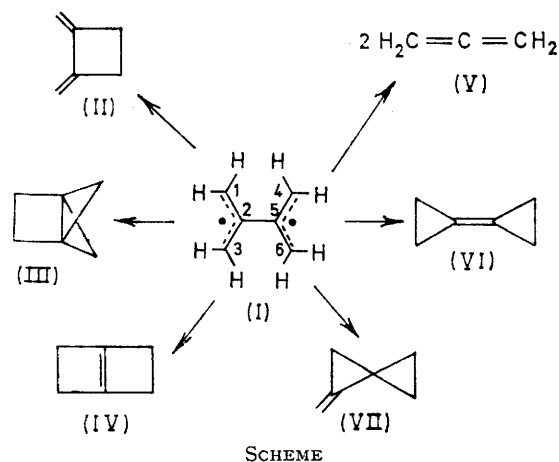


The 2,3-Dimethylenetetramethylene Biradical

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The 2,3-dimethylenetetramethylene biradical has a variety of interesting collapse products. We report extended Hückel and Pariser-Parr-Pople calculations of the electronic structure of this molecule as a function of twist around its central bond. Though our calculations point to a twisted triplet ground state they are not definitive. In any conformation the allyl moieties couple only weakly and the lowest singlet state is then a nearly equal mixture of two configurations. An orbital symmetry analysis of the interconversions of the biradical and its collapse products predicts the stereochemical consequences of concertedness in these transformations.

THE biradical (I), named here as 2,3-dimethylenetetramethylene, may be formally formed or decomposed in a remarkable variety of pathways illustrated in the Scheme.



SCHEME

It has thus been an attractive intermediate to postulate in the thermal reactions of its collapse products.¹ We present here some quantum mechanical calculations of its electronic structure.²

Among the many ways in which two allyl radicals can be coupled, the species (I) represents about the least efficient. The two allyl moieties are linked at their central atoms. At these sites the allylic non-bonding orbital has no electron density and so the coupling of the two allylic units must depend on more remote and correspondingly weaker 1,4-interactions. In a simple Hückel calculation there are two accidentally degenerate non-bonding orbitals in (I). When non-nearest-neighbour interactions are included these levels split slightly. The rough form of the molecular orbitals of (I) is shown in Figure 1. The splitting between b_1 and a is 0.20 eV in an extended Hückel calculation.³ Since the splitting is small, one is tempted to postulate a triplet ground state for the planar molecule.² No low-lying state of the planar species is expected to show much 2-5-

π -bonding. Moreover there is a pair of potentially short hydrogen-hydrogen contacts in the planar geometry, and so one is led to examine the possibility of preferred twisting around the 2-5-bond.

We first studied the π -electron states of (I) by a Pariser-Parr-Pople procedure specifically adapted for examining twisting motions and non-planar π -electron

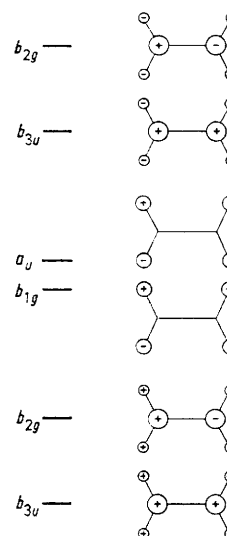


FIGURE 1 The π molecular orbitals of planar 2,3-dimethylenetetramethylene from the top. The co-ordinate system has the z axis along the central CC bond, the x axis perpendicular to the molecular plane

systems.⁴ As the molecule twists it goes from D_{2h} to D_2 to D_{2d} symmetry. The level correlation diagram of Figure 2 shows schematically the behaviour of the energy levels with angle of twist around the 2-5 bond. The non-bonding levels cross at about 40° of twist. The small splitting in the D_{2d} geometry places the b_1 level at lower energy and is clearly attributed to spiroconjugation.⁴ The splitting amounts to 0.15 eV in an extended Hückel calculation.

¹ (a) J. D. Roberts and C. M. Sharts, *Organic Reactions*, 1962, **12**, 1; (b) W. von E. Doering and W. R. Dolbier, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 4534; (c) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, 1967, **89**, 4532; 1969, **91**, 5900; (d) W. R. Moore, R. D. Bach, T. M. Ozretich, *J. Amer. Chem. Soc.*, 1969, **91**, 5919; (e) O. J. Muscio, jun., and T. L. Jacobs, *Tetrahedron Letters*, 1969, 2867; T. L. Jacobs, J. R. McClenon, and O. J. Muscio, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6038, and refs. therein.

² The electronic structure of (I) was first discussed by H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.

³ R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397, and subsequent papers. The parameters used here are the same except for a H 1s exponent of 1.3. The idealized geometry of (I) has 120° everywhere, and all C-C distances 1.45 Å, all C-H 1.10 Å.

⁴ R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, 1967, **89**, 5215; A. Imamura and R. Hoffmann, *ibid.*, 1968, **90**, 5379.

The important configurations in a π -electron description of 2,3-dimethylenetetramethylene are the following (we use the D_2 symmetry labels since this group of symmetry operations is maintained throughout the rotation): (i) $(b_3)^2(b_2)^2(b_1)^2 = {}^1A$; (ii) $(b_3)^2(b_2)^2(a)^2 = {}^1A$; (iii) $(b_3)^2(b_2)^2(b_1)^1(a)^1 = {}^1,{}^3B_1$. Since the a and b_1 levels

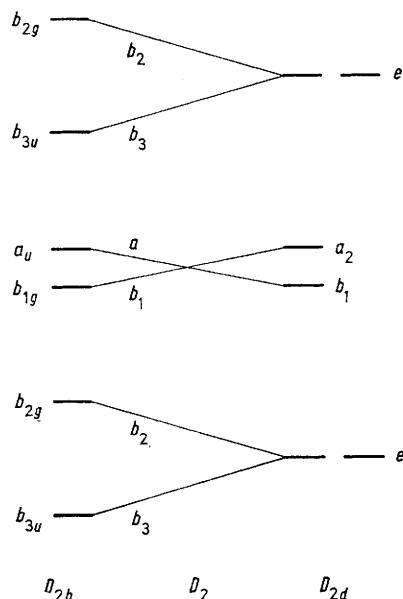


FIGURE 2 Level correlation diagram for twisting 2,3-dimethylenetetramethylene. The co-ordinate system is specified in the caption of Figure 1. Group theoretical designations follow E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill Book Co. Inc., New York, 1955.

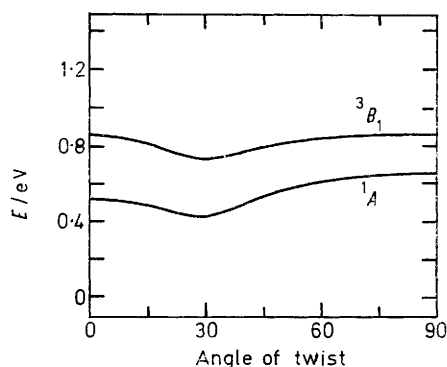


FIGURE 3 Calculated energy curves for the two lowest states of (I). Singly and doubly excited configurations only were included at this stage. The energy zero is arbitrary

are always close in energy, we expected extensive configuration interaction between (i) and (ii). This was confirmed; the lowest singlet, of A_1 symmetry, was primarily composed of configurations (i) and (ii), in nearly equal admixture.

Figure 3 shows the angular variation of the lower lying states of (I). In this calculation all single and double excitations were included in the configuration interaction treatment. The ground state at this stage is calculated to be 1A , with 3B_1 4–8 kcal/mol above it.

The potential energy does not vary much with twisting around the 2–5-bond, but there is a distinct minimum in both 1A and 3B_1 states near the level crossing at approximately 40° twist. Configuration interaction is extremely important for the description of biradical ground states, and so we stretched our resources to perform an SCF calculation in the planar geometry including nearly all configurations through triply excited ones. The 3B_1 state was extensively stabilized by this, and emerged approximately 1.5 kcal/mol below 1A .

Our conclusions as to the ground state and equilibrium geometry of biradical (I) are thus somewhat ambiguous. Given the measure of error in these calculations, we cannot safely predict whether 1A or 3B_1 is the ground state of the molecule. However, the two states cannot be far apart in energy. The π -electron calculation favours a planar or partially twisted geometry. Non-bonded interactions must be added on as a further energy component, and they will favour the twisted geometry. An extended Hückel calculation makes the D_{2d} geometry more stable than D_{2h} by ca. 4 kcal/mol. As expected there is no large barrier to twisting in any of the lower energy configurations.

Though the e.s.r. spectrum of triplet (I) has been recently reported,⁵ there is no structural information on its geometry. Stereochemical studies¹⁰ of thermal reorganization of dimethylenecyclobutanes have led to the conclusion that the lowest singlet possesses two effectively perpendicular allyl moieties.

We now consider briefly some of the orbital symmetry controlled⁶ interconversions of compounds (I)–(VII). Consider first the concerted collapse of planar (I) to the bicyclopropylidene (VI). If each cyclopropane ring can be formed in a conrotatory or disrotatory fashion, then there may be distinguished five distinct closure modes: two conrotatory in both rings, two disrotatory in both rings, one conrotatory in one ring, disrotatory in the other. A view of the transition state geometry along axis 1 in Figure 4(a) is convenient for visualizing these possibilities. The first four processes in Figure 4(b) retain at least two symmetry operations of the D_{2h} symmetry, and these may be used in the construction of correlation diagrams. One such diagram for the process dd_2 , preserving the mirror planes 1 and 2, is shown in Figure 5. The reaction is clearly symmetry-forbidden for any of the important configurations (i), (ii), or (iii) of (I). Similarly one finds that the processes dd_1 , cc_1 , and cc_2 are also forbidden. No symmetry is preserved in the dc process and so a correlation diagram is of no use in analysing the reaction. Following the orbitals through the reaction leads to the conclusion that this process, conrotatory in one ring, disrotatory in the other ring is allowed for configurations (i) or (ii).

For the collapse of (I) to the bicyclohexene (IV) one can again visualize five distinguishable modes. The transition state geometries may be labelled just as in the

⁵ P. Dowd, *J. Amer. Chem. Soc.*, 1970, **91**, 1066.

⁶ R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 1969, **81**, 797, and references therein.

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study of the collapse to dicyclopropylidene, except that the view is now along axis 2. The orbital symmetry

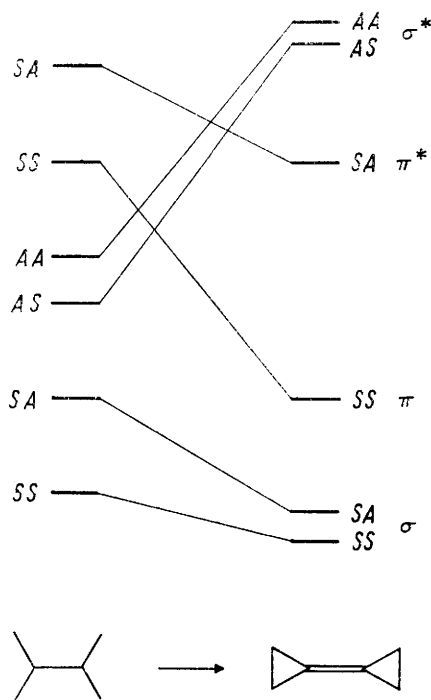
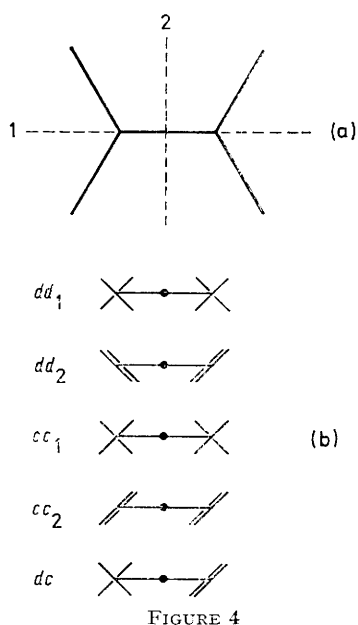
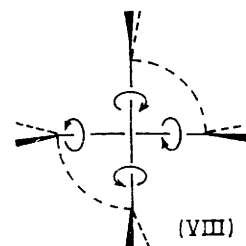


FIGURE 5 Level correlation diagram for the doubly disrotatory mode dd_2 for the collapse of (I) to bicyclopropylidene. The mirror planes are defined in the text

analysis yields the following results: the dd_1 and dd_2 modes are forbidden. The cc_1 and cc_2 modes are allowed for configuration (ii) only, and the dc mode is allowed for configuration (i). Since the lowest singlet is a nearly balanced mixture of configurations (i) and (ii), it is difficult to predict its stereochemical preference.

Were the collapse to bicyclohexene to begin in the twisted D_{2d} geometry then one definite twist mode would be directed by the torsions needed to form the bonds. This mode, shown in (VIII) is equivalent to cc_1 .



In the formation of the highly strained tricyclo-[2,1,1,0]hexane (III) from (I) we find that a concerted process is possible when either a conrotatory or disrotatory closure of the cyclobutane ring (forming bond 1-4) is coupled with a specific process in which bonds are made from 3 and 6 to 5 and 2 respectively on the *same* topological face at 3 and 6. Configuration (i) favours a disrotatory closure, while configuration (ii) prefers a conrotatory course. Were we to localize double bonds at C(3)-C(2) and C(5)-C(6) we could describe the bicyclobutane formation as a $2_s + 2_a$ cycloaddition.⁶

In the context of known chemistry most pertinent is the collapse of (I) to the dimethylenecyclobutane¹ (II). Let us begin the analysis with a planar geometry of (I). Correlation diagrams for conrotatory and disrotatory closure are shown in Figure 6, which correlation diagram has also been constructed by Muscio and Jacobs.^{1e} Configuration (i) allows the disrotatory process, configuration (ii) the conrotatory process. To the extent that (i) predominates slightly in the lowest singlet state

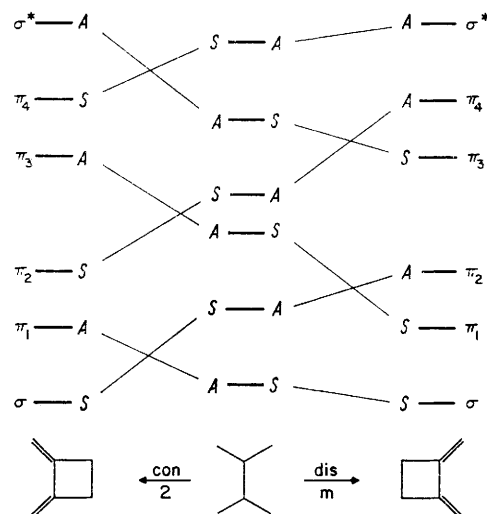


FIGURE 6 Level correlation diagram for disrotatory and conrotatory closures of (I). The symmetry elements used are a mirror plane at right and a two-fold rotation axis in the heavy atom plane at left

of the planar form one might expect a preference for disrotation. As mentioned previously, however, the 1A state is a mixture of configurations (i) and (ii) in nearly

equal proportions, and so we do not feel secure in predicting a striking preference for disrotation.

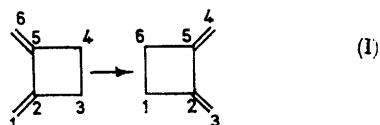
Were the reaction to begin in a twisted D_{2d} geometry, the same configurational relationships would hold. However in the twisted 1A state the configuration (ii) predominates slightly and a corresponding small preference for conrotation would be expected.

The interconversion of the bicyclohexene and the dimethylenecyclobutane is a normal electrocyclic reaction expected to be conrotatory in the ground state, disrotatory in the first excited state.

The direct rearrangement of (VI) to (IV) may be classified as a cycloaddition of two σ bonds. It is geometrically constrained to proceed with inversion at all centres, and thus is classified as $^1_02_s + {}_02_s$, ground-state forbidden, photochemically allowed.

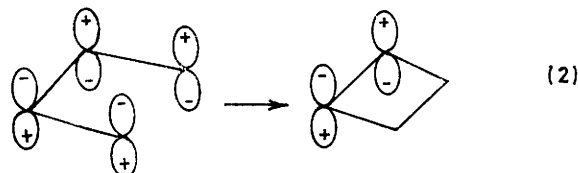
The stereochemical results of an elegant experiment on the dimerization of optically active cyclononadiene^{1d} are consistent with the allowed $\pi 2_s + \pi 2_a$ process. The observed stereospecificity is however also accounted for^{1d} by a sterically controlled formation of (I) and its orbital symmetry controlled closure to (II).

We finally discuss the degenerate rearrangement (1) of (II). This reaction is formally a Cope rearrangement,

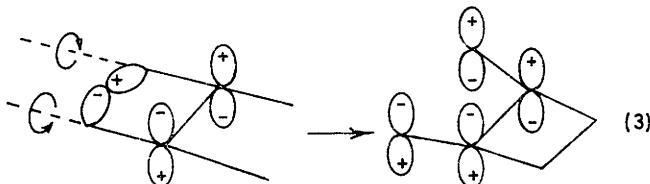


and can be analysed as such, or as a $\pi 2 + {}_02 + \pi 2$ cycloaddition. The thermally allowed processes are those conrotatory at both ends or disrotatory at both ends. Of special interest is the allowed double disrotatory process, since stepwise performance of this process, *via* the bicyclohexene, is a sequence of two forbidden reactions. It is interesting to analyse how this can occur.

In the isolated disrotatory electrocyclic closure the orbital which moves to high energy in the transition state is χ_2 of butadiene; χ_1 having formed the new σ bond, χ_2 can only correlate (2) to a π^* orbital of the cyclobutene.⁶



In the case of the doubly disrotatory Cope rearrangement this same orbital is kept bonding by mixing with a σ^* orbital of the breaking σ bond. It becomes χ_2 of the new butadiene [reaction (3)].



In addition to symmetry factors there is an overlap requirement for effective reactions. In dimethylenecyclobutane there is little initial overlap between the two double bonds and the breaking σ bond. The concerted reaction is not expected to be easy. The experimental evidence on the thermal rearrangement of labelled dimethylenecyclobutanes implicates a non-concerted process proceeding through a relatively freely rotating 2,3-dimethylenetetramethylene biradical.^{1b,c}

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