A Theoretical Approach to the Investigation of the Photochemical Internal Cycloaddition in Penta-1,4-diene and Hexa-1,5-diene

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A theoretical calculation has been performed on the photochemical internal cycloaddition reaction of non-conjugated dienes by an *ab initio* SCF MO procedure. The ground-state geometries of the species in several rotamers were investigated and the geometries in the excited triplet state were analysed in the same way. This enabled clarification of the stable and/or preferred molecular geometries of penta-1,4-diene and hexa-1,5-diene in both ground and excited triplet states for the first time. Total energies along the reaction co-ordinates were followed systematically. From these results preferred mechanisms for the addition reactions were proposed. Previous experimental results are explained in the light of the present calculations, *viz.* the prevalent parallel compound from the 1,4-diene, the cross compound from the 1,5-diene, and the ratio of the parallel/cross products in each reaction species. The potential for internal rotation about the skeletal bond was calculated for some cases in connection with the facility of the reaction. Reaction orbitals were selectively extracted and analysed, and the factors governing the [2 + 2] internal cycloaddition reaction were considered. The calculations also clarified the position of initial closure in the molecule.

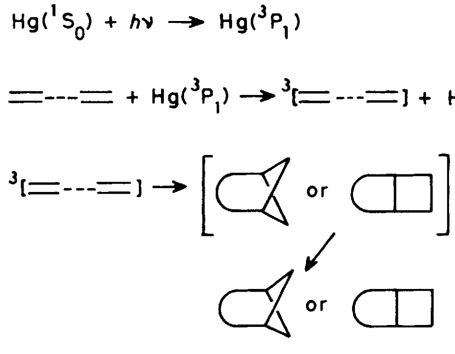
It is well known that non-conjugated aliphatic dienes give bicyclic alkanes on sensitization by mercury ($^3P_1$).[1–6] The photosensitized isomerization of dienes has been investigated since the very early days of photochemistry.[7–9] The reaction affords 1,2-bridged cycloalkanes *via* parallel addition or 1,3-bridged cycloalkanes *via* cross addition (see Scheme). The ratio of parallel to cross products depends on several factors, principally the number of methylene groups between the double bonds and the kind and the number of substituent groups. To explain the experimental results, Srinivasan *et al.*[5] proposed the 'rule of five' for 1,4-, 1,5-, 1,6-, and other dienes, Wolff *et al.*[10] argued in terms of the 'effect of substitution' at C(5) and the 'ring effect' in 1,5-dienones, and Bünzli *et al.*[11] and Gleiter *et al.*[12] discussed the effect of 'through-space interaction' and 'through-bond interaction'. Osawa *et al.* discussed steric effects for many ring dienes in the light of empirical force field calculations.[13] The 'rule of five' is valid for a variety of dienes.[14–16]

In recent years a group of theoretical treatments of photochemical reactions has appeared.[17–20] Stereochemistry has been discussed very widely.[21–27] There are still however some unclear points concerning the present reaction, and some exceptions to the rule.[28–30] To be able to predict selectivity, and parallel or cross closure, is of interest. In a preliminary communication[31] we have reported the result of MO calculations on this type of reaction, for penta-1,4-diene and hexa-1,5-diene as examples. Yet another interest of the present work was to determine the position of initial closure of the reactant molecules.

We describe here in detail the result of the SCF MO treatments of penta-1,4-diene and hexa-1,5-diene.

Calculation

All MO calculations were performed by using the Gaussian 80 program package[32] and geometry optimization was carried out by the energy-gradient procedure.[33] The basis set used for all calculations was STO-3G.[34] When the ground-state diene molecule is excited by triplet-state Hg or by u.v. light the molecule may become a triplet excited state according to the Wigner–Witmer spin-correlation rule.[35,36] The ground state of the molecules is, therefore, calculated by the RHF method and the excited triplet state by the UHF method. The calculations for the *trans,trans* (TT), *trans,cis* (TC), and envelope forms were performed for the 1,4-diene and the all-*trans* (TTT), *trans,cis,trans* (TCT), and envelope forms were taken into account for the 1,5-diene. These three forms were considered in both ground and excited states. In the excited state of the 1,4-diene, several additional forms were also energetically optimized. It was assumed that cross closure of the 1,4-diene started from the TC form and parallel closure from the envelope form in the triplet excited state, and that cross closure of the 1,5-diene started from the envelope form and parallel closure from the TCT form. Some singlet-point calculations were also performed to test the energy. The final products of the reactions were tentatively geometry-optimized.



Scheme.

Results and Discussion

Optimized Geometry.† —1,4-*Diene.* The values of the geometrical parameters seem reasonable in the ground state

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† Tables of geometrical parameters, bond lengths, and angles, are available as Supplementary Publication no. SUP 56678 (4 pp.). For details of Supplementary Publications see Instructions for Authors (*J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1).

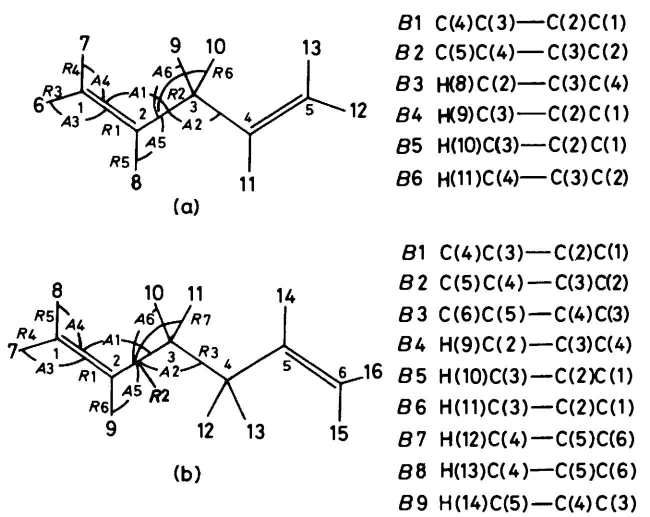

Figure 1. Schematic structures and atom numberings of (a) penta-1,4-diene and (b) hexa-1,5-diene

with reference to the observed values for, *e.g.*, but-1-ene:[37] $C(1)H_2{=}C(2)H{-}C(3)H_2{-}C(4)H_3$ (skew form) C(1)–C(2) = 1.342, C(2)–C(3) = 1.493, C(3)–C(4) = 1.536, C(1)–C(2)–C(3) = 125.4, C(2)–C(3)–C(4) = 112.1; (*cis*-form) C(1)–C(2) = 1.336, C(2)–C(3) = 1.507, C(3)–C(4) = 1.536, C(1)–C(2)–C(3) = 126.7, C(2)–C(3)–C(4) = 114.8 (bond lengths in Å, angles in degrees). With the ground-state geometrical parameters obtained among the rotamers there appears only a small difference in one bond length (*R*2) and one bond angle (*A*2) (see Figure 1). The bond concerned is the single C–C bond and it is understood that the value varies with the variation in rotational angle around this bond. The change in angle *A*2 is analogous to that of the observed values for C(2)–C(3)–C(4) of but-1-ene.[37]

Let us examine the geometries obtained for the triplet excited state. The most marked difference appears in the bond length *R*1 which in the ground state is the double bond. This bond is markedly elongated by triplet excitation; the increase is especially large in both TT (1.470 Å) and envelope (1.471 Å) forms, almost to the extent of loss of double-bond character. This elongation makes rotation about the bond possible. The bond angles *A*1 and *A*2 differ a little among the rotational isomers. In the case of the form 7 (Figure 2), *R*1 reaches a maximum (1.492 Å) and the difference between *R*1 and *R*2 (1.532 Å) becomes very small. The value of *R*1 decreases from form 5 (1.417 Å) to form 8 (1.408 Å) and increases again from form 8 to form 9 (1.429 Å).

There are some interesting differences in internal rotation angles (*B*1—*B*6), for example, between the forms 3 (R) and 6 (U).

The distances between the non-bonded C(1) and C(5) in the envelope form and between C(2) and C(5) in the TC form are of interest. The distances between C(1) and C(5) in the forms 3, 6, and 7 are estimated to be 4.36, 3.78, and 3.52 Å, respectively. The distances between C(2) and C(5) in the forms 2, 5, 8, and 9 are calculated to be 3.01, 3.02, 3.12, and 2.79 Å, respectively. In going from form 3 to form 6, and from form 6 to form 7, the distance between the ends of the molecule [C(2) ••• C(5)] decreases monotonically. This may be understood by considering the stereochemistry of the reaction course. In going from form 2 to form 9 the distance between C(2) and C(5) behaves differently from other distances. Thus the distance then varies little in going from form 2 to form 5, increases a little from form 5 to form 8, and then decreases abruptly from form 8 to form 9. The increase in going from form 5 to form 8 may be due to repulsive forces between H(8) and H(13). The distance between the H(8) and H(13) is 1.96 Å in form 5 and 1.93 Å in form 8. The abrupt decrease in going from form 8 to form 9 may also be due to the reduction of repulsion between the hydrogen atoms. The reaction scheme presented here for the TC form is only hypothetical, and does not show a definite mechanism/route for cross closure for the 1,4-diene.

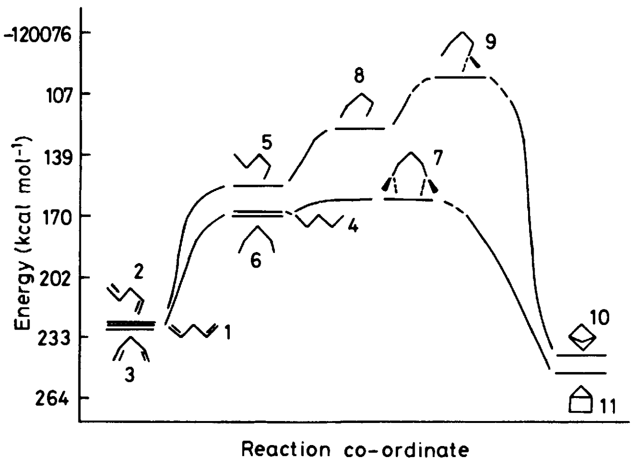

Figure 2. Relative energies (kcal mol^{-1}) for the system penta-1,4-diene–bicyclopentane

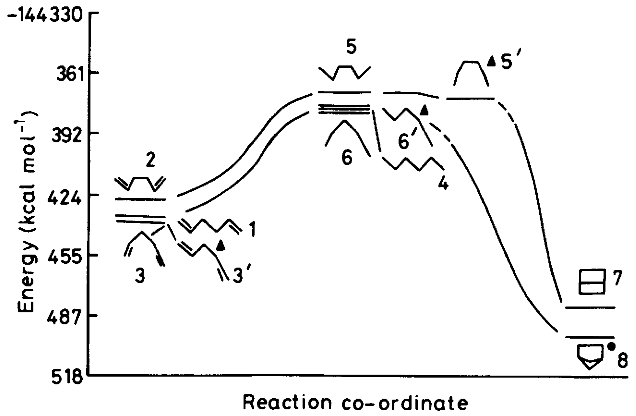

Figure 3. Relative energies (kcal mol^{-1}) for the system hexa-1,5-diene–bicyclohexane: (▲) single point calculation; (●) from ref. 38

1,5-*Diene*. The bond length *R*3 depends largely on the skeletal conformation in the ground state. In the case of the TCT form, the repulsive forces between H(9) and H(14) are greater, resulting in a large *R*3 value (1.581 Å; *cf.* TTT form 1.551 Å). The same is true in the excited triplet state. The values of the bond angles *A*2 and *A*5 also depend on the skeletal conformation in the ground state. However there are no clear bond angle differences between the ground and excited states. With the internal rotation angles, only the value of *B*4 is markedly different between ground and excited states. In this species we did not find the large differences between internal rotation angles in the ground and excited states which were observed in the case of the 1,4-diene.

Nevertheless there is some geometrical change in going from the ground to the excited state. The distance between C(2) and C(5) decreases in going from form 2 to the form 5 (Figure 3) (3.05 to 3.01 Å), and the distance between C(1) and C(5) decreases in going from form 3 to form 6, *i.e.* from 3.44 to 3.29

Table 1. Total energies (kcal mol^{-1}) for the system penta-1,4-diene–bicyclopentane

Form^a	RHF	UHF
1/4	−120 225.46	−120 169.41
2/5	−120 224.54	−120 155.36
3/6	−120 229.08	−120 170.32
7		−120 162.15
8		−120 126.09
9		−120 100.05
10	−120 242.51	
11	−120 251.63	

^{a} See Figure 2.

Table 2. Total energies (kcal mol^{-1}) for the system hexa-1,5-diene–bicyclohexane

Form^a	RHF	UHF
1/4	−144 435.33	−144 379.67
2/5	−144 426.15	−144 371.25
3/6	−144 436.82	−144 381.45
3′/6′	−144 436.75	−144 378.79
5′		−144 374.00
7	−144 481.57	
8	−144 495.11^b	

^{a} See Figure 3. ^{b} From ref. 38.

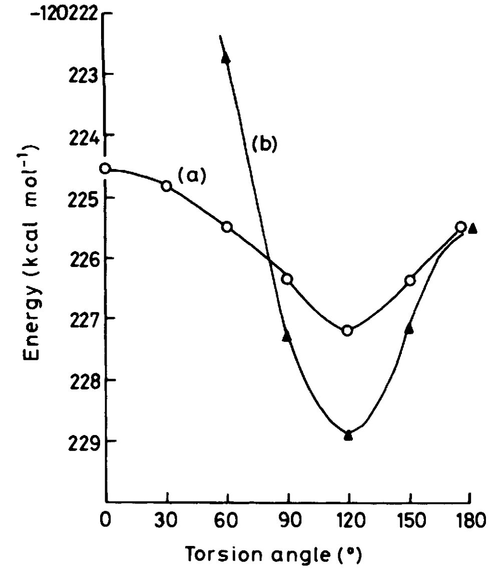

Figure 4. Total energy as a function of the rotational angle around the C–C bond in the ground state of penta-1,4-diene (RHF): (a) rotation around the C(3)–C(4) bond; (b) simultaneous rotation around the C(2)–C(3) and C(3)–C(4) bonds

Å. These changes are reasonable in view of the mechanism of internal closure of the molecule.

Optimized geometries of the products. The optimized geometries of the reaction products, bicyclo[1.1.1]pentane, bicyclo[2.1.0]pentane, bicyclo[2.1.1]hexane, and bicyclo[2.2.0]hexane, obtained by the *ab initio* SCF MO procedure, have appeared elsewhere.[38–40] These molecules however were also geometry-optimized in the present work, except for bicyclo[2.1.1]hexane. The geometries obtained reproduced excellently the previous *ab initio* work, and agreed quite well with the published geometrical parameters for bicyclo[1.1.1]pentane,[41] bicyclo[2.1.0]pentane,[42] and bicyclo[2.2.0]hexane.[43] We therefore did not carry out the computation for bicyclo[2.1.1]hexane.

Total Energies.—The relative energies for the systems penta-1,4-diene–bicyclopentane and hexa-1,5-diene–bicyclohexane are shown in Figures 2 and 3. Values of the energies are summarized in Tables 1 and 2.

1,4-*Diene*. The relative energies of the rotamers in the ground state are in the order: envelope < *trans* zigzag (TT) < TC. The energy difference between TT and TC in the ground state is small (*ca.* 1 kcal mol^{-1}).* However the difference between the envelope and TT forms in the ground state is *ca.* 4 kcal mol^{-1}. In the excited state the energies of the TT and envelope forms are close to each other. However, the destabilization is much larger in the case of the TC form than in the others. In the excited triplet state, forms 8 and 9 are considered as the most unstable forms, *i.e.* very close to the transition state (TS). Form 8 is the one in which the left-hand vinyl group has rotated 90° around the CC–CCC bond from form 5. In form 9 the right-hand methylene group has rotated by 90° around the CCCC–C bond from form 8. The total energies of the products bicyclo[1.1.1]pentane and bicyclo[2.1.0]pentane are also summarized in Table 1; the energy difference between them is *ca.* 9 kcal mol^{-1} and bicyclo[2.1.0]pentane is more stable than bicyclo[1.1.1]pentane. The present result agrees well with the previous *ab initio* work.[38] The order of the total energies of the products is closely related to the ease of cycloaddition. Srinivasan *et al.* reported [5] that the predominant product from the 1,4-diene was the parallel one, and that the cross/parallel ratio was 0.10. The energy difference between the TC and envelope forms in the excited triplet state (*ca.* 15 kcal mol^{-1}) seems too much for coexistence of the TC and envelope forms in this ratio in this state, even at the temperatures around 80 °C (b.p. of benzene). However, the minimal basis set used in the present work (STO-3G) does not take configuration interaction (CI) into account. Energetics obtained should therefore be regarded as merely qualitative. Use of a large basis set and a CI calculation might well give a smaller energy difference. The present calculation gives a difference between ground-state and excited state energies of the order of 60—70 kcal mol^{-1}. The excited mercury atom may have 112.2 kcal mol^{-1} in excess of the ground state,[7] *i.e.* enough to excite all the forms from ground to the excited state. Once all the forms are triplet-excited, the molecule exists in accordance with triplet-state energy, and when the difference in energy becomes reasonable, the TC and envelope forms may coexist; the competitive reaction will then take place.

1,5-*Diene*. The energies of the TTT and envelope forms in the ground state are nearly the same. However, the energy difference between TCT and envelope forms in the ground state is fairly large (*ca.* 10 kcal mol^{-1}). In the excited triplet state, the energy trends are analogous to those in the ground state. In order to save computing time the envelope form in the ground state was geometry optimized with the assumption that the bond lengths were the same as those of the *trans*-form. For geometry optimization in the excited triplet state, both the bond lengths and the bond angles were transferred from the *trans*-form. The internal rotation angles alone were optimized. If the full geometry optimization were carried out in these cases the energies obtained for the envelope form would be altered to some extent. The 10 kcal mol^{-1} difference between the envelope and *trans*-forms in the ground and excited states seems still too great to allow the coexistence of the two forms under experimental conditions. The improvement of the basis function

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* 1 kcal = 4.184 kJ.

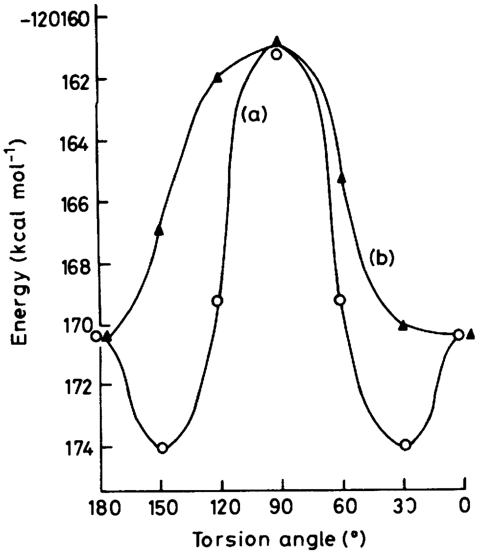

Figure 5. Total energy as a function of the rotational angle around the C–C bond in the excited triplet state of the envelope form of penta-1,4-diene (UHF): (a) conrotatory simultaneous rotation around the C(1)–C(2) and C(4)–C(5) bonds; (b) disrotatory simultaneous rotation around the C(1)–C(2) and C(4)–C(5) bonds

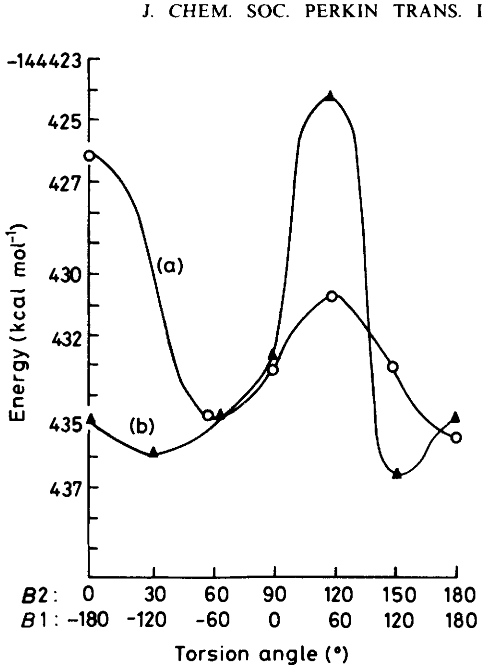

Figure 6. Total energy as a function of the rotational angle around the C–C bond in the ground state of hexa-1,5-diene (RHF): (a) rotation around the C(3)–C(4) bond; (b) rotation around the C(2)–C(3) bond by fixing the *gauche* conformation around the C(3)–C(4) bond

and inclusion of CI calculations might diminish the energy difference between the rotational isomers. Destabilization by the triplet excitation is calculated to be *ca.* 55 kcal mol^{-1}, *i.e.* somewhat less than for the 1,4-diene and sufficiently less than the excess of energy (112.2 kcal mol^{-1})[7] of the triplet state mercury atom.

The energies of the products bicyclo[2.2.0]hexane and bicyclo[2.1.1]hexane are shown in Table 2. The energy difference between them is *ca.* 14 kcal mol^{-1}, and bicyclo[2.1.1]hexane is more stable than bicyclo[2.2.0]hexane. Here the energy of the bicyclo[2.1.1]hexane is the literature value.[38]

In the triplet excited state the energy difference between the envelope and TC/TCT forms is rather more for the 1,4-diene than for the 1,5-diene. This can be reconciled with the experimental large cross/parallel ratio (2.53) for penta-1,5-diene; *cf.* 0.10 for the 1,4-diene.[5]

Barrier Height due to Internal Rotation.—1,4-*Diene.* The internal rotation potential around the CCC–CC bond was calculated in the ground state by the RHF procedure; the result is shown in Figure 4. Here the optimized geometry in the TT form was used and we have assumed that the rotation around the bond is rigid. The results showed that the TG form is at the energy minimum and that the TT and TC forms follow it. This shows that the most stable conformation around the single bond is the *gauche*. From this, the barrier for *gauche* to *cis* rotation is *ca.* 2.6 kcal mol^{-1} and that from *gauche* to *trans* is *ca.* 1.6 kcal mol^{-1}. These values are not high enough to prevent rotation about the bond at the usual temperatures. However most of the molecules probably exist in the G form in relation to the single bond, in accord with Boltzmann's distribution.

The internal rotation potentials around the CC–C–CC bonds were analysed simultaneously at the ground state by the RHF method (see Figure 4). The geometry optimized in the TT form was used again. In this case it was expected that the most stable form would be the envelope (GG). This is well reproduced by the calculations. The *cis,cis*-form is extraordinarily high in energy because of approach of the terminal methylene groups.

Simultaneous rotation around the C–CCC–C bonds in the envelope form was investigated in the excited triplet state by the UHF method; the result is shown in Figure 5. Here the geometry used was the one optimized for the GG form. These bonds became as long as an ordinary single bond in the excited state, as discussed in the preceding section. Thus rotation around them may not be difficult. Either conrotatory or disrotatory rotations were performed around both bonds simultaneously, and two curvatures were obtained. Both curvatures have energy maxima around τ[H(6)C(1)–C(2)C(3)] and τ[H(7)C(1)–C(2)C(3)]; or τ[C(3)C(4)–C(5)H(12)] and τ[C(3)C(4)–C(5)H(13)]: = 90° and −90°. These may correspond to the transition states for these rotations. However, the envelopes of the curvatures are different from one another. The conrotatory curve has energy minima at around 30 and 150°, and the disrotatory curve at around 0 and 180°. In both cases the barrier heights are of the order of 10 kcal mol^{-1}. This value is small enough in comparison with the excitation energy.

1,5-*Diene.* The internal rotation potential around the single CCC–CCC bond was investigated by the RHF method; the result is shown in Figure 6. There are two energy minima at the *gauche* and *trans* conformations in curve (a). The estimated barrier height in going from the *gauche* to the *trans* form is *ca.* 4 kcal mol^{-1} and that for *gauche* to *cis* is *ca.* 9 kcal mol^{-1}. Here the rotation is rigid except at the *cis* form, and the geometry used is the one which was optimized in the *trans* form. For this reason the potential curve around the *cis* form is not well resolved.

Rotation was performed around the left-hand-side single bond (*B*1) by fixing the central single bond (*B*2) in the *gauche* conformation in the ground state, by use of the RHF method. This gave curve (b). Two energy minima appeared at 120 and −120° and an energy maximum at 60°. The barrier height in going from the *gauche* (−120°) to the *trans*-form (−180°) is *ca.* 1 kcal mol^{-1}; that for *gauche* (−120°) to *trans* (180°) is *ca.* 12 kcal mol^{-1}, and that for *gauche* (120°) to *trans* (180°) is *ca.* 2 kcal mol^{-1}. These barriers are not high in comparison with the usual u.v. excitation energy. This calculated result shows that in this molecule there is no particularly high barrier to the formation of cross or parallel compounds from the triplet excited state.

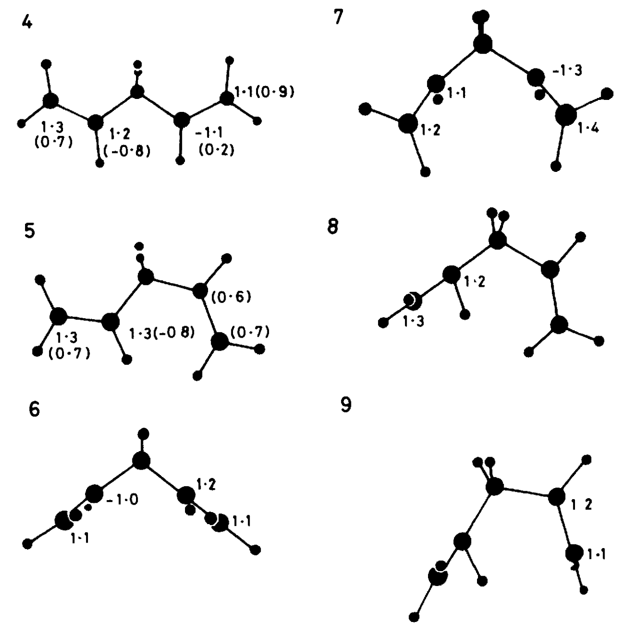

Figure 7. Atomic spin densities and coefficients of the SOMOs (in parentheses) of penta-1,4-diene (UHF)

Analysis of the Reaction Orbitals.—The orbitals which play an important part in the reaction are shown in Figures 7 and 8. In these Figures the coefficients of the SOMOs and atomic spin densities are summarized in order to rationalize the selectivity of the reaction and to find the initial closure point for the cycloaddition.

From these data we obtain answers to the following questions: (i) which takes place more easily, cross or parallel closure? (ii) where does closure begin? In the case of the TC form of the 1,4-diene, the atomic spin density is localized almost entirely at C(1) and C(2). However, it is spread over C(1)/C(2), and C(4)/C(5) in the case of the TT and envelope forms. This corresponds very well to the experimental fact that the reaction product is almost entirely the parallel compound.[5] For parallel closure, there are two possibilities: closure can begin between C(2) and C(4) or between C(1) and C(5). According to the SOMOs, C(1)···C(5) closure is the more reasonable. These calculations support the concept of 'the rule of five'.[5]

With the 1,5-diene, the largest spin densities are on C(1)/C(2) and C(5)/C(6). This tendency is nearly the same among the TTT, TCT, and envelope forms. This implies that there may exist strong competition between parallel and cross closure of the 1,5-diene and this may cause the larger cross/parallel ratio in the 1,5- than in the 1,4-diene. There are two possibilities for initial closure in parallel and in cross addition. According to the SOMOs, initial closure in the parallel reaction may take place between C(1) and C(6) rather than between C(2) and C(5). For the cross closure, we envisage prevalent C(1)···C(5) closure rather than C(2)···C(6).

In the present molecules the positions of greatest atomic density and the largest SOMO coefficients are almost coincident. Therefore by reference to the SOMO coefficients we can obtain information on the selectivity of cross/parallel additions and the position of initial closure.

Conclusions

(1) The stable conformations of the title compounds have been determined in both ground and excited states.

(2) Initial closure to give the parallel product takes place from the envelope form and to the cross product from the TC form in the case of the 1,4-diene. The same analysis is valid in the case of the 1,5-diene, *i.e.* parallel closure starts from the TCT form and cross closure from the envelope form. This means that the energy of the envelope form is one of the factors controlling cross or parallel closure in these dienes.

(3) Study of the variation of potential for internal rotation gave us information in relation to the energy barrier of the reaction.

(4) The SOMOs and the atomic spin densities of the molecules have clarified the position of the initial closure for both cross and parallel additions during internal cycloaddition. In some cases these data justify 'the rule of five'[5] in the selection of the cross or parallel closure. The result also implies that the cross/parallel ratio can be determined qualitatively by consulting SOMOs and atomic spin densities calculated for the excited triplet state.

Studies of the substitution effects on the internal cycloaddition reaction in the molecules concerned are in progress.

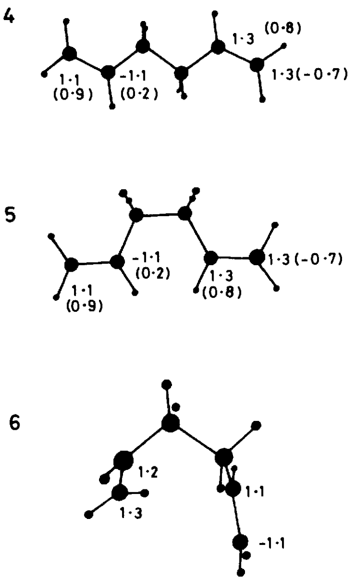

Figure 8. Atomic spin densities and coefficients of the SOMOs (in parentheses) of hexa-1,5-diene (UHF)

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