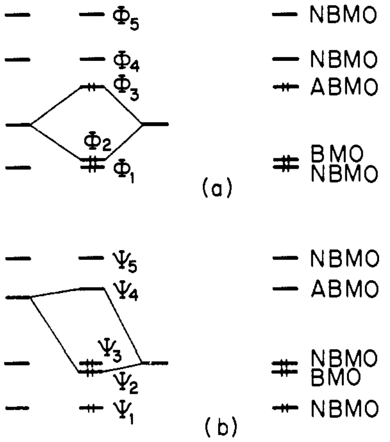


Figure 14. The MO's of the inversion (a) and retention (b) transition state complexes of a case I AD anionic 1,4 migration.

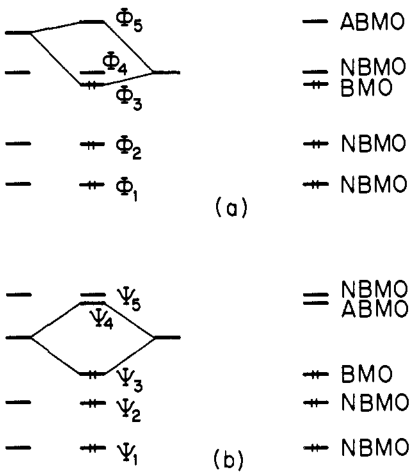


Figure 15. The MO's of the inversion (a) and retention (b) transition state complexes of a case II AX anionic 1,4 migration.

the forbiddenness of a least motion process is removed whenever there can be strong configuration interaction. This result is similar to results obtained in the cases of intermolecular cycloadditions and sigmatropic reactions. The full implications of these results will be discussed in greater detail in the next article.

Finally, it is rather apparent that approximate indices for locating a particular ionic migration on the reactivity spectrum are rather readily available as in the cases of intermolecular cycloadditions and sigmatropic reactions. In the case of cationic rearrangements, an AD migration will occur whenever the ionization potential of the migration framework and the ionization potential of the formal radical, which corresponds to the migrating formal cation, are similar in magnitude. On the other hand, an AX migration will obtain whenever the ionization potential of the migration framework and the ionization potential of the formal radical corresponding to the migrating formal cation are extremely different in magnitude. In the case of anionic rearrangements, an AD migration will obtain whenever the ionization potential of the migration framework and the electron affinity of the migrating formal anion are extremely different and an AX migration will obtain whenever the ionization potential of the migration framework and the electron affinity of the migrating group are similar.[12]

---

(12) In this work we only examined the stereochemistry of suprafacial migrations. The same approach can be used to examine the stereochemistry of the less probable antarafacial migrations.

Configuration Interaction and Organic Reactivity. IV. Concepts and Generalizations

Nicolaos D. Epiotis[1]

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540.

Received March 22, 1972

Abstract: On the basis of our previous findings it is concluded that configuration interaction can reverse the stereoselectivity of $4N$ electron pericyclic processes but not that of $4N + 2$ electron pericyclic processes. The importance of configuration interaction in reducing or removing the forbiddenness of certain pericyclic processes is further illustrated by consideration of front-side nucleophilic displacement on saturated carbon. Some important implications of these findings are also discussed.

In the previous articles, we examined the effect of configuration interaction on the stereoselectivity of pericyclic reactions. The results of this study are collected in Table I. An examination of Table I leads to the following generalizations.

(a) All pericyclic reactions form a reactivity spectrum which varies continuously from AA to AZ pericyclic processes.

(b) Configuration interaction is important in most pericyclic AX processes and can be neglected in most AD pericyclic processes.

(c) Configuration interaction can lead to reversal of stereoselectivity in $4N$ electron pericyclic processes by rendering the stereoselectivity of the AX reactions opposite to the stereoselectivity of the AD reactions. In such $4N$ electron pericyclic processes, the intermediate region of the reactivity spectrum will be constituted of reactions which are nonstereoselective. The

---

(1) Address correspondence to the Department of Chemistry, University of Washington, Seattle, Wash. 98105.

Table I. Stereochemistry of AD and AX Pericyclic Reactions

Type of reaction	AD	AX
2 + 2 cycloaddition	$2_s + 2_a$	$2_s + 2_s$
4 + 2 cycloaddition	$4_s + 2_s$	$4_s + 2_s$
Butadiene ring closure	Conrotatory	Disrotatory (?)[a]
Hexatriene ring closure	Disrotatory	Conrotatory (?)[a]
1,3 sigmatropic shift	Suprafacial–inversion	Suprafacial–retention
1,5 sigmatropic shift	Suprafacial–retention	Suprafacial–retention
1,2 cationic shift	Suprafacial–retention	Suprafacial–retention
1,4 cationic shift	Suprafacial–inversion	Suprafacial–retention
1,2 anionic shift	Suprafacial–inversion	Suprafacial–retention
1,4 anionic shift	Suprafacial–retention	Suprafacial–retention

[a] In these cases, reversal of stereoselectivity may be obtained only in cases of extreme substitution.

nonstereoselectivity is the result of two competing concerted processes.

(d) Configuration interaction will not lead to reversal of stereoselectivity in $4N + 2$ electron pericyclic processes and these reactions will occur with the same stereoselectivity through the entire range of the reactivity spectrum.[2]

These generalizations lead to the identification of two categories of pericyclic processes.

(1) Unistereoselective processes which exhibit the same stereoselectivity independent of the nature of the reactants. The 4 + 2 cycloaddition is a typical example of a unistereoselective process.

(2) Multistereoselective processes which exhibit different stereoselectivity depending on the nature of the reactants. The 2 + 2 cycloaddition is a typical example of a bistereoselective process. It is probably necessary to fully explain our choice of the term multistereoselective. In the present work, we have examined reactions which were either unistereoselective (4 + 2 cycloaddition) or bistereoselective (2 + 2 cycloaddition). The term multistereoselective is general and it includes not only bistereoselective but also tristereoselective, tetrastereoselective, etc., reactions. The photocycloaddition of carbonyls and olefins is in a sense a tristereoselective reaction since it can occur in a concerted suprafacial manner, a biradical-like manner, or a concerted antarafacial manner depending on the position of the specific reaction on the reactivity spectrum.[3] Thus, we prefer the term multistereoselective as a general term although we recognize that most pericyclic reactions will be unistereoselective or bistereoselective.

It is important to recognize that the results of our analysis form a very interesting and intuitively satisfying pattern. In particular, we have argued that the stereochemistry of $4N + 2$ pericyclic processes does not depend on substituents. In other words, an aromatic transition state is not influenced by substitution. On the other hand, we have argued that the stereochemistry of $4N$ pericyclic processes does depend on substituents. In other words, an antiaromatic transition state is influenced by substitution. These results are entirely consistent with the concepts of aromaticity and antiaromaticity. For example, a benzene ring is an aromatic nucleus no matter what substituents are present. On the other hand, the orbital properties of cyclobutadiene and its antiaromaticity strongly depend on substitution and geometry.[4]

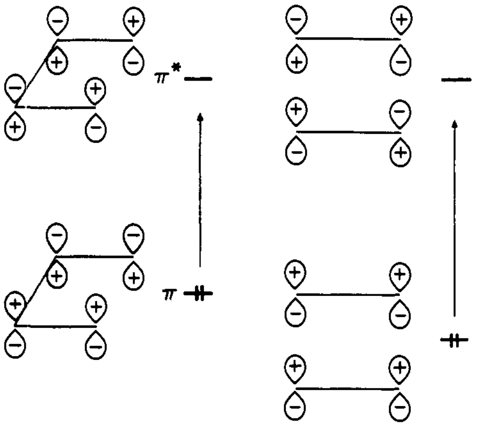


Figure 1. The effect of excitation on bonding in the cases of butadiene and the $2_s + 2_s$ transition state complex.

Some conceptual aspects of this work merit our attention. It should be emphasized that in this series of articles we considered just the bonding properties of the lowest diexcited configuration of the transition state complex and neglected the effect of configuration interaction in reducing Coulomb repulsions. In this respect, the ideas expressed in this work are very much related to some familiar notions of organic chemistry. The change of bond order which accompanies photoexcitation of a polyene is a textbook illustration of how bonding is affected by electronic redistribution.[5] The effect of π,π^* excitation on the double bond character of the central bond of butadiene is shown in Figure 1. This electronic transition involves removing one electron from an orbital which is antibonding along the central butadiene bond and placing it in an orbital which is bonding along the central butadiene bond. Hence, a π,π^* electronic transition results in increased bonding of the middle two carbons of butadiene. The same idea is central in our consideration of configuration interaction as a means of removing the forbiddeness of pericyclic reactions. The effect of promoting two electrons from ψ_2 to ψ_3 of the transition state complex of a thermal 2 + 2 cycloaddition of two ethylenes is shown in Figure 1. This diexcitation involves removing two electrons from an orbital which is antibonding along the uniting sites and placing them in an orbital

---

(2) However, $4N + 2$ electrocyclic reactions might be exceptions in extreme substitution situations.

(3) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924, 1935, 1941, 1946 (1972).

(4) For example, see R. Hoffmann, *Chem. Commun.*, 240 (1969).

(5) For the original work, see R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

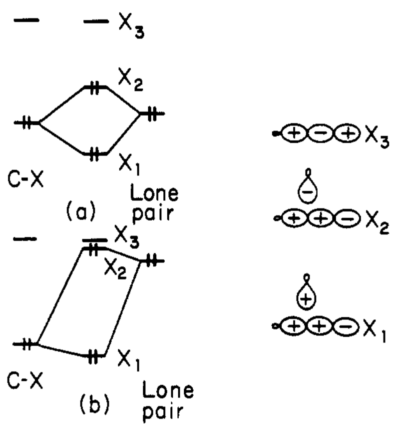


Figure 2. The MO's of the transition state complex for front-side displacement on saturated carbon. Substitution pattern I (a) and substitution pattern II (b).

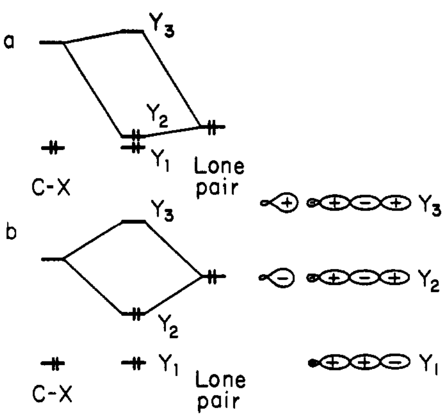
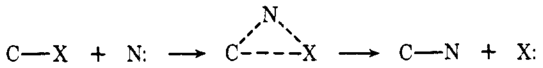


Figure 3. The MO's of the transition state complex for back-side displacement on saturated carbon. Substitution pattern I (a) and substitution pattern II (b).

which is bonding along the uniting sites. Hence, diexcitation results in increased bonding of the two ethylenes. In the photochemical example energy is provided by light, while in the thermal cycloaddition example energy is thermally provided. In forbidden AD pericyclic reactions, the thermal energy which is necessary for a two-electron promotion is substantial because the energy gap separating the HOMO and the LUMO of the transition state complex is large. On the other hand, in forbidden AX pericyclic processes the thermal energy which is necessary for a two electron promotion is small because the energy gap separating the HOMO and the LUMO of the transition state complex is small. Accordingly, diexcitation results in the removal of the forbiddeness of AX but not AD pericyclic processes.

It is interesting to remind ourselves how theoretical analysis of organic problems has evolved. In the computation field we have seen rapid progress which has taken us from the Hückel method to highly sophisticated *ab initio* methods.[6] On the other hand, in the field of "down to the bench" theoretical analysis our view of reactivity has been for decades a one-electron view. In this work, we have moved a small step ahead and considered reactivity from the standpoint of configuration interaction. The general conclusions that we arrived at are significantly different from conclusions based on one-electron treatments. It is rather remarkable that a configuration interaction approach has led to a drastically different outlook of electrocyclic reactions and it is worth speculating how other mechanistic concepts will be altered when configuration interaction is taken into account. As a prelude to a potentially exciting general reinvestigation of mechanistic concepts, we now consider the problem of front-side nucleophilic displacement at a saturated carbon.[7]

The problem of front-side nucleophilic displacement at saturated carbon can be treated simply by considering the interaction of a lone pair of electrons with a σ bond. The lone pair belongs to the nucleophile and the σ bond is the bond which is broken during the reaction.



$$\mathrm{C{-}X} + \mathrm{N{:}} \longrightarrow \overset{\mathrm{N}}{\mathrm{C{-}{-}{-}{-}X}} \longrightarrow \mathrm{C{-}N} + \mathrm{X{:}}$$

There are two characteristic substitution patterns and they are listed as follows. (I) The substituents on the C–X bond are inductively releasing groups and the lone pair has a high ionization potential. (II) The substituents on the C–X bond are inductively withdrawing groups and the lone pair has a low ionization potential. The MO's of the transition state complexes involved in front side displacement are shown in Figure 2. It can be seen that for both substitution types the ground state configuration of the transition state complex has the same energy as the two isolated reactants. A diexcited configuration will involve promoting two electrons from an ABMO to a NBMO of the complex, and this will give rise to net bonding between the lone pair and the C–X bond. Mixing of the ground state configuration and the diexcited configuration will become increasingly favorable as one goes from substitution type I to substitution type II. This occurs because the energy difference between the ground state and the diexcited configurations decreases in this order. Unfortunately, the stabilization of back-side attack also increases in the same direction and one expects back-side displacement to be uniformly of lower energy than front-side displacement. This is shown in Figure 3. However, this analysis shows that there is nothing sacred and absolutely forbidden about front-side displacement at a saturated carbon. In fact, when back-side displacement is rendered impossible then one might reasonably expect front-side displacement to occur. A reaction belonging to substitution type II where back-side displacement is sterically forbidden can lead to the observation of a genuine front-side displacement. It is interesting to note that our discussion of the interaction of a lone pair with a σ bond led to the conclusion that such an interaction becomes increasingly attractive in nature as the ionization potential of the lone pair decreases and the electronegativity of the C–X bond increases. This discovery is relevant to problems in conformational and geometric isomerism and will be discussed in detail in a forthcoming publication.

---

[6] (a) R. McWeeny and B. T. Sutcliffe, "Methods of Molecular Quantum Mechanics," Academic Press, New York, N. Y., 1969; (b) O. Sinanoglu and K. B. Wiberg, "Sigma Molecular Orbital Theory," Yale University Press, New Haven, 1970.

[7] For an excellent monograph on this subject, see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

In conclusion some general remarks are in order. We have argued that configuration interaction has profound effects on chemical reactivity. The condition for maximum configuration interaction is that there exists a diexcited configuration of similar energy to the lowest state configuration of the transition state complex or molecule. This criterion has been consistently utilized in our discussions. However, it should be pointed out that the matrix element between the lowest state and diexcited configurations should also be greater than zero and appreciable in magnitude for configuration mixing to be strong. Fortunately, this condition is almost always met, since the crucial matrix element reduces to an exchange integral which, for some appropriate geometry of the transition state complex or of the molecule, is usually significantly greater than zero. Many configuration interaction calculations of ground state and excited molecules can be cited in support of this argument. One should also be cautioned against semantic pitfalls. A pericyclic transition state complex can be either symmetrical or unsymmetrical. In all likelihood, most pericyclic transition states are unsymmetrical in nature since asymmetry lifts the prohibition to extensive configuration mixing which is otherwise imposed by symmetry itself. Thus, a pericyclic transition state can resemble a singlet dipolar or diradical species, but can never be equated to them since such entities do not exhibit bonding along the polar or radical termini, by definition. Finally, it is important to single out people who have expressed related ideas with respect to the importance of configuration interaction. In this respect, the important contributions of Bader,[8] Salem,[9] and Pearson[10] merit our attention. More recently, the effect of configuration interaction on specific organic reactions has been discussed in interesting papers by Buenker and Peyerimhoff[11] and Trindle.[12] Finally, an interesting paper on concertedness has recently been contributed by Schmidt.[13]

Acknowledgment. I wish to express my appreciation to Professor P. v. R. Schleyer for his helpful comments and interest in this work. I am indebted to Professor L. Salem for his critical comments. Professor C. Trindle kindly made available some of his work prior to publication and Professor R. C. Cookson informed us of similar ideas regarding the problem of sigmatropic reactions. Finally, discussions with Professor J. A. Berson and comments of Professor P. D. Bartlett are gratefully acknowledged. The author is pleased to acknowledge the support of the Petroleum Research Fund (Grant 2653-G1) and the Research Corporation.

(8) R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962).

(9) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969); also L. Salem, unpublished work reported in the Brandeis Mechanism Conference, 1968.

(10) R. G. Pearson, *Accounts Chem. Res.*, 4, 152 (1971).

(11) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *J. Amer. Chem. Soc.*, **93**, 5005 (1971), and previous papers in this series.

(12) F. S. Collins, J. K. George, and C. Trindle, *ibid.*, **94**, 3732 (1972).

(13) W. Schmidt, *Tetrahedron Lett.*, 581 (1972).

Absolute Configuration and Chiroptical Properties of Optically Active 1,1′-Spirobiindan, 1,1′-Spirobiindene, and 1,1′-Spirobiindanone[1]

James H. Brewster* and Robert T. Prudence

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. *Received April 27, 1972*

Abstract: (*R*)-(+)- and (*S*)-(−)-1,1′-spirobiindan, (*S*)-(−)-1,1′-spirobiindene, and (*S*)-(+)-1,1′-spirobiindan-3-one and the related *R*-(+) monoolefin and *R*-(−) monoketone have been prepared in a state of high enantiomeric purity. Their configurations, as assigned by Horeau's method, concur with those assigned independently by others. The long-wavelength rotations can be accounted for by coupling (B-mode) of major local polarizability axes, in a simple form of the helical conductor model. The ultraviolet Cotton effects are discussed in terms of sector rules and various coupled oscillator models of optical activity.

Chiral substances with C_2 symmetry (one twofold rotation axis) are of interest because their chiroptical properties ([M]D, ORD, and CD) may reveal the ways in which the chromophores interact with one another under the influence of light.[2] For example, 1,1′-spirobiindan (**5**, Chart I) contains two phenyl groups that could interact with light (a) essentially independently, (b) cooperatively as a composite chromophore *via* diphenylmethane homoconjugation (π transmission), (c) as oscillators coupled through dipole–dipole interactions (through-space transmission), or (d) as parts of a framework in which a collection of electrons suffers small, but concerted and cooperative, displacements along bonds (σ transmission). In the first case, the Cotton effects would correspond in location to those of suitably analogous mononuclear indans and be about twice as large. In the second case a Cotton effect not seen in monoindans would appear, potentially quite strong and with a sign corresponding to the chirality of the composite chromophore.[3] In the third case, as

(1) (a) A Useful Model of Optical Activity. X. (b) Part IX: J. H. Brewster and R. S. Jones, Jr., *J. Org. Chem.*, **34**, 354 (1969).

(2) G. Wagnière and W. Hug, *Tetrahedron Lett.*, 4765 (1970); *Tetrahedron*, **28**, 1241 (1972).

(3) (a) A. Moscowitz, "Optical Rotatory Dispersion," C. Djerassi, Ed., McGraw-Hill, New York, N. Y., 1960, Chapter 12; (b) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961); (c) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).