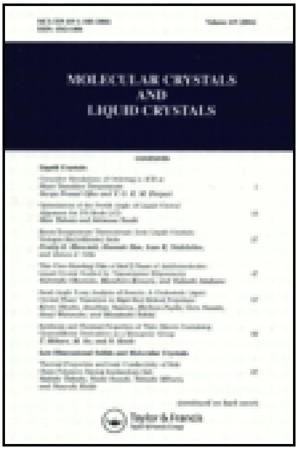

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Using Molecular Mechanics to Model the Movement and Relaxation of Radical Pairs Created By Photolysis of Single Crystals of Acetyl Benzoyl Peroxide (ABP)

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USING MOLECULAR MECHANICS TO MODEL THE MOVEMENT AND RELAXATION OF RADICAL PAIRS CREATED BY PHOTOLYSIS OF SINGLE CRYSTALS OF ACETYL BENZOYL PEROXIDE (ABP)

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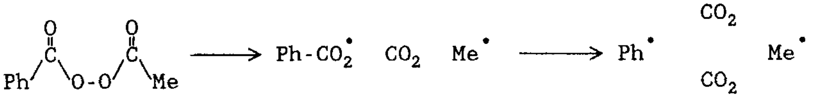
Abstract The structure of isolated crystal defects is studied by molecular mechanics techniques, using experimental data to constrain the relaxation of configurational energy and to escape from local energy minima. A "Surface Walking" algorithm helps determine the reaction path among the metastable intermediate structures that evolve upon warming. Applying these techniques to ABP gives good results even without relaxing surrounding molecules.

INTRODUCTION

A crystalline environment restricts the number of possible pathways available for a reaction. By a combination of theory and experiment one can hope not only to identify intermediates but also to delineate reaction paths with precise atomic coordinates and trajectories. Here we show how molecular mechanics can help to clarify experimental results and predict structural features that are inaccessible by current experimental techniques. We have tested this method on acetyl benzoyl peroxide (ABP), because we have available a large body of experimental data for checking the computational results.[1]

Reactions Occuring in Single Crystals of ABP

Limited photolysis of crystalline ABP with UV light creates isolated radical pairs.[1] Careful irradiation forms a Benzoyloxyl-Methyl (BM) radical pair by liberating a single CO_2 molecule; further irradiation splits off another CO_2 leaving a Phenyl-Methyl (PM) pair. Both these radical pairs are stable at low temperatures (<77K) and can be studied by EPR spectroscopy. The radical pairs eventually collapse to methyl benzoate and toluene, respectively. Isotope labelling has shown that each product arises by combination of a radical pair generated from a single peroxide molecule. Thus the surrounding molecules of ABP form a cage confining these radicals, and this set of fragments can be treated as an isolated defect within the crystal.



ABP BM PM

USING MOLECULAR MECHANICS TO MODEL THE REACTION SITE

We wish to determine how intricate molecular mechanics[2] calculations must be in order to give pictures of a solid-state reaction which are reliable to the extent of reproducing various experimental observations. The goals of the calculations are:

(1) To determine the location and orientation of the radical fragments; we can check a model geometry against EPR data by calculating the zero-field splitting tensor (zfs) and the orientation of hyperfine splitting (hfs) and g-tensors.

(2) To predict the arrangement of reaction products that are not directly associated with the radical centres, and to predict how much the surrounding environment is perturbed and the state of local stress. For radical pairs in ABP, the location of the CO_2 molecules has not yet been determined experimentally at low temperatures.[3] For the PM pair the CO_2s can be investigated by IR techniques, but information about CO_2 in the BM pair is accessible only by calculation, because BM photolyses so easily to PM.

(3) To reveal the sequential arrangements of molecular fragments as local stress is relaxed upon warming, and, more challenging still, to map out the detailed relaxation route and the structure and energy of transition states between successive metastable arrangements. This is less important for ABP, which shows only one structure for each radical pair, than for other systems which show as many as eight successive structures for a single set of fragments.[3]

In approaching these goals two problems arise. First, how to express the extent of agreement between calculated radical pair geometries and experimental data? Second, how to choose a reasonable path in multidimensional space from one stable configuration of the fragments to another and avoid becoming trapped in local potential energy minima?

We solve the former problem by using the experimental data in the form of constraints on the relaxation of the system, and comparing constrained with unconstrained structures. Modifying the configurational potential energy surface by adding various constraint functions also favours escape from local energy minima that are unrelated to experiment. A more direct solution to the problem of finding reaction paths involves a special optimisation algorithm which uses analytic first and second Cartesian derivatives of the potential energy; this enables full characterisation of stationary points of the system and yields eigenvectors of the second-derivative or Hessian matrix, which are "normal modes" of the structure at any desired point on the potential energy surface. The algorithm, which was first implemented for "surface walking" on quantum mechanical potential energy surfaces,[4] allows us to travel between minima via transition state structures. This feature permits us to model the routes between the successive configurations of radical pairs that develop upon warming.

Relaxing the Radical Pairs Generated by Photolysis of ABP

The present calculations held the surrounding, intact molecules at their crystallographic positions. The PM and BM pairs gave the minimum energy structures shown in Figure 1 from a variety of initial conditions. For example, the same PM configuration was reached by cleaving the second CO_2 from the intermediate BM radical pair and by splitting both CO_2s simultaneously from the starting peroxide. Unconstrained simulation of the BM radical pair reproduced the 30 degree in-plane rotation of the benzoyloxyl radical, which was previously suggested by analysis of the hfs and g tensors.[5,6]

IMPLEMENTING EXPERIMENTAL CONSTRAINTS

The program can use zfs, hfs, and g tensor information as constraints on the relaxation of the system. The constraints are implemented as penalty terms that are included in the energy function being minimized.

For the zfs tensor, the square of the difference between the calculated and observed tensor components formulates the penalty term as shown in Eq. 1, where $K = 9284$ Gauss/Å^3, and W_{ten} is a weighting parameter, which is increased until the calculated tensor matches the observed tensor within experimental error. If desired,

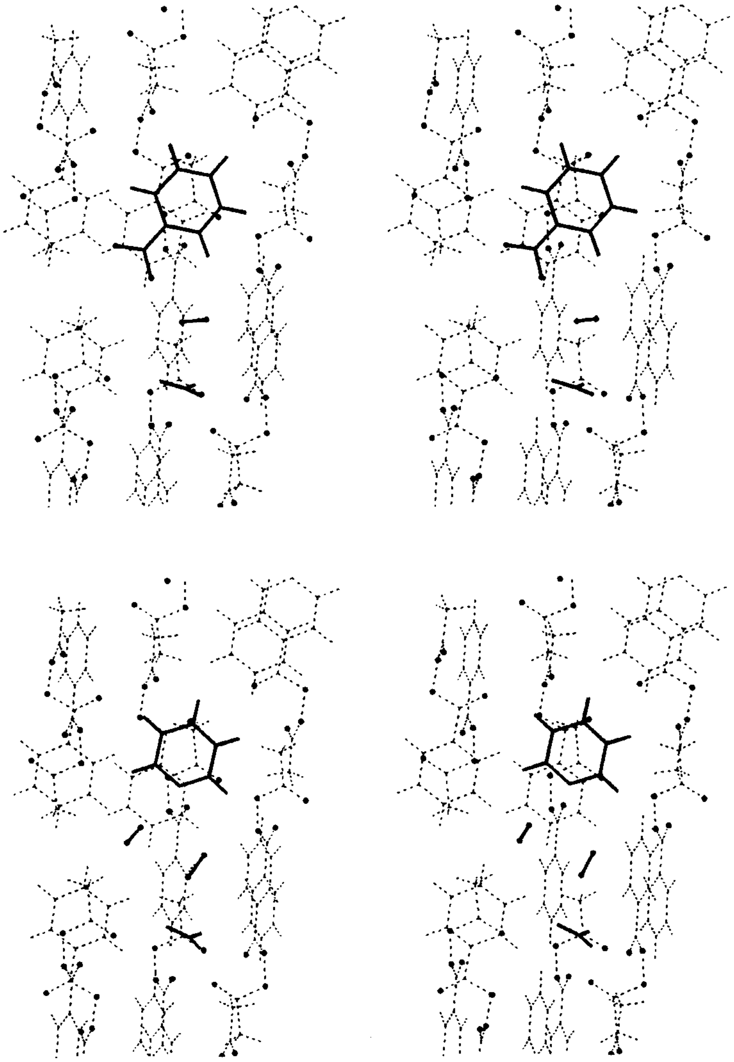


Figure 1. Stereo views of the reaction site with the fully relaxed configurations of the BM (above) and PM (below) radical pairs. Before decomposition the fragment atoms were related by translation to the cage molecule in the upper right.

$$E_{tensor} = W_{ten} \sum_{i} \sum_{j \geq i} w_{ij} \left(zfs^{cal}_{ij} - zfs^{obs}_{ij}\right)^2 \qquad (1)$$

$$zfs^{cal}_{ij} = K \langle r^{-5}(r^2 \delta_{ij} - 3 r_i r_j) \rangle$$

$$\equiv K \sum_{a} \sum_{b} \rho_a \rho_b r_{ab}^{-5} [r_{ab}^2 \delta_{ij} - 3(r_{ab})_i (r_{ab})_j]$$

contributions of the individual elements can be weighted independently, according to their experimental reliability, using w_{ij}. The i and j subscripts specify the tensor element. Subscripts a and b refer to the discrete spin density locations of the different radicals, and ρ_a, ρ_b are the corresponding spin densities at each location. The theoretical electron spin density is partitioned into discrete locations modelled by pseudo-atoms attached rigidly to the molecular framework.

TABLE I Comparison of defect structures obtained by free and constrained (starred) relaxation.

	E_{int}[a]	E_{sur}[b]	TOTAL[c]	E_{pen}[d]	D_{zz}[e]	D_{yy}	D_{xx}
ABP	7.1	-31.2	-24.2				
BM	4.8	-25.9	-21.1	37.2	-119.6(4.0)[f]	59.2(5.1)	61.4(6.2)
BM*	5.2	-25.5	-20.3	0.5	-125.1(0.0)	60.5(0.6)	64.6(0.6)
Experimental (RMS error 1.5)					-125.0	58.8	66.2
PM	2.1	-23.1	-21.0	16.8	-77.3(4.2)	38.5(51)	38.9(51)
PM*	2.5	-22.9	-20.4	0.4	-86.5(0.3)	43.0(39)	43.5(39)
Experimental (RMS error 2.5)					-86.2	41.6	44.7

[a] Molecular mechanics energy within and among the fragments; neglects the energy of bond breaking. [b] Nonbonding energy of the fragments with surrounding, intact molecules. [c] TOTAL = $E_{int} + E_{sur}$. [d] Penalty function contribution. All energies are measured in kcal/mol. [e] D_{zz}, D_{xx} and D_{yy} are diagonalized zfs tensor components (Gauss). [f] The angle in degrees between calculated and experimental eigenvectors is given in brackets. Experimental errors in orientation are 0.2° for D_{zz} and 4° for the other directions.

Figure 2 shows the model for the electron spin density[7] and also shows how the experimental zfs tensor is oriented with respect to the relaxed fragments. D_{zz} shows the magnetic field direction for maximal splitting, which corresponds to the average direction between the odd electrons. Table I shows that imposing constraints on the energy minimization can force excellent agreement between the model and experiment for both the direction and the magnitude of D_{zz}. Orthogonal to D_{zz} are the D_{xx} and Dyy axes showing the directions which characterize departure of the dipolar splitting from axial symmetry. If there is axial symmetry ($D_{xx} = D_{yy}$), the orientation of these axes is arbitrary. This is almost the case for the PM radical pair, which explains discrepancy between the calculated and experimental eigenvector directions for that pair (see Table I).

We can also force conformity between the orientation of certain fragments and their associated hfs and g tensors. This can be achieved by constructing a penalty function that favours the parallel alignment of two Cartesian vectors, see Eq. 2 where $\underline{u}$ is an experimentally determined unit vector

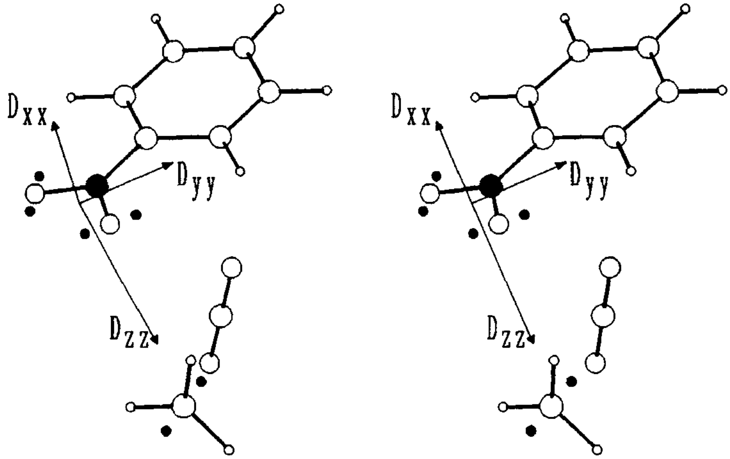


Figure 2. The zfs tensor orientation and the electron spin density locations (dark circles) for the BM radical pair.

and $\underline{r}$ is the corresponding calculated vector for a particular orientation of a molecular fragment. Minimizing the summation of Eq. 2 is mathematically equivalent to minimizing the angle between the vectors. W_{vec} is a weighting factor chosen to enforce alignment within experimental error. For the BM pair, the acyloxyl radical was constrained to match vectors derived from the unique eigenvectors of the ^{17}O hfs tensors for oxygens O3 and O4 ($\underline{R}$ and $\underline{S}$). Figure 3 shows how this was done.

$$E_{vector} = W_{vec} \sum_{i} (u_i - \frac{1}{|r|} r_i)^2 \qquad (2)$$

For the BM radical pair of ABP we found that the structure which was constrained to fit both the hfs and zfs tensors was closely similar to the structure which was energy-minimized without these eight numerical constraints,[8] as shown in Figure 4. The difference in energy is only 0.8 kcal/mol and the RMS displacement between corresponding non-hydrogen atoms is 0.14 Å, much less than the RMS displacement of 1.1 Å from the atomic positions in the precursor molecule. Releasing the constraints on the fitted structure for BM returned the molecular configuration to that of the unconstrained structure, showing that the two structures correspond to the same local energy minimum. It is particularly significant that this level of agreement was achieved without any relaxation of the surrounding environment. This suggests that *molecular mechanics calculations with a relatively small number of atoms can be quite useful for understanding reactive defects in crystalline solids.*

For the PM radical pair, with four molecular fragments, the zfs-constrained and unconstrained structures were also closely similar, differing in energy by 0.6 kcal/mole and in RMS atomic displacement by 0.12 Å.

Table II gives the coordinates for the energy minimized, constrained structures for both radical pairs.

WALKING ALGORITHM AND NORMAL MODE ANALYSES

In a typical molecular mechanics calculation the goal is to minimize potential energy for all motions of atoms or sets of atoms. The walking algorithm differs by moving in the wrong way, toward increasing energy, for one particular direction of concerted atomic motion while aiming to minimize energy for all orthogonal directions of motion. If

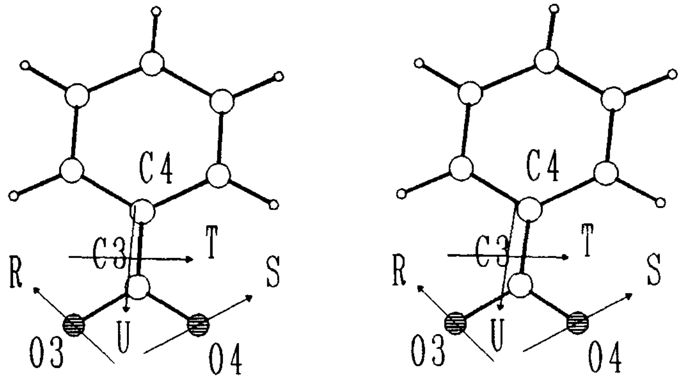


Figure 3. Vectors R and S are the largest valued eigenvectors of the ^{17}O hfs tensors. The C4-C3 atom-atom vector is aligned with U (S + R) and 03-04 is aligned with T (S - R).

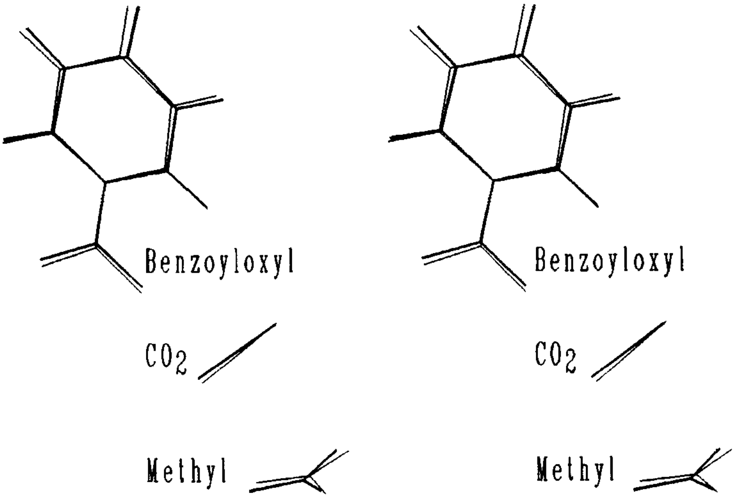


Figure 4. Comparison of the unconstrained relaxation of the BM radical pair (thick) with the configuration obtained by constraining the structure to the experimentally observed hfs and zfs tensors (thin).

the unique direction is properly chosen, the walk will move into a region of the potential energy surface where the force constant for displacement in that direction becomes negative. It is then possible to locate a transition state structure by the Newton-Raphson procedure and to proceed by standard techniques to the next local minimum of energy.

The key to success in this procedure is choosing the proper direction for maximization in this multidimensional space. We choose normal modes (eigenvectors of the Hessian matrix) as a convenient reference frame, because it is easy to identify feasible displacements by their small force constants, the modes are readily defined, and they are orthogonal to one another. Following the lowest eigenmode, the direction corresponding to the smallest force constant, is the simplest to accomplish but does not always lead to a significant new structure. Following higher eigenmodes is

TABLE II Cartesian coordinates (a,b,c*) for the experimentally constrained radical pair structures. The fragmented molecule is the same as that reported in Reference 1.

Atom	Benzoyloxyl-methyl pair			Phenyl-methyl pair		
C1	-3.8989	0.4045	-1.1887	-3.6000	0.2863	-1.5828
H1	-4.2110	0.8503	-2.1314	-3.7634	0.9664	-2.4168
H2	-3.3628	1.0029	-0.4532	-3.1451	0.6518	-0.6628
H3	-4.1219	-0.6396	-0.9841	-3.8908	-0.7580	-1.6694
C2	-1.7015	-0.1554	-2.9994	-1.1090	0.1001	-3.3843
O1	-2.3306	-0.7210	-3.7329	-1.8494	-0.6185	-3.8231
O2	-1.0729	0.4157	-2.2677	-0.3705	0.8199	-2.9456
O3	-1.0214	1.8664	-4.7209	-0.8197	3.0135	-5.0808
C3	-0.3050	2.0942	-5.6887	-1.4665	2.2619	-5.5956
O4	-0.8744	2.7781	-6.5317	-2.1197	1.5142	-6.1061
C4	1.0253	1.6683	-5.8058	1.2862	1.2168	-5.6630
C5	1.5748	0.7888	-4.8517	2.2999	0.4118	-5.1328
H5	1.0010	0.4601	-3.9994	2.1334	-0.1292	-4.2167
C6	2.8865	0.3177	-5.0054	3.5356	0.3392	-5.7860
H6	3.3051	-0.3547	-4.2760	4.2999	-0.3052	-5.3983
C7	3.6643	0.7524	-6.0874	3.7774	1.1198	-6.9265
H7	4.7055	0.4950	-6.1427	4.7579	1.1330	-7.3655
C8	3.1040	1.5855	-7.0642	2.7530	1.9091	-7.4712
H8	3.6966	1.9205	-7.8945	2.9252	2.5045	-8.3543
C9	1.7850	2.0344	-6.9324	1.4979	1.9342	-6.8520
H9	1.3825	2.6849	-7.6917	0.7116	2.5423	-7.2670

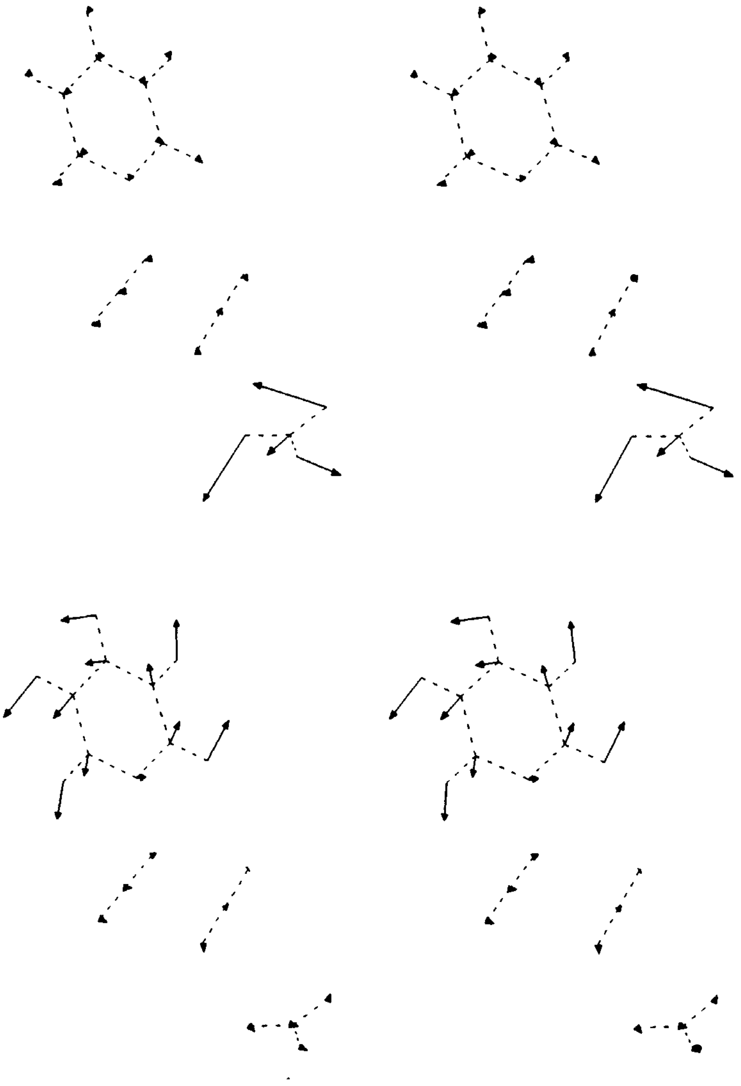


Figure 5. Lowest (above) and second lowest (below) eigenmodes for PM radical pairs. The lowest mode leads to a degenerate structure; the second, to the new structure of Figure 6.

far more tricky and constitutes most of the challenge to this research.

Visualizing the normal modes of the equilibrium configuration as a set of atomic 3-dimensional Cartesian shift vectors, one can identify certain modes which are likely to lead to alternative structures. For instance, the lowest eigenmode for PM (Figure 5) will only rotate the methyl radical about its largest inertial axis. Because the methyl hydrogens are equivalent, their reorientation will not lead to a new configuration. Following the second mode seems to rotate the phenyl radical to a new configuration. Figure 6 demonstrates the use of the walking algorithm by starting "up-hill" in this direction. A stationary point on the potential energy surface with a single negative eigenvalue was found (transition energy of -13.2 kcal/mol, 7.8 kcal/mole above the initial radical pair) and led to a new energy minimum (-18.9 kcal/mol). In this case the new structure is 2.1 kcal/mol above the starting geometry, but in other systems we hope to discover sequences of exothermic rearrangements, which have been observed experimentally.

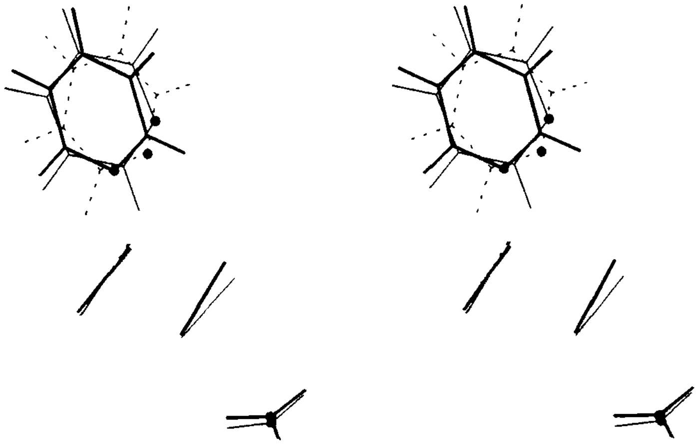


Figure 6. Three superimposed configurations of the PM radical pair: the global minimum (dark) can reach the local minimum (light) via movement through a transition state configuration (dashed).

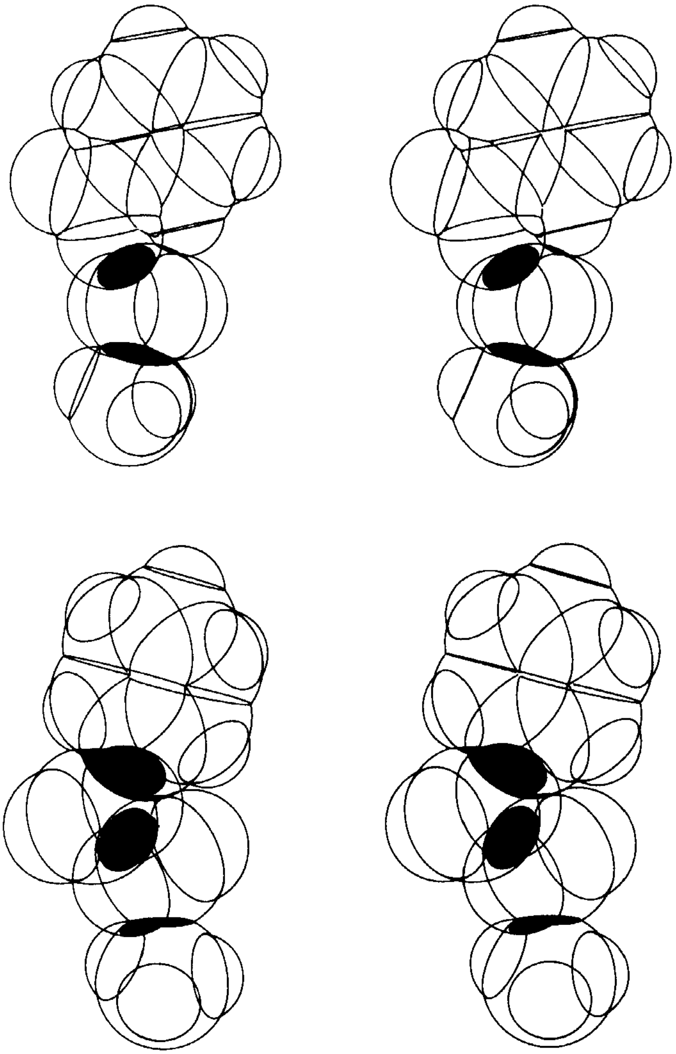


Figure 7. Intersections of van der Waals envelopes among fragments of the relaxed BM pair (above) and PM pair (below). These stereo drawings in the glass mode illustrate stress within the defects.

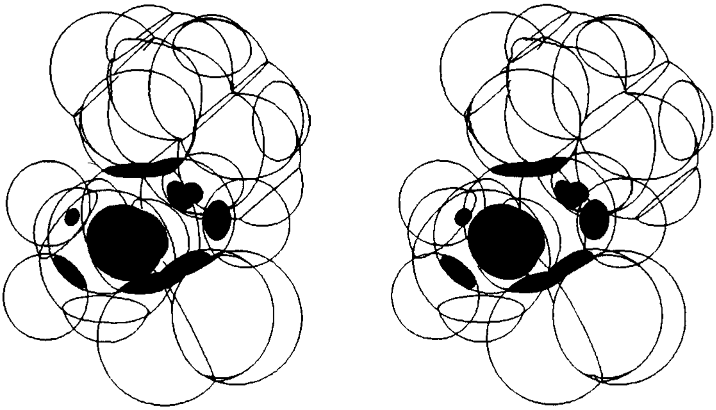


Figure 8. The black spherical intersections show how the CO_2 is wedged between the BM radicals and the atoms of the a neighbouring phenyl ring (the three atoms on the lower right). The ends of the CO_2 are held in place by hydrogen atoms.

VISUALIZATION OF LOCAL STRESS

Molecular mechanics is well suited for quantitative evaluation of local stress at crystal defects, but thus far we have studied stress only qualitatively by examining plots like those shown in Figure 7. These stereoplots in the "glass" mode, a novel feature of our graphics package, illustrate the overlap of van der Waals envelopes among the defect fragments of PM and BM. Analogous plots show overlap of the defect fragments with atoms of the surrounding cage molecules, as shown in Figure 8.

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