K. Itoh, H. Hayashi and S. Nagakura, *Mol. Phys.* **17**, 561 (1969); G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.* **95**, 2735 (1973).

[11] For related discussions see [a] L. Salem and C. Rowland, *Angew. Chem. Int. Ed. Engl.* **11**, 92 (1972); [b] J. Katriel and R. Pauncz, *Adv. Quantum Chem.* **10** 143 (1977); [c] R. L. Snow and J. L. Bills, *J. Chem. Ed.* **51**, 585 (1974).

[12] W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **99**, 4587 (1977).

[13] Anisotropic thermal parameters appear in the Ph.D. dissertation of M. W. Vary, Yale University (1979).

[14] J. M. McBride and D. W. Walter, submitted to *J. Am. Chem. Soc.*

[15] P. H. Kasai, E. Hedaya and E. B. Whipple, *Ibid.* **91**, 4364 (1969).

[16] The 72° and 70° values are likely underestimated. See the following paragraph.

[17] We assume that the carboxyl C is 2.86 Å from the phenyl center (1.37 Å ring diameter + 1.49 Å exocyclic C–C distance), that the C–O distance is 1.25 Å, and that the angles at the carboxyl carbon are 120°. We have also guessed that the phenyl radical in the PB pairs and the unrotated benzoyloxyl radical in the BB pairs derive from the half of BPO with higher numbers in Table 1. The arbitrariness of this guess, its irrelevance to intramolecular interactions, and its importance to some intermolecular interactions are discussed in Ref. 2.

[18] We thank M. D. Newton for performing this GAUSSIAN76 calculation.

[19] [a] S. P. McGlynn, T. Azumi and M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, p. 345. Prentice–Hall, Englewood Cliffs (1969); [b] D. W. Pratt, *Excited States*. Vol. 4. Academic Press, New York (1979).

[20] See Ref. 19*a*, p. 196. For an alternative view see H. F. Hameka, (Edited by A. B. Zahlan) pp. 10–11. *The Triplet State*. Cambridge University Press, Cambridge (1967).

[21] J. M. McBride, *J. Am. Chem. Soc.* **99**, 6760 (1977).

[22] These represent the amount of spin on each side of the carbon nucleus for an sp^8-hybridized Slater orbital, and the average value of the axial component of distance in each of its lobes. For orbitals which point toward one another it is better to use the mean component rather than the r.m.s. component.[6]

[23] The value from an unrestricted 4-31G SCF calculation of $^2B_2$ formyloxyl radical.[18] INDO calculation of $^2B_2$ benzoyloxyl radical gives an even smaller carbon spin density of -0.10.[6]

[24] It is not obvious how "hot" the radical pairs may be at the instant of their formation, or how rapidly they cool.

[25] J. S. Binkley, R. A. Whitehead, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre and M. D. Newton, *Q.C.P.E.* **11**, 368 (1978).