# Diphenylcarbene: INDO Calculations on Several Geometrical Conformations

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INDO Calculations on diphenylcarbene indicate that the triplet state is more stable than the singlet by *ca.* 4 kcal mol$^{-1}$ † and that the two states should interconvert very rapidly. These results are compared with experimental data on diphenylcarbene and also with those of the parent, methylene. The calculations confirm the planar fluorenylidene to have a triplet ground state, whereas two as yet unknown carbenes are predicted to have singlet ground states.

DIPHENYLCARBENE has been extensively studied for >15 years,[1] but like its parent, methylene, which has been under even more extensive experimental and theoretical investigation, its nature is still incompletely understood.[2]

MO Calculations, using the extended Hückel method, have shown that the non-bonding orbitals, which in unsubstituted methylene are localised on the carbon atom, interact with those of the phenyl rings.[3] Since these effects are expected to be important in determining the properties of the singlet and triplet states, the calculations were repeated using a method that takes spin explicitly into account. The size and complexity of the system precludes *ab initio* calculations so, of the common semi-empirical methods, we chose INDO,[4] which has been shown to be of considerable value to the understanding of the nature of transient species.[5] Moreover, since methylene has been well studied using accurate *ab initio* methods [2c] as well as the INDO method,[5c] the comparison allowed us to avoid some of the pitfalls associated with semi-empirical methods. Hutchison and Kohler have shown that INDO calculations are useful to the understanding of e.s.r. spectra of diphenylcarbene.[6]

Experiments have yielded the following general information on methylene and diphenylcarbene. Except for a brief study in the gas phase,[7] the chemical properties of the latter are those derived from extensive experimentation in condensed phases. Hence, the properties of methylene to which they will be compared are principally those derived from experiments in similar media.

The ground states of both molecules are bent triplets,[6,8] and, in the case of diphenylcarbene, the phenyl rings are twisted. The energy differences between the ground-state triplet and the first singlet state are thought to be 8 and <3 kcal mol$^{-1}$ for methylene and diphenylcarbene respectively.[2c,9] When the two carbenes are prepared in similar ways they react rather differently both with olefins and with saturated hydrocarbons.

Methylene adds to olefins to give cyclopropanes and there is also a small amount of insertion into CH bonds. Unless an inert compound, which can induce intersystem crossing, is present in great excess, the addition to double bonds is stereospecific.[10] Diphenylcarbene reacts with olefins either by way of partial, non-stereospecific addition to give cyclopropanes or by abstracting a hydrogen atom, depending on the substitution pattern of the olefin.[11] The stereospecificity of the addition is not increased when a triplet scavenger, oxygen, is added to the system.

Methylene, when generated photochemically, reacts with saturated hydrocarbons by insertion into CH bonds,[12] which has been shown by isotopic labelling experiments to be a non-radical process.[13] When triplet methylene, which is apparently not produced in the above experiments, is specifically present, it participates in abstraction–recombination reactions with saturated hydrocarbons.[14] The reaction of diphenylcarbene with saturated hydrocarbons proceeds overwhelmingly by an abstraction–recombination mechanism [1a] rather than by direct insertion.

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† 1 kcal mol$^{-1}$ = 4.184 kJ mol$^{-1}$.

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These results and others [9a,15,16] have been explained by postulating that thermal equilibrium is maintained between singlet and triplet species in diphenylcarbene but not in methylene.

## CALCULATIONS

The computer program used for the calculations was a modified version of the CNINDO program obtained from the Indiana University Quantum Chemistry Program Exchange [17] and has been previously described.[5a] The molecular geometries fed into the INDO program were computed from bond angles and bond lengths by standard methods.

Triplet states were calculated from open-shell Slater determinants, and singlet states from closed-shell Slater determinants. Because of this the only singlets which could be studied were those with double occupancy of the highest occupied molecular orbital (HOMO); in our case this was invariably one of the carbene centre's two non-bonding orbitals. Ordinarily it is safe to assume that a closed shell configuration corresponds to the lowest singlet state, however it is conceivable that in certain geometries the singlet state in which each of the non-bonding orbitals is singly occupied can become lower in energy. We were able to eliminate this possibility by calculating the empirical exchange integrals using parameters from the INDO program and estimating the energy of the singlet states with singly occupied orbitals. This lies above the closed-shell singlet state in all the geometries that we calculated, in agreement with the finding that the corresponding $^1B_1$ state in methylene does not become more stable than the closed shell $^1A_1$ state in any geometry.[5c]

The INDO program used fails to take explicit account of configuration interaction; however its neglect probably does not have serious consequences, as has been shown to be the case for methylene.[5c]

## RESULTS AND DISCUSSION

*Methylene.*—As our calculations on methylene are almost identical with recently published INDO calculations,[5c] they are not reported but merely taken as confirmation of our computational procedures. For discussions of these, and other relevant results we refer to recent reviews by Harrison [2c] and by Wadt and Goddard.[5c]

*Diphenylcarbene.*—It is inconvenient to use group theoretical notation to define the ground state and excited states of diphenylcarbene because, as the molecule bends and twists, it passes through several symmetry point groups. Therefore the ground state, which is a triplet, will be referred to as $T_0$ and subsequent states as $T_1$—$T_n$. The first singlet state is then $S_1$ and subsequent states are $S_2$—$S_n$. This is in complete analogy with the conventional enumerative notation, which uniquely assigns the subscript 0 to the ground state, ordinarily a singlet.[18]

*Molecular Geometry and Energy.*—Even when all the bond lengths, as well as the internal angles of the phenyl rings, are fixed, the complete description of the molecular geometry of diphenylcarbene requires that the values of three variable parameters be specified. As shown in Figure 1, these are the angle $\alpha$ between the two bonds joining the central carbene carbon atom to the phenyl rings and two angles $\theta_1$ and $\theta_2$, each being the dihedral angle between one of the rings and the central plane, *i.e.* the plane containing $\alpha$. INDO Calculations were carried out at several different values of $\alpha$, $\theta_1$, and $\theta_2$.

Two basic types of concerted ring rotation had to be considered: conrotatory motion, in which the two rings rotate in the same sense, and disrotatory motion, in which they rotate in opposite senses. Any independent rotation of the two rings could then be expressed as a suitable superposition of a conrotation and a disrotation. However, in order to reduce the number of calculations, the angles $\theta_1$ and $\theta_2$ were further restricted, in each mode, to two sets of conditions: (A) one ring achieves coplanarity with the central plane when the other is at right angles to it; (B) both rings achieve coplanarity with the central plane at the same time.

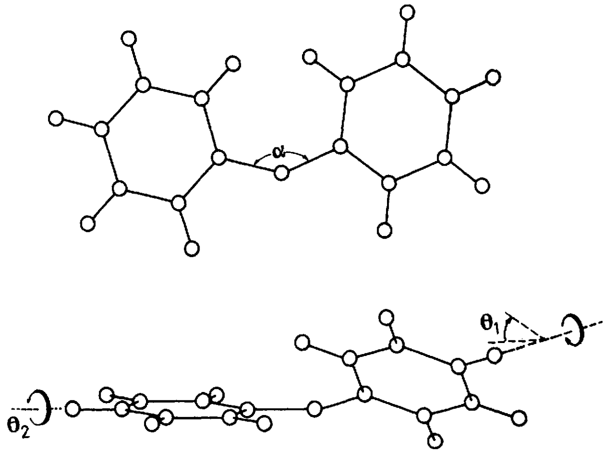

FIGURE 1 Views of diphenylcarbene along two orthogonal axes, showing the angle of bend of the bonds connecting the carbene centre and the phenyl groups ($\alpha$) and the angle of ring twist of the phenyl groups ($\theta_1$ and $\theta_2$)

The co-ordinates describing these two variants of each of the two modes of internal rotation are as follows. For disrotation $\psi = (\theta_1 - \theta_2)$ with the restriction that $\theta_1 + \theta_2 = \theta_1^0 + \theta_2^0$. $\psi$ describes the angular dependence of the motion and $\theta_1^0$ and $\theta_2^0$ are the values of $\theta_1$ and $\theta_2$ for $\psi = 0$. Two different initial sets of conditions are considered: (A) $\theta_1^0 = 45$, $\theta_2^0 = 45°$; (B) $\theta_1^0 = \theta_2^0 = 0$. For conrotation $\chi = (\theta_1 + \theta_2)$ with the restriction that $\theta_1 - \theta_2 = \theta_1^0 - \theta_2^0$. Again two different initial sets of conditions are considered: (A) $\theta_1^0 = 45$, $\theta_2^0 = -45°$; (B) $\theta_1^0 = \theta_2^0 = 0$.

Perspective views of various stages of motion along these four co-ordinates are depicted in Figure 2. It should be noted that $(\theta + 180°)$ represents a ring

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orientation that is physically indistinguishable from that of $\theta$, since each ring has local $C_2$ symmetry with respect to an axis through the bond joining it to the central carbon.

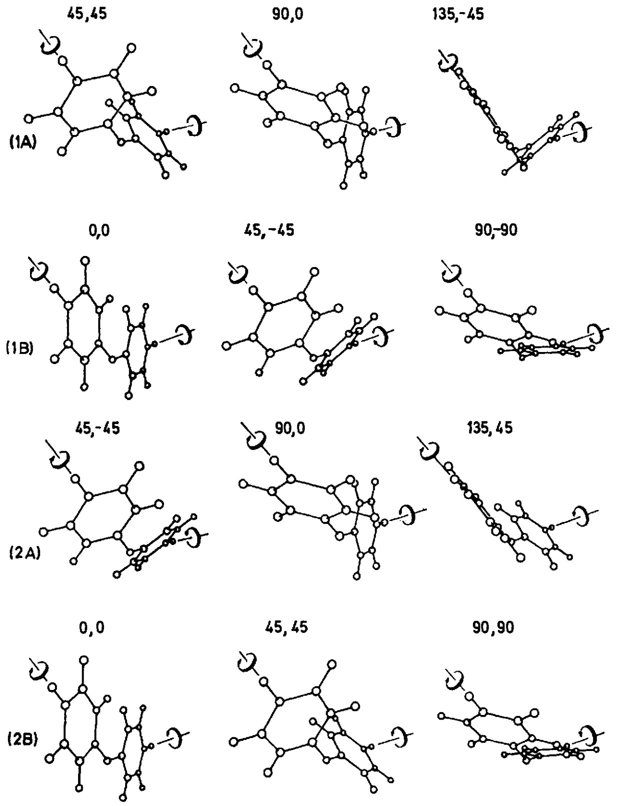

FIGURE 2 Four symmetrical concerted rotations [disrotations (1A) and (1B) and conrotations (2A) and (2B)] of the phenyl groups in diphenylcarbene. The numbers above each configurational drawing are the values in degrees of $\theta_1$ and $\theta_2$ respectively in that configuration

Hence one arrives at a series of sections through the potential energy surface, as one varies either the bond angle $\alpha$ at fixed angle of ring twist (Figure 3) or varies the degree of ring twist at constant bond angle $\alpha$ (Figure 4a—d). For each geometry the energy of the closed shell singlet state and the lowest energy triplet state are shown. To simplify the presentation all energies are expressed as kcal mol$^{-1}$ above the energy of the most stable configuration. The program outputs the energy in terms of the binding energy of the molecule, which is *ca.* 80 000 kcal mol$^{-1}$, so interpretation of energy differences of the order of a few kcal mol$^{-1}$ must be made with extreme caution.

The energies of the singlet and triplet levels of different geometrical configurations of diphenylcarbene seem to depend mainly on two factors: (*a*) the strength of the repulsive interaction between the *ortho*-hydrogen atoms on the phenyl rings and (*b*) the amount of overlap between the molecular orbitals of the ring systems and the orbitals on the carbene centre. The singlet state is expected to be stabilized by overlap to only one of the non-bonding orbitals on the carbene centre, while the triplet state will be favoured when both non-bonding orbitals on the carbene are equally stabilised by overlap. Both multiplicities are expected to be equally destabilised by the repulsion between the ring hydrogens.

Figure 3 shows the change in energy of diphenylcarbene on varying the bond angle $\alpha$ at three pairs of values of $\theta_1$ and $\theta_2$. Repulsive overlap between the hydrogens on the rings causes a destabilisation of both multiplicities at small values of $\alpha$ when the molecule is planar, but this is relieved by rotating the rings ($\theta_1$ and/or $\theta_2 \neq 0$) out of the central plane defined by the two bonds to the carbene carbon atom. The triplet state is clearly favoured at large values of $\alpha$ and the singlet state at small values, except in the planar molecule, which is extremely unstable at small values of $\alpha$. This behaviour is to be expected on the basis of overlap between the ring and the carbene centre's non-bonding atomic orbitals. In the linear molecule the latter are degenerate $p$ orbitals, each of them equally capable of entering into conjugation with the $\pi$-system of a suitably oriented phenyl ring, thus favouring the triplet state. In a highly bent molecule, these two orbitals will be non-degenerate, and would be expected to interact with the rings to different extents, so the singlet state would be preferentially stabilized.

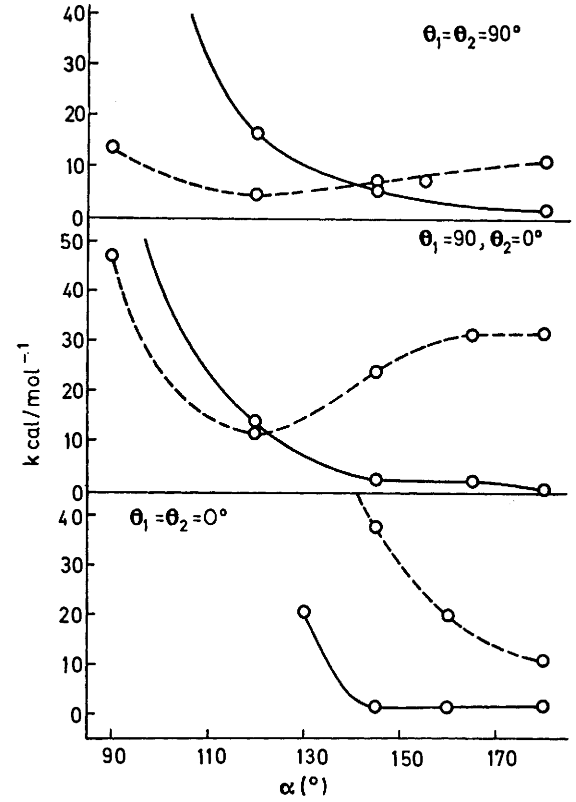

FIGURE 3 Variation of the energy of diphenylcarbene with respect to the angle $\alpha$ at constant amount of ring twist ($\theta_1$ and $\theta_2$ constant): full line, triplet state; broken line, singlet state

The energy dependence of the concerted rotations (1A and B) and (2A and B), depicted in Figure 2, are shown in Figure 4 as a—d respectively. The calculations in each case were carried out at three different values of α, namely 180, 145, and 120°. At α 180° both disrotations become molecular rotations about the longitudinal axis of the molecule, which thus remains at constant energy with respect to the rotation. Similarly, at α 180°, the distinction between conrotations (2A and B) disappears, since both reduce to the same internal rotation about the longitudinal axis. A general feature of our results is the virtually isoenergetic nature of the triplet state, under all the concerted motions, when α is greater than 145°. The potential energy diagrams shown in Figure 4 are therefore limited for the most part to α 120°, where motion along any of the four co-ordinates causes the singlet and triplet curves to cross; only two diagrams at the larger values of α, one for each, are included.

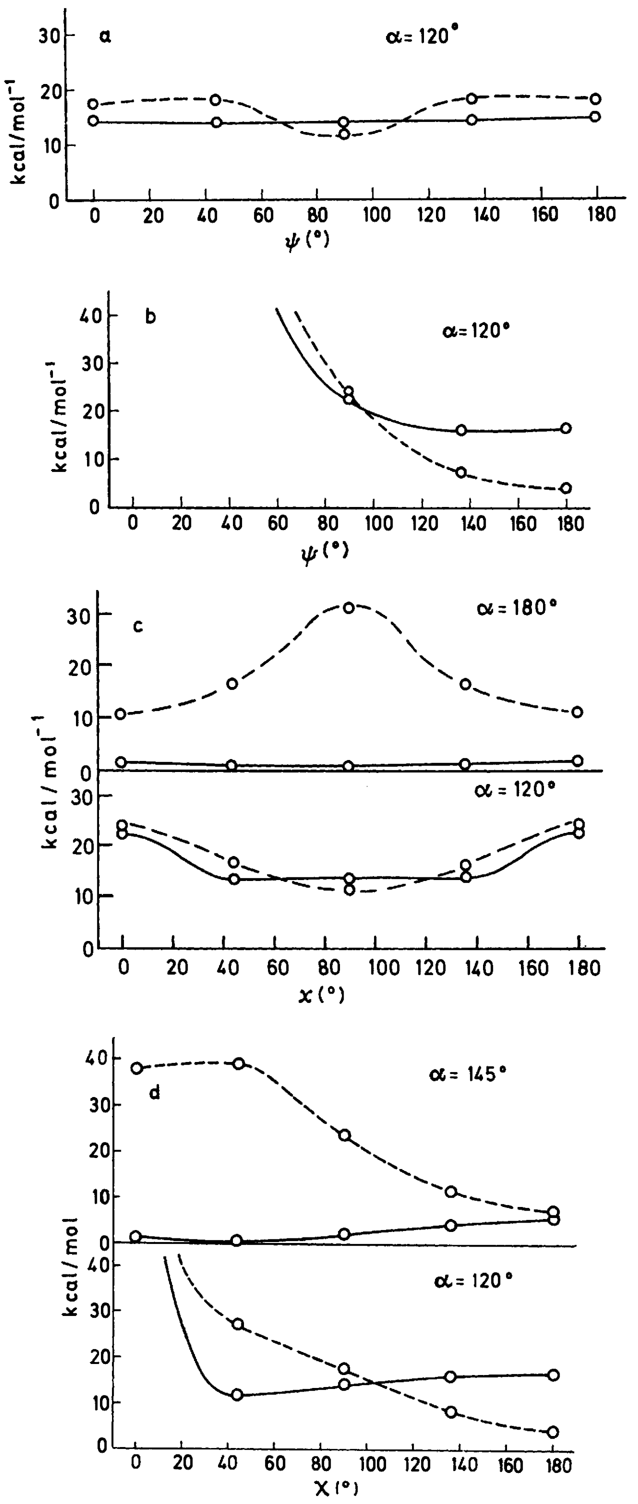

FIGURE 4 Variation of the energy of diphenylcarbene with respect to rotation of the phenyl rings at constant angle α: (a) disrotation (1A); (b) disrotation (1B); (c) conrotation (2A); (d) conrotation (2B). Full line, triplet state; broken line, singlet state

The co-ordinates that define the four motions discussed fall into two groups: (1A) and (2A), in which a variation of $\psi$ or $\chi$ by 180°, or, equivalently, of $\theta_1$ and $\theta_2$ by 90°, regenerates a physically identical conformation; (1B) and (2B), in which $\psi$ or $\chi$ have to be changed by 360° ($\theta_1$ and $\theta_2$ each by 180°) to return to the initial geometry. These two groups will be discussed separately.

The energy of the singlet state is, like that of the triplet, insensitive to disrotation (1A), except at small values of α, when, as shown in Figure 4a for α 120°, it does bring the singlet below the triplet. This insensitivity is probably a result of the fact that disrotation (1A) can be regarded as being the perturbation of a molecular rotation, where no change in overlap between the ring π-systems and the carbene *p* orbitals occurs. In contrast, as shown in Figure 4c, conrotation (2A) causes a large variation in the energy of the singlet, because the twist angle between the phenyl rings changes during the rotation and thus affects the amount of overlap into which each can enter with the two orthogonal carbene *p* orbitals. The difference in the effect of this motion on singlet energy at α 180 and 120° is striking.

The variation in energy of diphenylcarbene under the influence of disrotation (1B) and conrotation (2B) is similar at α 120°, as shown in Figure 4b and d respectively. Along both co-ordinates the singlet is strongly stabilized and the triplet weakly destabilized as the phenyl rings become perpendicular to the central plane. At α 120° the repulsion between the *ortho*-hydrogens is large enough to prevent the molecule from becoming planar. Moreover, at α 120°, disrotation (1B) is more difficult than conrotation (2B), because repulsion between the *ortho*-hydrogen atoms on the phenyl rings is relieved more effectively by the latter. When α becomes appreciably larger than 120°, the singlet energy remains higher than the triplet energy along both disrotation (1B) and conrotation (2B), as shown for the latter in Figure 4d. In the former, the effect, which presumably arises from the variation of the overlap between the ring π-systems and the *p* orbitals of the carbene carbon atom, is less marked, and vanishes as α approaches 180°, when disrotation (1B), like disrotation (1A), becomes a molecular rotation.

A discussion of some of these conformations, with stereoscopic drawings, has been presented by van der Heijden *et al.*[19]

The state of diphenylcarbene calculated to be the most stable is a linear triplet with rings at 90° to each other. However, an energy of $<3$ kcal mol$^{-1}$, which is smaller than warranted by the accuracy of our calculations and is, in any case, easily accessible by thermal excitation at room temperature, separates it from a continuum of states in which the rings can rotate freely and the molecule can bend to almost 145°. As a result, we expect that triplet molecules can be found in almost any of these geometrical conformations, the relative stability of which might well be determined by environmental effects. It is thus hardly surprising that analysis of spectra in condensed phases at low temperatures indicates a non-linear, twisted molecule.[6]

The most stable singlet state is calculated to be highly bent ($\alpha$ 120°) with both the phenyl rings at 90° to the central plane. This state is computed to be *ca.* 4 kcal mol$^{-1}$ less stable than the triplet state in its own most stable conformation. Although our calculated value of the energy gap is too small to be reliable, it is compatible with the recent estimate,[9a] based on experimental data, that the singlet state lies $<3$ kcal mol$^{-1}$ above the triplet state.

*Molecular Orbitals.*—The INDO calculations also evaluate the contributions from the atomic orbitals to the molecular orbitals. As far as carbene chemistry is concerned, the most important orbitals of the singlet state are the HOMO and the lowest unoccupied molecular orbital LUMO. The triplet state has two singly occupied molecular orbitals, SOMOs I and II, in order of decreasing stability, which correspond to the HOMO and LUMO orbitals of the singlet. In methylene, these orbitals consist of either pure $p_y$ and $p_z$ orbitals on the carbon centre or of linear combinations of the two. Surprisingly enough, these molecular orbitals on diphenylcarbene also consist essentially of $p$ orbitals at the carbene carbon centre, with only a small amount of delocalisation due to overlap with the phenyl $\pi$ systems, in all the calculated geometries.

Our results on diphenylcarbene are not in conflict with those of Hoffmann *et al.*[3] whose most stable geometry ($\alpha$ 165°, $\theta_1 = \theta_2$ *ca.* 45°) lies within our rather large region of maximum stability. Also, our calculations confirm Hoffmann's geometry of the singlet state (corresponding to his $A\sigma^2$) in which the phenyl rings are perpendicular to the angle of bend ($\theta_1 = \theta_2 = 90°$), our angle $\alpha$ being *ca.* 20° smaller than his. We do, however, contest his conclusion that the difference in energy between the singlet and triplet states is large.

*Intersystem Crossing.*—The most striking difference between the chemistry of methylene and that of diphenylcarbene seems to be the absence and presence respectively of a rapid equilibrium between the singlet and triplet species. Salem and Rowland[20] discuss intersystem crossing between singlet and triplet diradical states *via* spin–orbit coupling, the most facile mechanism by which this can occur. As they point out the two fundamental pre-requisites for effective spin–orbit coupling are (*a*) the orbitals involved in intersystem crossing should be orthogonal and (*b*) the separation between singlet and triplet levels must be as small as possible. It will be seen that in all known methylenes condition (*a*) is satisfied, because there are two orthogonal substantially non-bonding $p$ orbitals on the carbene centre. Therefore the intersystem crossing rate should be directly dependent on the energy gap between the states and their energy level density. Examination of the energy–configuration plots for diphenylcarbene (Figures 3 and 4) shows that in many of the regions where the singlet and triplet levels are isoenergetic, the energy variation along the co-ordinate is quite small on both sides of the crossing, indicating the presence of a dense manifold of energy levels on both sides of the barrier. Moreover this crossing occurs, at an energy not far above the lowest energy configuration of each state, each time the molecule vibrates through the angle $\alpha$ *ca.* 140° when the rings are approximately perpendicular to the central plane. Thus effective intersystem crossing is to be expected, and, since the singlet–triplet energy difference is not very large compared to $kT$, thermal equilibrium between these states should be easily set up. In contrast, methylene would not be expected to undergo such facile intersystem crossing because (*a*) it is a small molecule which has only one low energy vibrational mode, ' variation of the H–C–H angle ' and no internal rotations, so the density of states is much lower; and (*b*) both experimental and theoretical studies make it probable that the singlet–triplet energy gap in methylene is larger than that in diphenylcarbene.[5c,9]

*Geometrically Stabilized Singlet and Triplet Carbenes.*—Our calculations show that the triplet state generally lies below the singlet state. However, the singlet becomes more stable than the triplet when the angle $\alpha$ is small and both rings are twisted relative to the central plane ($\theta_1$ and $\theta_2$ large). Fluorenylidene represents a rigid molecule which should have a triplet ground state, while 2,2′:6,6′-diethanodiphenylcarbene (DADC) or 2,2′:6,6′-diethenodiphenylcarbene (DEDC) should have singlet ground states. DADC is shown in Figure 5. The Table, which contains the calculated energy differences between the singlet and triplet states of these molecules, confirms this conclusion. The geometry of fluorenylidene used in the calculation was taken from

| Compound | $(T_0 - S_1)$[c]/ kcal mol$^{-1}$ |
|---|---|
| Fluorenylidene | −21 |
| DADC[a] | 66 |
| DEDC[b] | 59 |

[a] 2,2′ : 6,6′-Diethanodiphenylcarbene. [b] 2,2′ : 6,6′-Diethenodiphenylcarbene. [c] A positive energy indicates that the singlet state is the ground state and thus the labelling should be $T_1 - S_0$ as noted earlier in the text.

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[19] S. P. N. van der Heijden, E. A. H. Griffith, W. D. Chandler, and B. E. Robertson, *Canad. J. Chem.*, 1975, **53**, 2084.

[20] L. Salem and C. Rowland, *Angew. Chem. Internat. Edn.*, 1972, **11**, 92.

ref. 21; those of DADC and DEDC, which are as yet unknown, were estimated using realistic values for the bond lengths and angles.

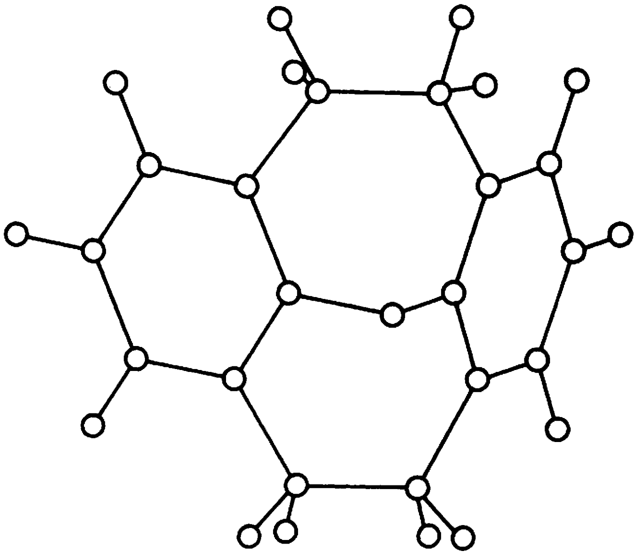

FIGURE 5 2,2′:6,6′-Diethanodiphenylcarbene (DADC)

Fluorenylidene has been found experimentally to have a triplet ground state.[22] Considering the arguments used in the discussion of intersystem crossing, one would not expect this to be a particularly rapid process in fluorenylidene because of a relatively large singlet–triplet energy gap and the absence of low energy modes. Therefore one would expect the chemical behaviour of fluorenylidene to be more similar to that of methylene than to that of diphenylcarbene. This is indeed the case, because it adds to $\pi$-systems without participating in a large amount of hydrogen abstraction,[23] the addition being largely stereospecific. A slow rate of intersystem crossing has been confirmed by the observation that the addition of an inert moderator to cause collision-induced intersystem crossing greatly affects the degree of stereospecificity of cyclopropane formation.[23b]

One would predict that DADC or DEDC, if generated in a similar way to methylene and fluorenylidene, would also react similarly, even though the former two are expected to have ground states of multiplicity different from that of the latter two. This is because their chemistry would presumably be governed by the nature of the initially prepared state, rather than that of the thermodynamically most stable state.

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