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Computational studies of transition states of reactions

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Abstract

The most direct way of understanding and controlling chemical reactions is to obtain detailed information about transition states. It is now fairly straightforward to compute transition-state geometries and energies of complex chemical reactions using semiempirical, Hartree–Fock, Møller–Plesset perturbational and density functional theoretical methods. Detailed insights which can be obtained from such studies are illustrated with representative applications to stereoselective cycloadditions, electrophilic additions, and Claisen rearrangements. The potential of computational transition state modelling in the design stage of antibody catalysis research is pointed out.

Keywords: Transition states, MO theory, stereoselectivity, catalytic antibodies.

1. Introduction

One of the primary goals of chemistry is to understand chemical reactivity in as great a detail as possible. Rational synthesis is possible only if transformations can be carried out in a predictable manner. While empirical data continue to provide the guiding principles in most cases, subtle problems of stereoselectivity require a deeper level of understanding.

At the fundamental level, study of chemical reactivity begins with the complete characterisation of the potential energy (PE) surface. The problem is complex because a system with N atoms involves a 3N-6 dimensional hypersurface. Detailed study is possible only for systems with 3 or 4 atoms. For the more important larger systems, a simplified description is used. An idealised one-dimensional cross-section of the PE surface, known as minimum energy pathway, connecting the reactant to the product is the focus of interest. The geometry change along the path represents the reaction coordinate and is characteristic of each mechanism. Additional minima along the reaction coordinate correspond to reactive intermediates. The highest energy point is the transition state.

Most studies have attempted to obtain detailed information about possible intermediates and transition state for a given reaction. Kinetics experiments provide energetic details about these key points on the PE surface. But only indirect information is obtained through these methods about molecular and electronic structure. While spectroscopic characterisation is possible for reactive intermediates,[1] such as carbocations and carbenes, transition states (with rare exceptions)[2] remain outside the purview of direct experimental observation.

Modern computational methods provide an attractive and, perhaps, the exclusive means of characterising transition states. Geometries, energies and additional properties can be obtained

sion) or a suitable combination of parameters (e.g. a pair of bond lengths for concerted cycloaddition reactions). The highest energy point on this surface is located with a fair degree of precision. This geometry is then used as the starting point in a more involved effort of gradient minimisation with the constraint that the Hessian is unity. Many algorithms have been implemented for this purpose with varying degrees of success. After refining the transition state structure, it is important to ensure that the Hessian is one through a vibrational frequency calculation. This has the added advantage of providing data for computing the entropy of activation. Finally, it must be confirmed that the transition vector truly connects the minima of interest. It is advisable to scan the PE surface on either side of the transition state along the reaction coordinate and to ensure that no other intermediates exist. Systematic procedures for following the transition vector have been developed for this purpose.[5]

The above sequence of studying reaction mechanisms can be employed with a variety of theoretical methods. Modern computer programs for performing semi-empirical[6] molecular orbital as well as *ab-initio* calculations[7] have built-in algorithms for transition state optimisations. Since gradients can be computed efficiently at the Hartree–Fock and MP2 (Møller–Plesset second-order perturbation theory) levels, transition state searches are relatively straightforward. Density functional methods can also be employed for studying transition states.

3. Studies on idealised substrates

Transition state optimisation programs have been used systematically to study various common reaction types with idealised substrates. The first step is to confirm that the theoretical methodology employed correctly reproduces the experimental activation parameters. Usually, activation energy is the property of interest. However, entropy of activation provides an additional reference for comparison. Conformational effects and substituent effects on activation parameters, where available, are also of interest. After ensuring that the calculations are consistent with the primary kinetic data, further analysis can be made.

The computed molecular and electronic structures of the transition state provide a wealth of information. Intricate details of the reaction mechanism, e.g. isotope effects, can be derived. Alternative pathways can be evaluated and the preferred one predicted. From electronic structures and additional details like charge distributions, the factors stabilising or destabilising the transition state can be unravelled.

Detailed computational studies as described above have been carried out on a number of important reactions. For example, the cycloaddition of ethylene and 1, 3-butadiene is one of the most exhaustively investigated reactions.[8] In addition to the concerted symmetrical pathway, an asynchronous mechanism as well as a step-wise process involving a biradical intermediate (Fig. 1) have been thoroughly evaluated. The activation barriers, entropies of activation and kinetic isotope effects have been computed at different theoretical levels. Similarly, three different types of transition states have been considered for the Cope rearrangement of 1,5-hexadiene (Fig. 2). Besides attempting to reproduce the experimental kinetic data, theory has been used in an innovative manner for this reaction. Chemical shifts and magnetic susceptibility have been computed for the energetically preferred transition state in order to assess its aromatic character.[9]

with as much rigour and reliability as for ground state minima. Multiple mechanistic pathways can be analysed. Even reactions which involve a high barrier can be studied. Calculations are ideally suited for studying problems of stereoselectivity and for obtaining insights as to the structural or electronic origin of relative activation barriers.

The computational effort involved in studying transition states and some of the commonly employed theoretical methods are described in the next section. The procedures can be applied in different ways. One approach would be to consider the simplest or idealised substrates for various important types of chemical reactions and characterise the transition state in each case. The general features can then be extrapolated to corresponding reactions of more complex substrates. Alternatively, the larger systems of experimental relevance can be directly studied, generally using simplified theoretical procedures. In this paper, representative examples of theoretical studies using the above strategies are given.

2. Procedures for determining transition states

Stationary points on a PE hypersurface can be precisely defined. The atomic forces are identically zero for these structures. Equivalently, the gradients of energy with respect to arbitrary nuclear displacements are zero. The stationary point is further characterised by the number of negative eigenvalues of the second derivative Hessian matrix (i.e. force constants), which is the same as the number of imaginary vibrational frequencies.[3] This number is called the Hessian index.

True minima, such as the reactant, product and possible intermediates have a Hessian index of zero. That is, a minimum has 3N-6 positive force constants (3N-5 for a linear system) and equivalent real vibrational frequencies. A saddle point, on the other hand, has one and only one negative force constant and the corresponding frequency is imaginary. The Hessian index is one. In qualitative terms, the transition state corresponds to a structure with zero gradients, which is a maximum along one vibrational mode and at the same time a minimum with respect to all other modes. The eigenvector of the force constant matrix corresponding to the unique vibrational mode with the imaginary frequency provides a precise definition of the reaction coordinate. The mode is referred to as the transition vector connecting two minima (the reactant and the product for a reaction with no intermediates). Stationary points with a Hessian index greater than one are also often encountered in computational work, especially those which include symmetry constraints. A structure with a Hessian of two corresponds to a 'hill-top'. Higher-order stationary points are usually not of chemical interest.

Efficient algorithms are available for determining minima on PE surfaces. The problem is relatively simple, since we need to find structures with vanishing gradients and with the lowest possible energy. Location of a transition state is more tricky.[4] Although the search is again for a structure with vanishing gradients, it must be a maximum with respect to one normal mode. Importantly, this mode must correspond to the desired transition vector connecting the reactant to the product. Although automated procedures are being developed, use of chemical insight is highly recommended in transition state searches.

The usual procedure begins with a rough scan of the PE surface with an assumed reaction coordinate. The latter may be a single geometric variable (like a bond length or angle or tor-

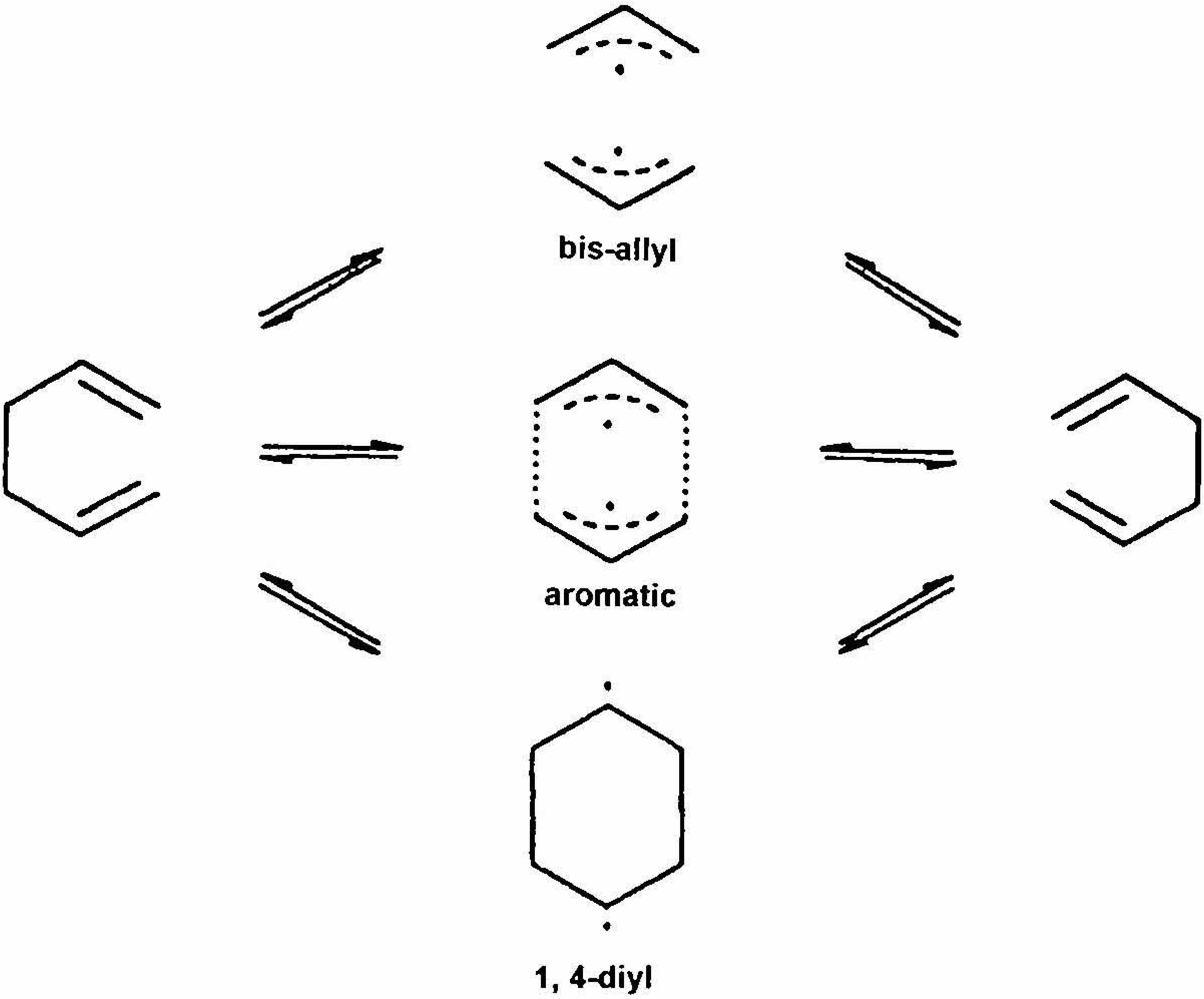


FIG. 2. Three possible mechanistic pathways for Cope rearrangement.

bon atoms of the enediyne unit is reduced has been successfully modelled[19] by the combined use of molecular mechanics with some parameters derived from semi-empirical calculations.

The above strategy is simple but assumes transferability of various interactions determining relative stability of the transition state. The procedure may not always be reliable. For example, the unusual changes in Bergman cyclisation rates in substrates with similar geometries could not be explained using hybrid quantum chemical/force field methods.[20] A better alternative would be to directly examine PE surfaces of complex substrates. Necessarily, semi-empirical and low-level *ab-initio* calculations have to be used.

A few illustrative calculations employing the two approaches effectively are discussed in the following.

4.1. *Face-selective cycloadditions*

By definition, the two faces of a π bond are equivalent. However, the symmetry can be broken through substitution. The possibility of selectivity directing a reagent to approach from one of

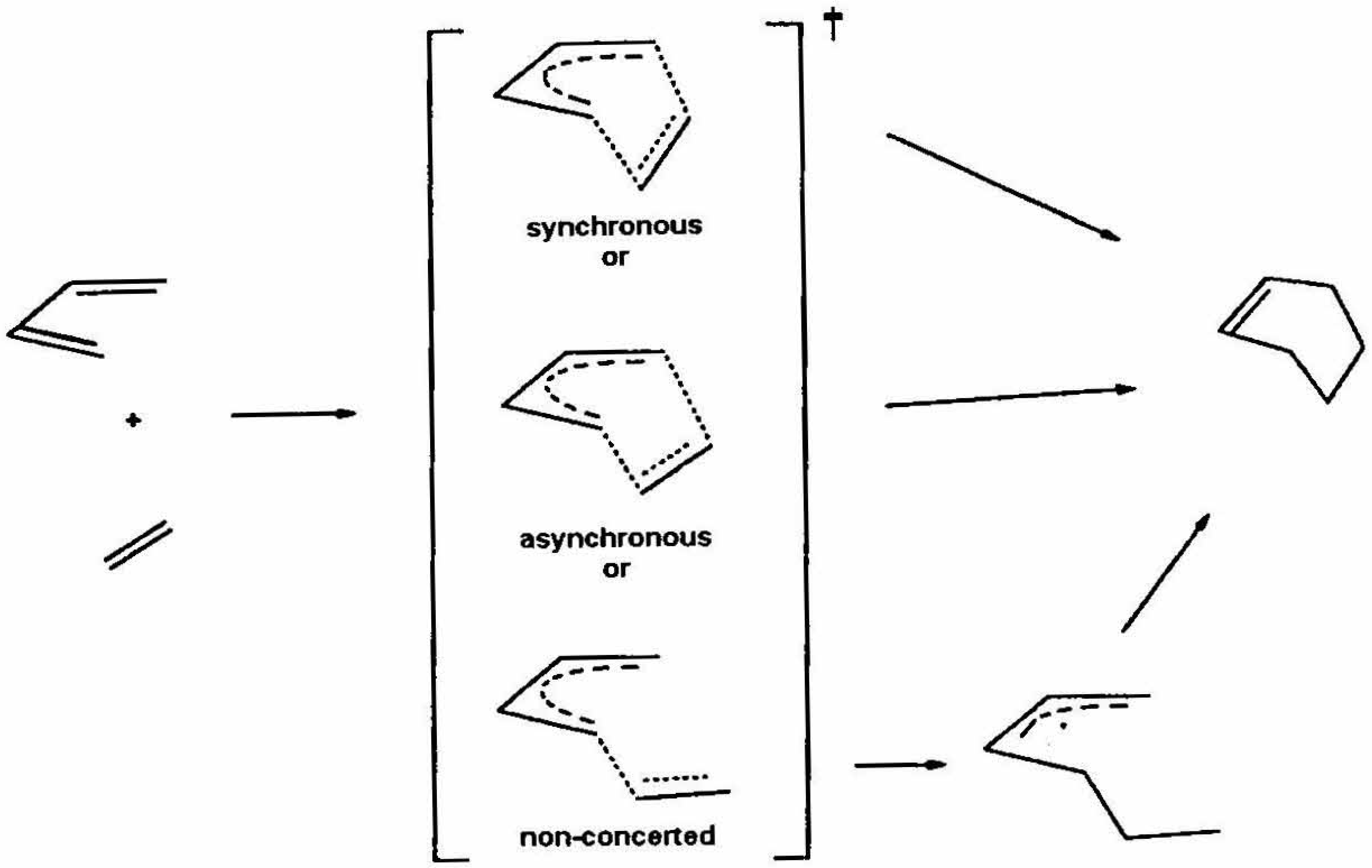


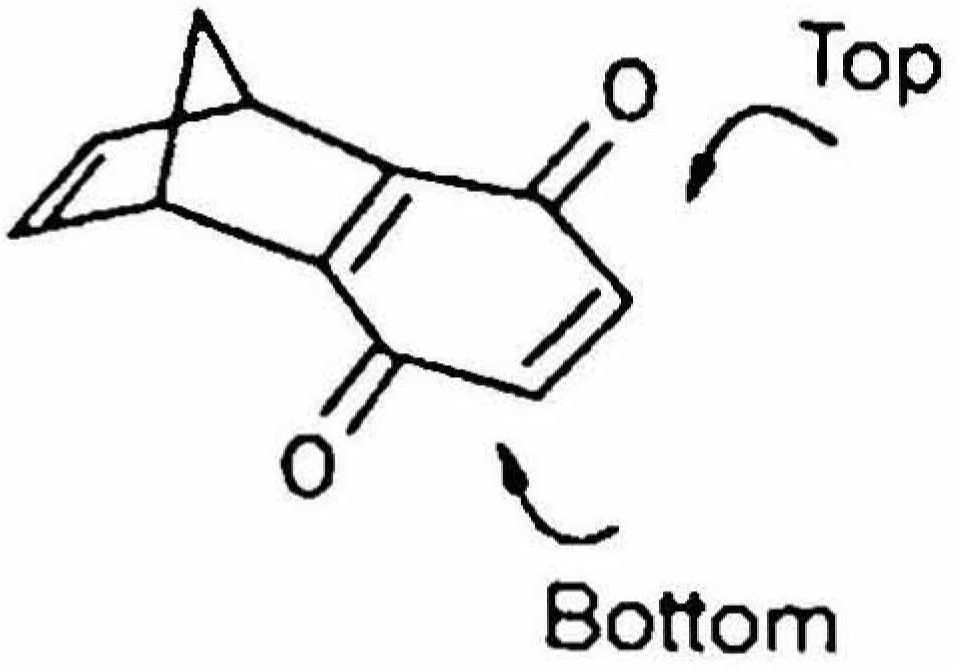
FIG. 1. Three possible mechanistic pathways of Diels–Alder addition.

Other reactions which have been extensively studied at high levels of theory include carbene addition to olefines,[10] nucleophilic addition to cyclohexanone[11] and other ketones,[12] Claisen rearrangement,[13] cycloaromatisation of hexaenediyne (Bergman cyclisation)[14] and Myers' cyclisation of an allene-ene-yne.[15] A series of catalytic processes involving organometallic systems have also been thoroughly examined in recent years.[16]

4. Studies on complex substrates

The examples considered in the previous section correspond to the simplest representatives of various reactions. While these are no doubt of fundamental interest, most experimental studies involve much more complex substrates. For theory to be of greater value, reactivity problems of such systems have to be addressed.

A simple approach is to extrapolate the key results on simple substrates to complex systems. The basic structures of the transition state may be assumed to be unchanged and the steric and electronic perturbations caused by substituents can be assessed. Steric effects in transition states, in particular, can be modelled quantitatively to a certain extent. Empirical force field parameters can be developed from the energetics of the model transition state. For example, from *ab-initio* calculated results on the cycloaddition reaction between ethylene and butadiene, a reasonable force field for Diels–Alder transition state has been developed.[17] Similar parameters are also now available for a variety of common organic reactions, such as the ene reaction, hydride transfer, hydroboration, radical addition, etc.[18] In an interesting application, the variation in the activation energy of Bergman cyclisation as the distance between the terminal car-



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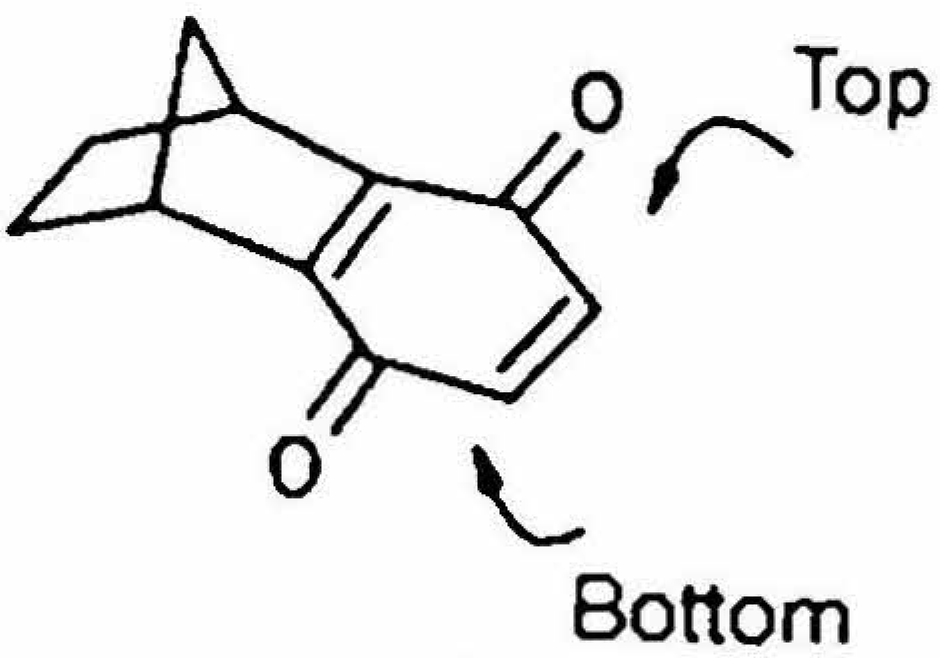

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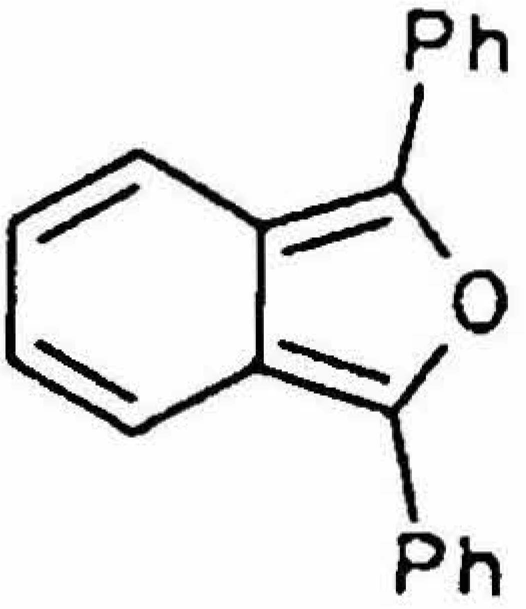

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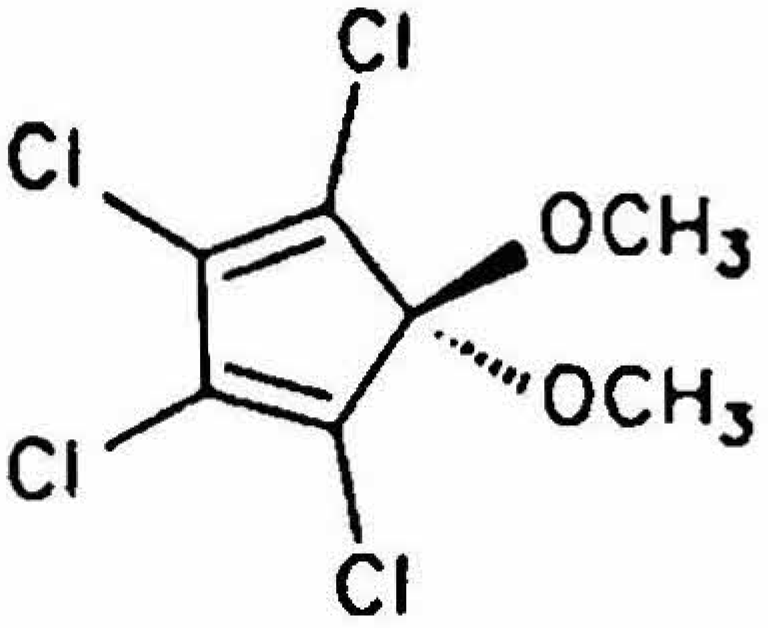

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While the above trends are qualitatively reasonable, the exclusive formation of the top face adduct in the case of two dienes has a more subtle origin. The calculated transition state geometry for the Diels–Alder reaction of the simple substrates, ethylene and 1, 3-butadiene, reveals several interesting features (Fig. 3). In addition to pyramidalisation of ethylene and twisting of the terminal methylene units on the diene, the hydrogen atoms on the central carbon atoms of the diene are also distorted. There is a clear out-of-plane bending of the hydrogen atoms towards the dienophile. This geometric feature is reproduced at all levels of theory and is in the range 10–15°. All the distortions, including bending, occur to maximise frontier orbital interactions. When bulky groups are present in the central carbon atoms of the diene, the out-of-plane bending can have important steric consequences. For example, such substituents would have greater repulsion with the *endo* hydrogen atoms for the bottom face addition to **2**. This is indeed the origin of the exclusive formation of the top face adduct in the case of dienes **3** and **4**, both of which have bulky groups at the central carbon atoms of the diene.

All the above interpretations could be quantified using a hybrid MO/MM2 procedure.[22] The MNDO-optimised geometry of the Diels–Alder transition state for ethylene + butadiene was used as the basic model. The geometry of **1**, **2** and the model diene, optimised at the MNDO level,[23] was grafted onto the transition state structure. The non-bonded interactions were then computed using the MM2 force field parameters.[24] This simple computational procedure yielded energy differences between top and bottom face addition transition states which are generally consistent with the observed product ratios (Table I).[21] Although the predictions were

Table I
Experimental and calculated product ratios (top: bottom) for the cycloaddition reactions of dienophiles 1 and 2 with various dienes

Dienophile	Diene	Observed	Calculated
1	cyclopentadiene	35:65	46:54
2	cyclopentadiene	78:22	34:66
1	isobenzofuran, **3**	81:19	34:66
2	isobenzofuran, **3**	100:0	100:0
1	chlorodiene, **4**	77:23	46:54
2	chlorodiene, **4**	100:0	100:0

the π faces through remote perturbation represents an interesting challenge, with considerable potential synthetic utility. Many studies have been carried out on cycloaddition reactions of sterically perturbed dienes, such as isodicyclopentadiene and related derivatives.[21] The first systematic investigation of face-selective Diels–Alder reactions of sterically biased dienophiles was carried out on the *p*-benzoquinones **1** and **2**. Several interesting trends were noted experimentally (Table I).[22] In most cases, a mixture of two products, corresponding to the top and bottom face addition to the distal double bond was obtained. Generally, the norbornyl derivative, **2**, gave more of the top face adduct. However, the magnitude of selectivity was dependent on the diene partner used. In two cases, viz. with isobenzofuran (**3**) and a chloro diene (**4**), exclusively top face attack was observed.

All the above trends can be traced mainly to steric interactions at the cycloaddition transition states. The diene normally prefers the *endo* approach. As a result, it encounters repulsion with the methylene or etheno (ethano) bridges for the top and bottom face attack, respectively. Face selectivity is determined by the relative van der Waals' repulsion. The etheno bridge involves the least repulsion and hence more of the bottom face adduct is obtained in the case of norbornenyl-fused derivative, **1**. The *endo* hydrogen atoms in the corresponding dihydro compound lead to enhanced repulsion with the diene, resulting in the major product corresponding to the top face attack.

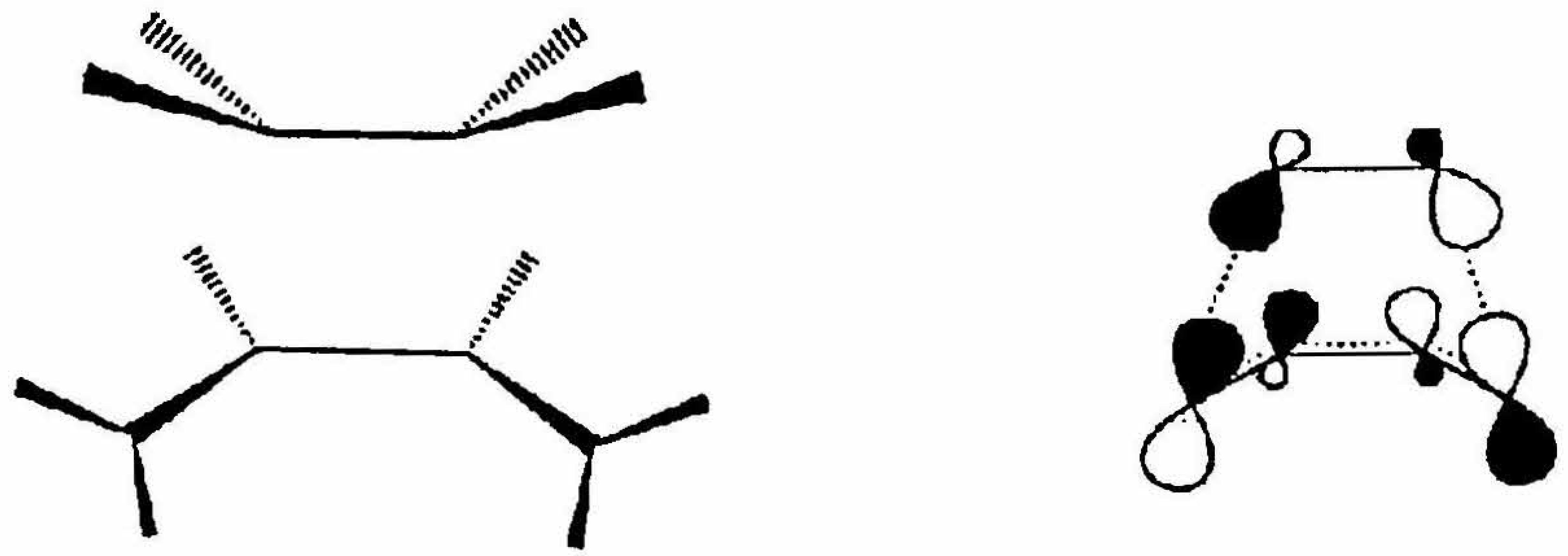


FIG. 3. Schematic representation of the optimised geometry of the Diels–Alder transition state. Note the pyramidalisation of the dienophile, twisting of the terminal units of the diene and the out-of-plane bending of the internal substituents which maximise the frontier orbital interaction shown on the right.

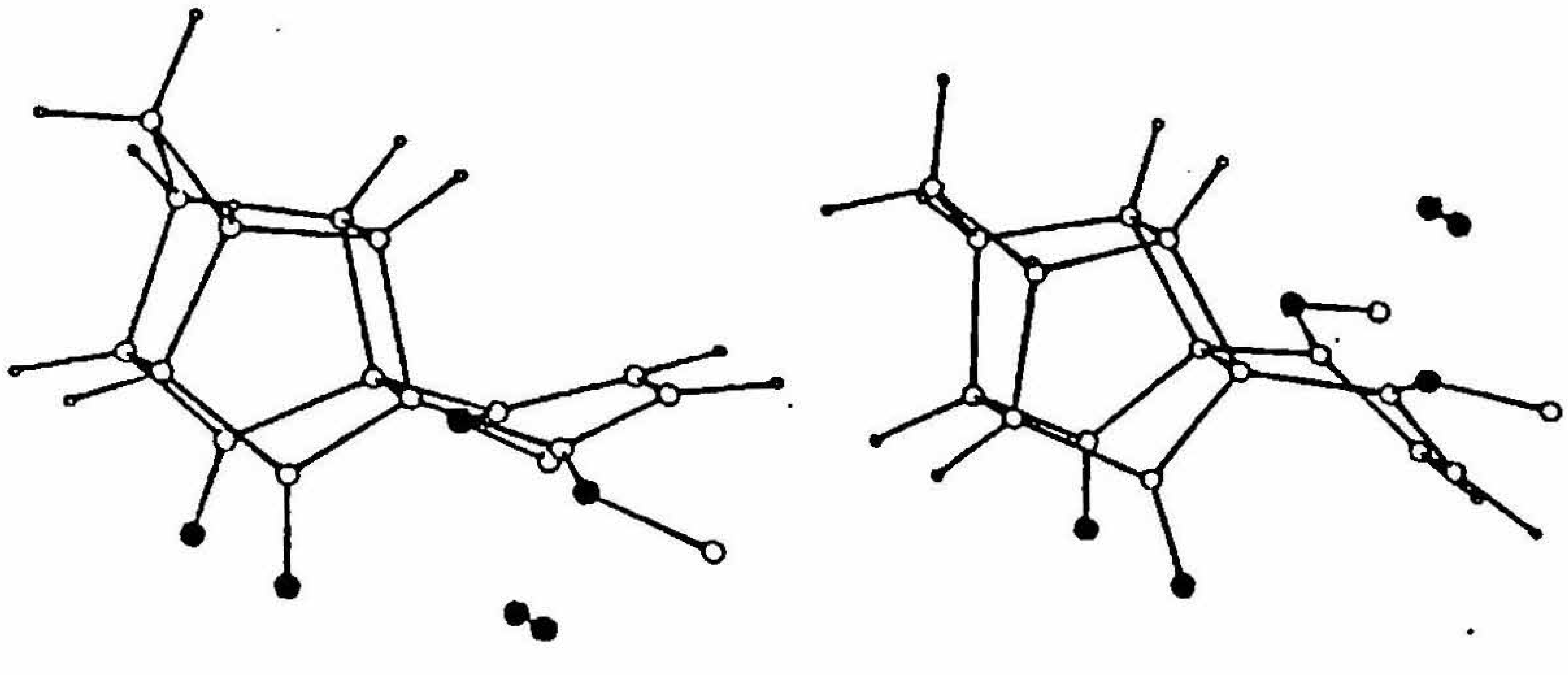


FIG. 4. Optimised geometries of the transition states for singlet oxygen addition to the carbonyl (left) and cyclobutane (right) faces of diene 5 with dimethoxy substituents. Note the closer contact between–OMe groups and carbonyl units in the former structure.

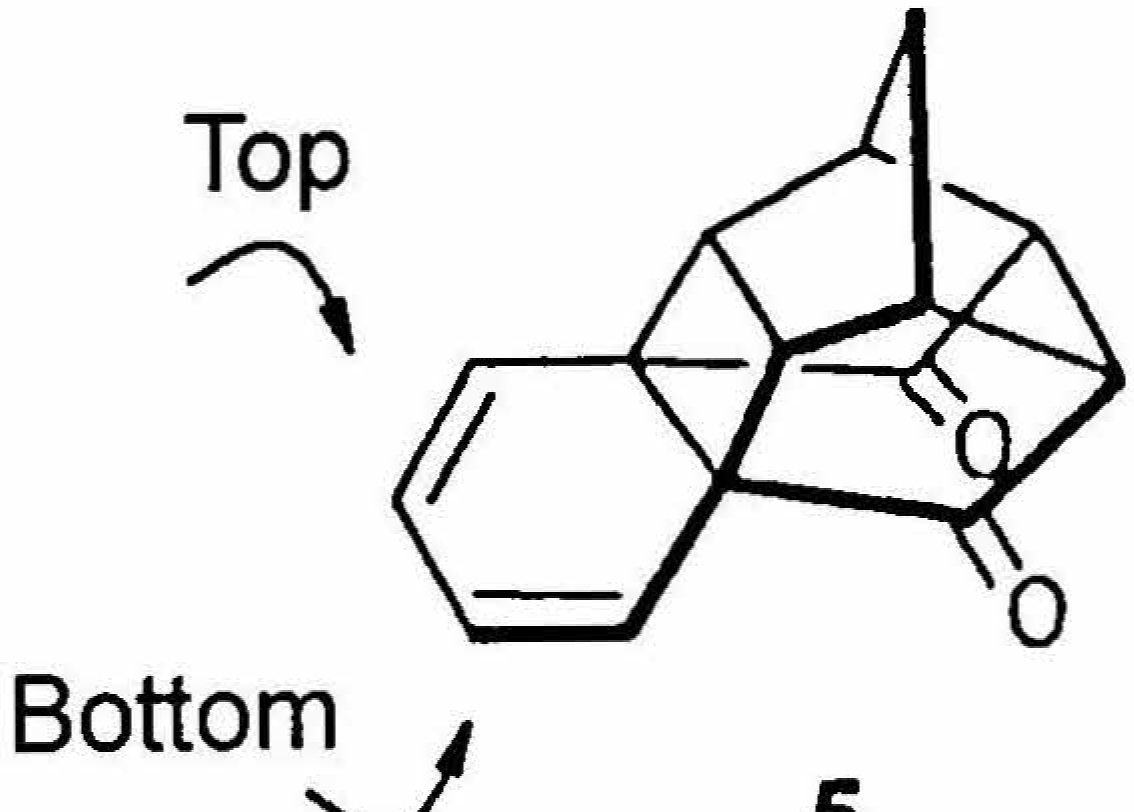
around in selectivity cannot be explained on the basis of ground state effects. The effect can be explained only by taking into account the additional interactions introduced at the transition state.

As noted earlier, the terminal groups of the diene twist towards the approaching dienophile (Fig. 3). In a cyclic derivative, the internal atoms necessarily have to be used to close the ring. Therefore, the substituents on the ring twist upwards in the direction of the dienophile. In the substituted dienes, the –OR groups distort towards the approaching singlet oxygen. For the bottom face attack, this will bring the –OR groups closer to the carbonyl groups resulting in destabilization (Fig. 4). Hence, more of the top face attack product is observed.

The above interpretations were confirmed through transition state energies computed at the MNDO and AM1 levels.[27] The enhanced top face preference in the substituted derivatives was correctly reproduced in the calculations.[26] As further support, model studies were carried out on hydroxy derivative. In this system, there is the possibility of hydrogen bonding between the hydroxy group and the carbonyl unit in the transition state for bottom face attack. Face selectivity is predicted to be indeed opposite to that of the methoxy derivative. Thus, calculations on transition states reproduce experimental trends and also provide an internally consistent interpretation.

4.2. *Face-selective carbene additions*

The origin of face selectivity in nucleophilic additions to sterically unbiased substrates, such as 5-substituted adamantanones (6) and *endo*-substituted norbornanones (7), has been a subject of intense debate.[28] According to Cieplak model,[25] the preferred direction of approach is antiperiplanar to the relatively electron-rich C–C bond. Hence, inductively electron-withdrawing groups are predicted to favor *syn* addition. Selectivity has also been attributed to electrostatic interactions.[29] A simple means of distinguishing between these models is to consider the complementary process, viz. electrophilic addition to the corresponding olefines. The preference



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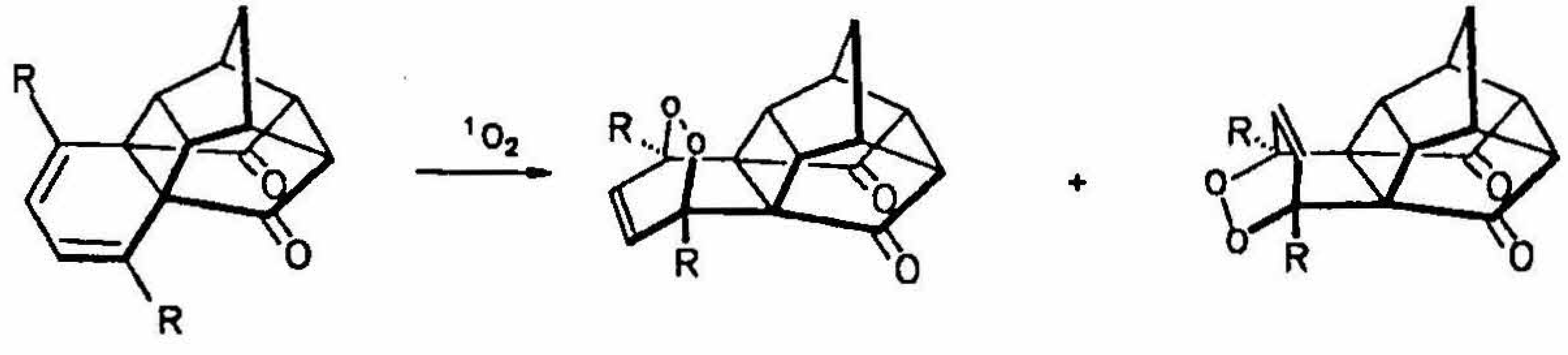
not quantitatively correct, small energy differences were obtained in systems which led to a mixture of products. In contrast, the calculated energy difference was quite large for the two cases in which exclusively top face addition was observed. More importantly, the computational model provides a means of verifying the interpretations. When the calculations were repeated assuming the substituents at C-2 and C-3 to be in the plane of the diene, very little face selectivity was predicted. This provides support to the importance of out-of-plane bending at the transition state in determining the face selectivity of cycloaddition in these systems.

The twisting of the terminal groups of the diene in the Diels–Alder transition state has also been implicated in another subtle face selectivity problem. Singlet oxygen addition to the polycyclic diene, 5, can occur from the non-equivalent top and bottom faces. The hydrogen atoms at the cyclobutyl unit would lead to some steric repulsion for approach from the top face. On the other hand, carbonyl groups would exert electrostatic repulsion for the bottom face approach of the hetero-dienophile. Further, the bottom face attack may be favoured according to Cieplak effect,[25] since the newly formed bonds would be stabilised by the electron-rich antiperiplanar cyclobutane ring bonds. The observed product ratio (4:1 favoring the bottom face attack) is thus a result of a complex interplay of steric and electronic factors.

Interestingly, face selectivity for singlet oxygen addition to this substrate can be altered by substituents in the π plane of the diene. Methoxy and acetoxy groups at the terminal carbon atoms of the diene lead to exclusive addition from the top face (Scheme 1).[26] This turn-



R = H	22	78
R = OMe, OAc	100	0

SCHEME 1.

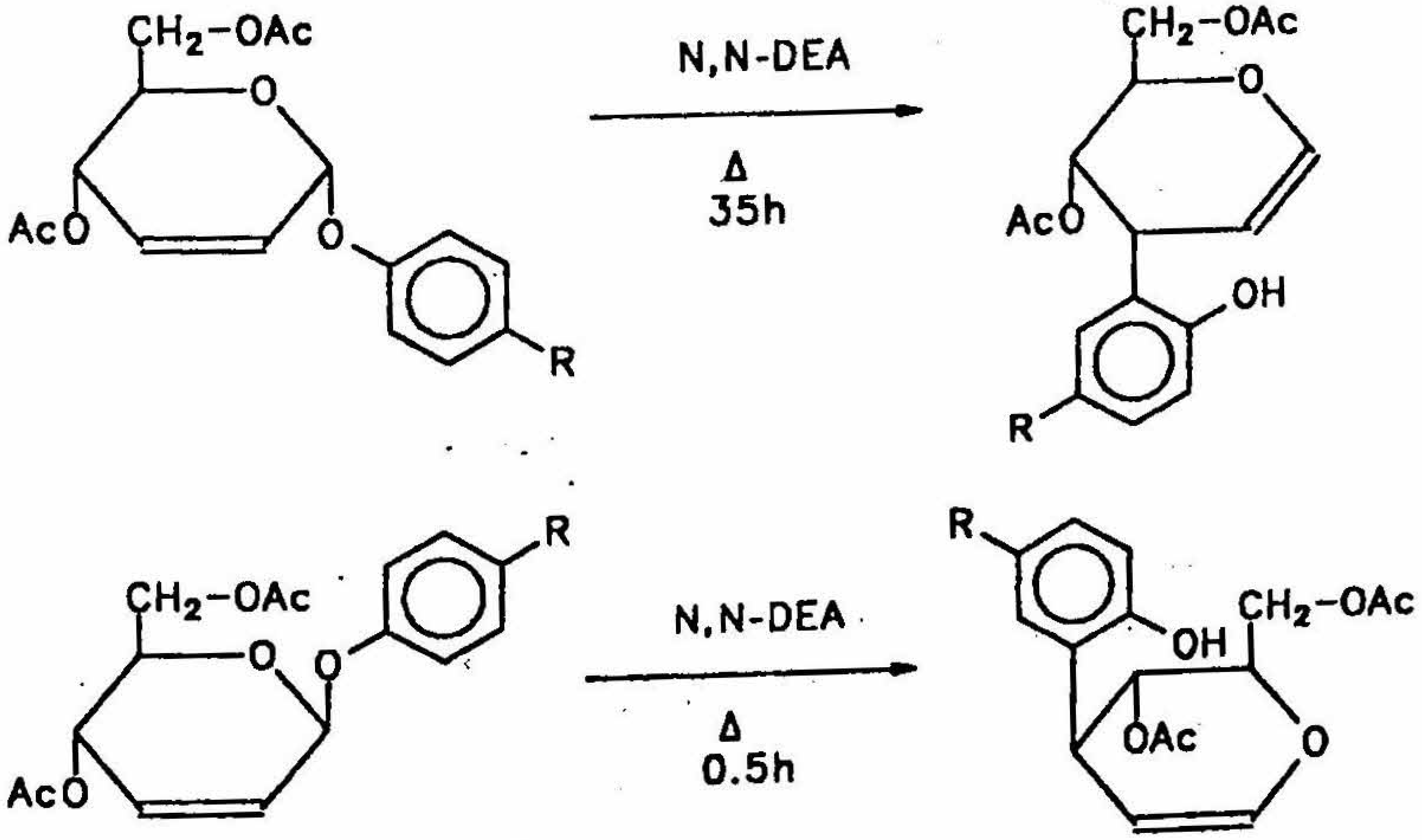
Table II
Calculated heats of formation (kcal/mol) of CCl_2 addition transition states to 2-*endo*-substituted-7-isopropylidenenorbornanes, relative preference for *syn* addition and observed product ratios

Substituent	Site of initial attack	*syn*	*anti*	Difference	Exp. *syn: anti*
–CN	C–7	91.53	92.37	0.84	78:22
	C–8	93.17	93.21	0.04	
–$COOCH_3$	C–7	–23.11	–22.52	0.59	60:40
	C–8	–21.66	–21.65	0.01	

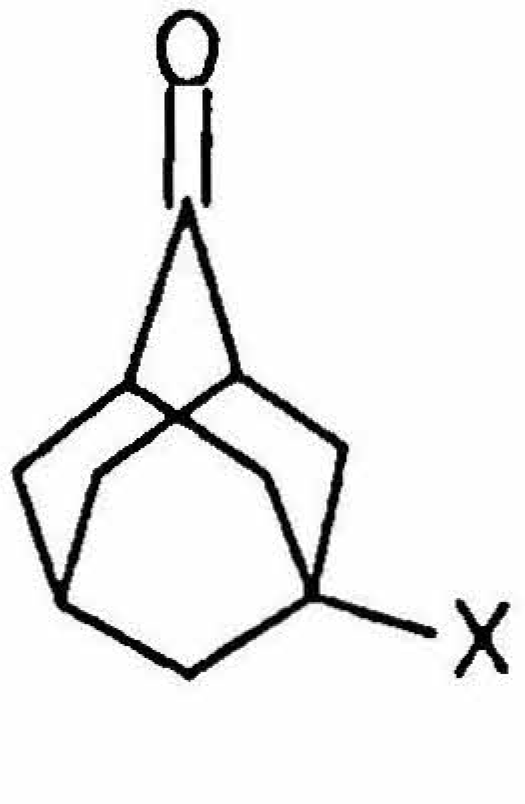
The computed energies also reveal that there would be no face selectivity for carbene attack at C–8 (Table II). The newly formed bonds are too distal to be influenced by hyperconjugative interactions. Overall, the calculations are in agreement with the experimentally observed face selectivities and establish the validity of Cieplak model in determining the trends.

4.3. *Face-selective Claisen rearrangement*

In the attempted synthesis of aflatoxins, an unusual rate difference was observed in the Claisen rearrangement of two unsaturated sugar substrates (Scheme 2).[34] The β isomer of 4, 6-di-O-acetyl-2, 3-deoxy-D-erythro-hex-2-enopyranoside on heating in N, N-diethylaniline medium underwent Claisen rearrangement readily in 30 minutes. In contrast, the α isomer reacted sluggishly with a half life of ca. 20 hours. The latter has the migrating group poised in the axial position, which is ideal for the formation of the cyclic 6-membered transition state. The stereocontrol of the rate is therefore unusual.



SCHEME 2



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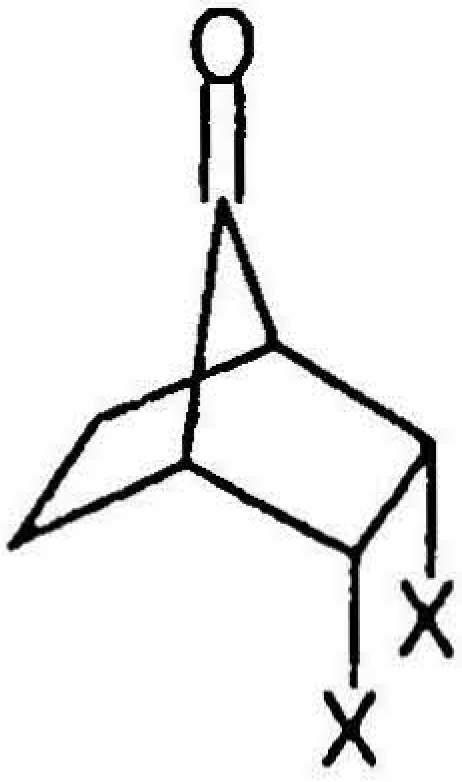

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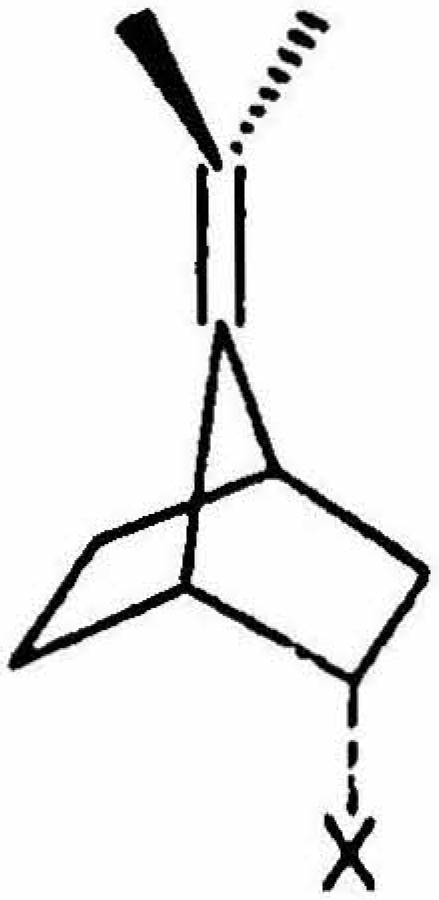

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should be unchanged as per Cieplak model, whereas electrostatic interactions should be absent or even be reversed. Initial experimental results were interpreted along these lines,[30] and supported the validity of Cieplak model. However, there is some uncertainty about the mechanistic details in these reactions. In particular, the initial direction of approach need not determine the ultimate product if the reaction involves more than one step.[31] The complication can be eliminated by choosing an appropriate substrate for which the mechanism is unambiguous. Alternatively, computational studies can be used to monitor face selectivity resulting from transition states corresponding to different mechanisms. The two approaches have been combined in a fruitful interplay of theory and experiment.[32]

With an isopropylidene group at the 7-position of a variety of *endo*-substituted norbornane, face selectivity for dichlorocarbene addition has been determined. Theoretical studies on these substrates (**8**) led to several useful insights. Although other electrophiles were examined, the results for the neutral carbene are discussed here, since electrostatic effects should be unimportant in this case.

The transition state for carbene addition to an olefin has an interesting structure. The least motion pathway to form a cyclopropane is a forbidden process.[33] Carbene approaches with its empty *p* orbital interacting with the π bond in an unsymmetrical fashion. At the transition state, one C–C bond is well formed while the remote carbon remains essentially planar. For an unsymmetrical olefin, there are two possible sites of attack. In the norbornyl substrates considered, there are four possible transition states. The site of attack can be C-7 or C-8 and the direction of approach can be *syn* or *anti* with respect to distal substituent.

AM1 calculations have been carried out for all possible transition state structures.[32] In the isopropylidene derivatives, attack at C-7 is favoured (Table II). As a result, the σ^* orbital of the newly formed C–C bond is more susceptible to hyperconjugative interaction with the ring C–C bond. A cyano or ester substituent leads to sufficient discrimination of the donor ability of the C1–C2 (C3–C4) and the C5–C6 (C4–C5) bonds. The preferred direction of approach of the electrophile is antiperiplanar to the latter. Hence, *syn* isomer is the major product.

higher barrier for rearrangement. This has been confirmed through experiments on appropriate substrates. Further, the vinylogous anomeric effect[35] is not a significant factor in these systems. Hence, the observed trends can potentially be exploited in cyclohexane derivatives too.

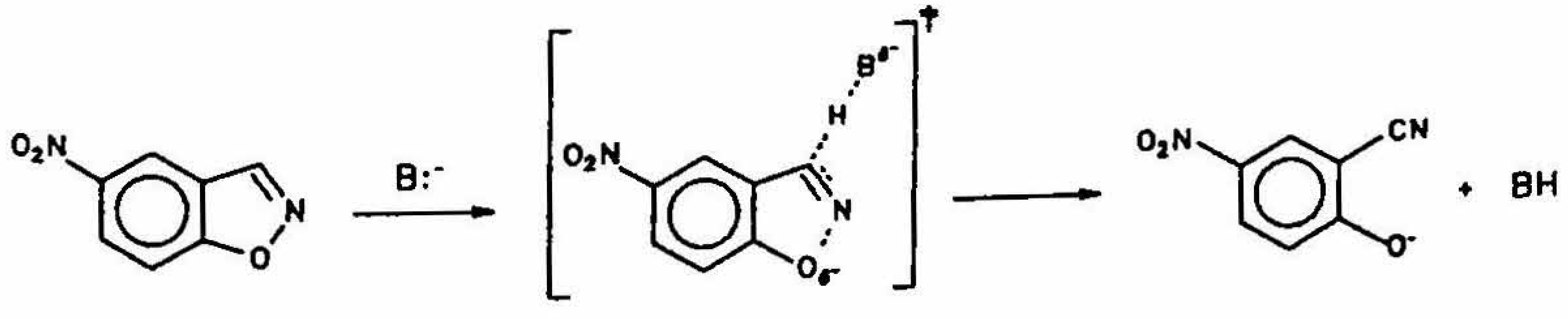
5. Transition state modelling and antibody catalysis

As is well known, the remarkable ability of enzymes to catalyse different reactions stereospecifically is due to their ability to efficiently stabilise the corresponding transition states. In principle, the transition state of a reaction can be mimicked through stable molecules with related structure and coordination properties. Such systems may be used to raise antibodies which are very efficient catalysts for the reaction of interest.[36] The key step in the development of catalytic antibody for a transformation is the design of a hapten which resembles the transition state as much as possible. Theoretical determination of transition state structures is increasingly being used for such innovative studies.[37 38]

A recent study illustrates the general strategy.[38] The base-assisted ring opening of nitrobenzisoxazole (Scheme 3) is a sluggish process in aqueous medium, whereas some enzymes can effect the transformation at diffusion-controlled rates. From the expected nature of the transition state for the reaction, a hapten was designed and used to raise antibodies. Two of these turned out to be quite effective in catalysing the reaction in aqueous medium, with turnover number greater than 10^8 and rate acceleration greater than 10^3. While these values are impressive, they do not compare favourably with the more efficient enzymes.

In order to design a better hapten, a systematic theoretical study of the reaction profile was carried out.[38] *Ab-initio* calculations were used to precisely locate the transition state for the formate-assisted ring opening of the model system isoxazole. These results were used in a more approximate AM1 calculation on benzisoxazole ring opening. The effect of a few solvent molecules was explicitly taken into account. Using these structures as the basis, several haptens were then proposed using a set of criteria, such as complementary hydrogen bond sites, ability to form strong complexes with acetate ion and acetic acid or methanol. The structures were superimposed on transition states to ensure maximum overlap. Three molecules, **9–11**, were identified as the most promising haptens.

An interesting variation in the above theme has been tried out.[39] A hydroxyalkyloxirane substrate was found to cyclise to form a tetrahydrofuran ring in aqueous acidic conditions. It was found that the mode of cyclisation could be altered to form a tetrahydropyran using an antibody elicited by a cyclic N-oxide derivative. Evidently, the antibody has an optimum binding site for the hapten as well as for the transition state leading to the formation



SCHEME 3.

AM1 calculations on model systems revealed that the β isomer also has the migrating group in the axial position, since the $^5H_0$ conformer is stabilised by anomeric interaction which overwhelms steric repulsions of the pseudo-axial groups. This conformational preference was confirmed by NMR coupling constant data and subsequently through X-ray structure determination. While this finding can explain why the β isomer also undergoes rearrangement, it cannot account for the large rate acceleration observed in this isomer. The origin of the rate enhancement is to be found exclusively in the transition state structures and energetics.

AM1 calculations confirm that the β isomer has a smaller activation barrier for rearrangement by 4 kcal/mol.[34] The significant difference is due to geometric differences at the transition state. The 6-membered ring of the Claisen unit prefers to have a chair conformation. This leads to a sterically encumbered structure for the α isomer, for which the sugar ring retains the chair conformation (Fig. 5, left). In contrast, the transition state for the β isomer undergoes a conformational change. While the Claisen unit is chair-like, the unsaturated sugar ring adopts a boat conformation (Fig. 5, right). This is enabled by the presence of oxygen and the nearly trigonal carbon atoms in the ring. The net result is reduction of steric repulsions between migrating unit and substituents on the sugar ring.

The above interpretation was confirmed by calculating the less favourable transition states with the Claisen unit having a boat conformation.[34] These are intrinsically less stable structures, but the migrating group does not sterically interact with the substituents on the sugar ring, either in α or β form. Hence, these higher energy transition states have nearly the same energies.

Quantitative MO calculations account for the unusual rate difference in the unsaturated sugar substrates. The proposed interpretation has important implications. If the sugar ring is prevented from changing its conformation, e.g. through ring fusion, the β isomer will have a

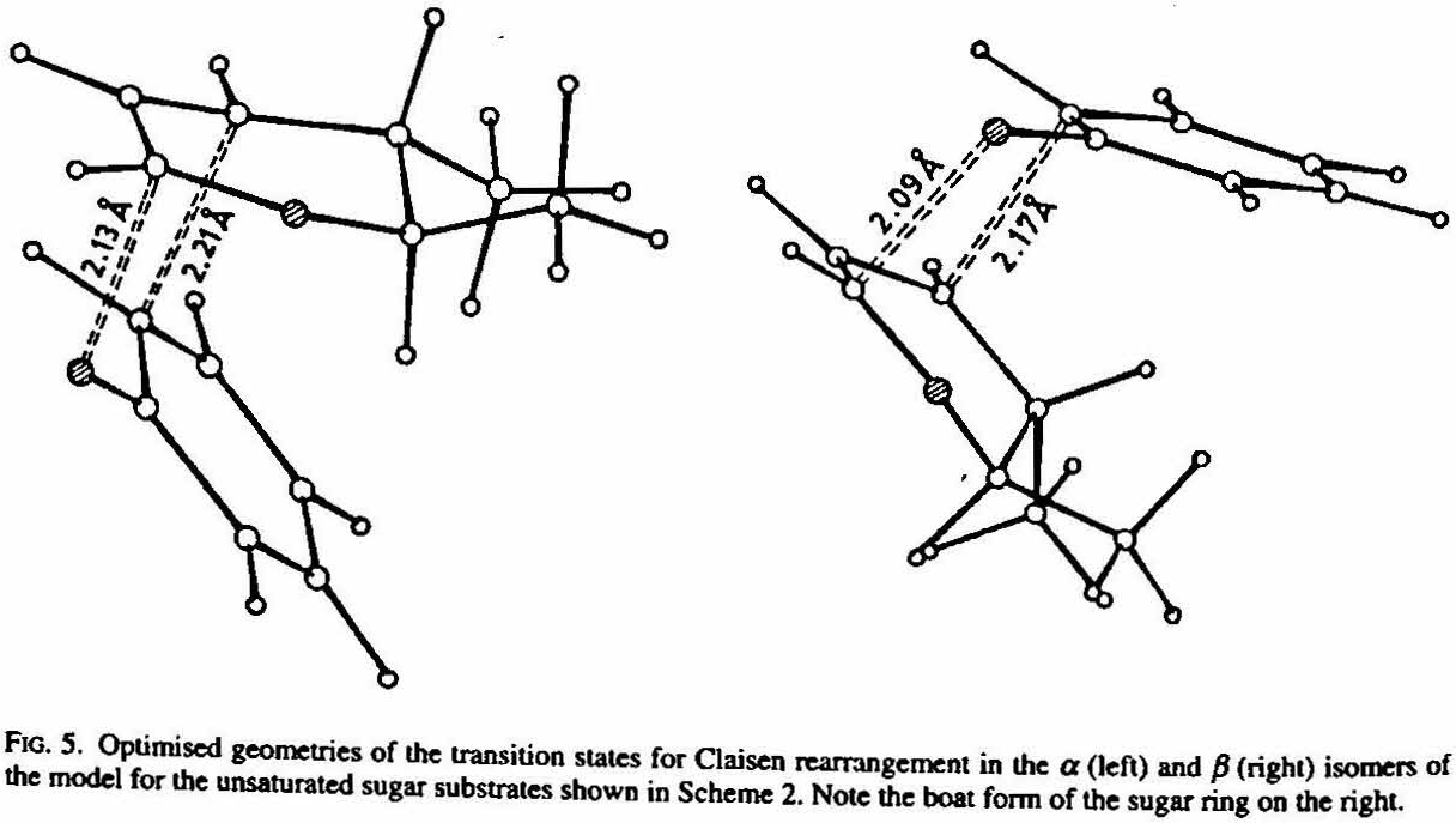


FIG. 5. Optimised geometries of the transition states for Claisen rearrangement in the α (left) and β (right) isomers of the model for the unsaturated sugar substrates shown in Scheme 2. Note the boat form of the sugar ring on the right.

Interesting reactions involving electronic excited states and solvation effects also cannot be routinely examined. Special procedures requiring considerable effort are needed in these cases. But, with rapid developments in computer hardware and algorithms, increasingly larger number of reliable computational studies on chemically interesting reactions are expected in coming years.

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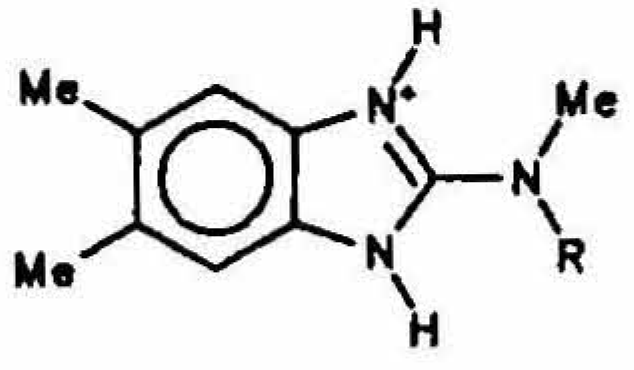

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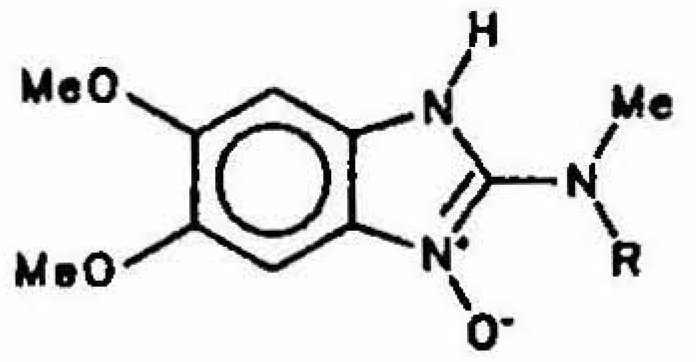

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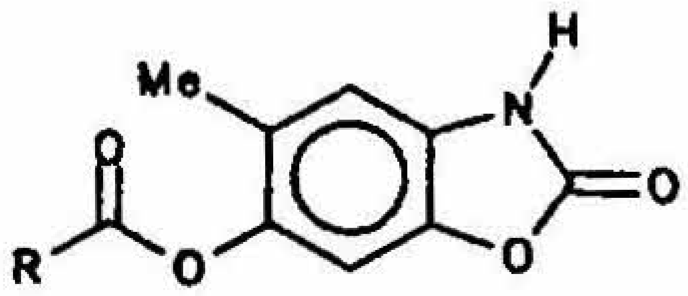

11

of the pyran ring. Using methanol and the formate ion as model acidic and basic sites, the geometry of the complex with the hapten was optimised using *ab-initio* procedures. When the hapten was replaced by the transition state for the two possible cyclisation modes, the more stable structure corresponded to the preferred pathway. The authors termed the model structure a 'theoretical enzyme' or *theozyme*.

In the next dramatic step, the authors tried to predict the selectivity of the theozyme in the reactions involving a different substrate.[39] The higher homologue of the oxirane was calculated to prefer the formation of a pyran (6-membered ring) in acidic conditions, but the preference is predicted to be altered in favour of an oxepan (7-membered ring) when complexed with the theozyme. The results were found to be consistent with independent experiments.[40]

More studies such as those described above for designing haptens and for predicting antibody catalyst selectivity using quantum chemical calculations are likely to be attempted in the near future, especially if consistently successful predictions are made.

6. Conclusions and outlook

Computational studies have contributed significantly to the fundamental understanding of reaction mechanisms. Many insights have been obtained which are often outside the scope of present experimental methods. The studies have also generated much controversy, among the theoretical groups themselves and with experimentalists. With improvements in methodology and greater degree of critical evaluation, the debates are carried out with maturity, leading to better overall understanding.

Model studies on small substrates have been used to rationalise complex transformation. Quantitative force fields have also been developed for some of the more common reactions. Approximate methods have been used to tackle reactivity problems involving large molecules. Many interesting and subtle questions concerning stereoselective reactions have been addressed.

Transition state calculations have also been used in novel applications. Attempts have been made in the design of haptens using appropriate transition state models for developing catalytic antibodies for specific reactions. Calculations have been employed to develop *theozymes* which are models for the binding sites of the catalytic antibodies and to predict their catalytic potential.

In spite of the enormous growth in the quality and quantity of computational studies of transition states, certain difficulties remain. The complexity of the 3N-6 dimensional problem associated with potential energy hypersurface can be approximated, but cannot be eliminated.

J. Indian Inst. Sci., Nov.–Dec. 1998, **78**, 463–472.

BOOK REVIEWS

Properties of III–V quantum wells and superlattices by Pallab Bhattacharya, The Institution of Electrical Engineers, Michael Faraday House, Six Hills Way, Stevenage, Herts, SG1 2AY, UK, 1996, pp. 420, £125.

The advent of molecular beam epitaxy and organometallic vapor-phase epitaxy in the mid-70s has made it possible to grow superlattices and quantum wells which have dominated the semiconductor technology. This has been particularly noticeable in the case of III–V-compound semiconductors. Unlike silicon which has found wide electronic applications on its own, gallium arsenide by itself has found very limited application. However, epitaxial technologies have made it possible to deposit layers of different materials as required. Today, almost all applications of III–V semiconductors for microwave and millimeter wave electronics, optical sources and detectors, etc. involve epitaxial layers of different materials tailored to suit the requirements. Thus, another tool is available in the hands of device designers to meet the ever-increasing stringent requirements of system designers.

The epitaxy of III–V-compound semiconductors started with liquid-phase epitaxy in mid-60s and slightly later by the VPE technique. Then it was assumed that unless the epilayer lattice matched the substrate, it could not be grown. In 70s, MBE and MOCVD reached maturity and achieved growth control at monolayer level making it possible to plan for quantum effect structures. It became possible to realize two- and one-dimensional electron systems. In mid-80s, the concept of strained layer epitaxy was perfected. This provided another tool to material engineers and the idea of band gap engineering was truly achieved. In the 90s, these techniques are now allowing a very wide range of materials to be deposited on a wide variety of substrates.

This book reviews the present status of technology and presents a comprehensive database for the benefit of workers in this field. It is a part of the Electronic Materials Information Service (EMIS) series of books brought out by INSPEC. And like all other volumes of this series, this one also maintains the high standard. All the authors have contributed to their fields a great deal and are acknowledged masters in their specialization.

The book starts with a historical perspective by three masters who have been the initiators of this revolution and have been in the middle of it all along. Their accounts of the growth of the subject make very interesting reading. The chapters on theoretical aspects cover details of the band structure, transport properties, excitons, as well as effects of electric, magnetic and strain fields. MBE and MOVCD growth techniques have been described briefly. Characterization of the superlattices and quantum wells by X-ray and electron diffraction is a special field and has been reviewed in this volume. Electronic and optical characterization by a wide variety of techniques has been thoroughly discussed. The application of superlattices and quantum wells as light emitters and detectors including attempts to detect far-infrared are also reviewed. The application of superlattices which has led to the development of millimeter wave transistors operating at W band and high frequencies has been possible because of the modulation doping of lattice matched and pseudomorphic structures. Their status is well reported in the relevant chapters. Resonance tunneling devices and self-electro-optic effect (SEED) devices have also been reported in detail. Thus, the volume is very comprehensive covering all aspects of the technology, material physics and device engineering. All chapters have large number of suitable references making it possible for any researcher to trace the literature.

Some of the materials such as gallium nitride which have attained prominence in early 90s are not covered as well. Similarly, another topic not discussed is metamorphic structures, using deposition of

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SI system of units has been used and review questions and problems are included at the end of each chapter and answers are provided at the end of the book.

This book will prove to be a boon for students, brilliant or average. Even professionals will love it as it will help in getting many concepts cleared and prove that there is a simpler way of understanding things. For example, till date I was not clear about the concept of reciprocal lattice, but Prof. Pillai has explained it so well that I have no hesitation to admit that the concept has become clear to me for the first time.

As Prof. Pillai has rightly said that there is one thing which all materials have in common, that is they are all composed of atoms and fittingly the book starts with Rutherford model of atom. But the experiment that helped Rutherford to construct his atomic model was not conducted by Rutherford as Prof. Pillai has written but at Rutherford's suggestion by Geiger and Germer in 1911.

As I was randomly going through the book, I found an error on page 111. Fig. 4.25 is in error, because direction OB is not correctly drawn and in page 74, name of van der Waalls is to be correctly spelt. There will be other errors, which I am sure, do not interfere with the text, but should be corrected in future editions. I also hope future editions will include the latest advances in the solid state such as superlattices and composites. Though these topics are not in syllabi of our universities yet, I hope they will come in the near future.

There are some mistakes in the index and the corrected forms are indicated below:

Vector atom mode	p. 669
Clausius–Mosoti equation	p. 669
Dispersion bonds	p. 670
Schrödinger	p. 673

Overall, this book will be valuable as a textbook to all students of solid-state physics at the M.Sc. level.

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Physics for engineers by M. R. Srinivasan, New Age International (P) Limited, 4835/24, Ansari Road, Darya Ganj, New Delhi 110 002, 1996, pp. 519, Rs 170.

This book is intended to be a textbook for the first-year engineering students studying in Karnataka. It has 17 chapters

Chapter 1 deals with acoustics. It discusses simple harmonic motion and free and forced vibrations. Acoustics of buildings is described in detail. Chapter 2 is on non-destructive testing. The principal techniques covered are ultrasonic testing and X-ray radiography. However, the contents on these two topics should have been a little more exhaustive.

Chapters 3–6 deal with optics. These chapters are dedicated to geometrical and physical optics. The contents are self sufficient and relevant to the needs of an engineering student. However, it would have supplemented the contents if Fresnel's equations for reflected and refracted wave amplitudes were included immediately after polarization. Some applications of interference techniques in some areas like measurement of thickness of thin films, production of antireflection coatings will be a desirable addition.

Chapters 7 and 8 on fibre optics and laser are informative but are too brief. It would be useful if the physical principles involved are also included to a reasonably appropriate level.

structures lattice matched to InP on GaAs substrates (using suitable quaternary buffer layers). However, these are more recent phenomena and in a field changing as rapidly as this one, it is only to be expected that some such topics will be left out.

This volume is a must for all students and professionals dealing with III–V semiconductors.

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Solid state physics by S. O. Pillai, New Age International (P) Limited, 4835/24, Ansari Road, Daryaganj, New Delhi 110 002, 1998, pp. 674, Rs 285.

Encounter with any book on solid-state physics is almost predictable—it is intimidating, even for a professional and for an uninitiated it is terrifying. In no time, vectors, matrices, integrals, polynomials and a host of impenetrable mathematical expressions knock out one. Prof. S. O. Pillai's book is a refreshing exception. As you open the book at random and try to read through, you wonder that you are not being overtaken by that indomitable desire of dropping the book dead on the table as it happens usually.

First published in 1995, the present volume is a revised and enlarged edition of its predecessor. *Solid state physics*, that is, physics of solids, or in modern jargon, physics of condensed materials has expanded enormously since the days of Rutherford. The subject has expanded both horizontally and vertically. Today the scope of solid-state physics is so varied and that data available are so voluminous that it is impossible to contain this knowledge and information, even in rudimentary form, in a reasonable size. Considering the enormity of the task, I have no hesitation to state that Prof. Pillai has done a remarkable job of it.

The present volume has altogether 11 chapters contained in about 675 pages. Chapter 1 is in the form of introduction contained in less than 2 pages and starts with a quotation from the Tamil poet Tiruvalluvar and gives an excellent introduction to this excellent book on solid state physics. Other chapters contain the following:

Ch. 2 Review of atomic structure
Ch. 3 Interatomic forces and bonding in solids
Ch. 4 Crystal physics
Ch. 5 Wave nature of material and X-ray diffraction
Ch. 6 Electrical properties of metals
Ch. 7 Thermal properties of solids
Ch. 8 Superconductivity
Ch. 9 Magnetic properties of materials
Ch. 10 Physics of semiconductors
Ch. 11 Dielectrics

Studded with quotations from scholars, poets and scientists each chapter is written in lucid style, use of mathematics is minimal and therefore on many occasions derivations are semirigorous but the treatment is easily digestible and more often throws better insight into the concept of physics involved. To quote Prof. Pillai, "the author has constantly tried to keep in mind the needs of the less than brilliant student and the student whose background may be spotty by retaining the steps in the calculations and by often offering multiple explanation to elucidate a point."

teachers and students, in spite of the current trend in India of education becoming subservient to examination.

The topics to be covered in a book of this type must be based on the practices of many universities. The author, using his experience in teaching for many years in one of the well-known colleges of Bangalore, has chosen a good compromise among the conflicting requirements. The electron, relativity theory, atomic spectra and molecular spectra form the first four chapters, while laser optics, scattering of light, X-rays and quantum mechanics form the next four chapters. Basic nuclear properties, radioactivity, particle detectors, particle accelerators, nuclear reactions and elementary particles form the next six chapters. The final four chapters are titled statistical physics, solid state, cosmic rays and space physics. There is a short appendix on SI units and a three-page index. Thus the coverage will satisfy the students of many universities.

The worked examples in the various chapters deal with analytical derivations and discussions in the beginning and with numerical examples later on. This is a good point, because physics students need to have a feel for the numbers and the magnitudes of the different quantities. The author then gives a set of problems to be solved by the students. Numerical answers are given in most cases to help the students. Therefore, if a candidate diligently studies the worked examples and solves the problems in each chapter, the person will surely get a good understanding of the subject.

The book also has a fairly large number of clear figures which help the student. By necessity they have to be schematic but they adequately convey the main features. The author has also added sketches of prominent physicists at the beginning of each chapter to give a human touch, whose absence can make the book into a dry collection of derivations, questions and answers. The book is also moderately priced.

All these features are likely to make the book popular among the students and the teachers. Therefore, one must ensure that it does not contain mistakes or gives wrong impressions. On this count many comments can be made. Starting with the selection of thumb-nail sketches of famous and modern physicists, a few are misplaced like Pauli in the chapter on nuclear reactions or Galileo (modern physicist?) in connection with SI units. Hertzberg died several years ago. Schawlow is misspelt. The picture of W. Henry Bragg alone gives the wrong history; the Bragg's law was developed by the son W. Lawrence Bragg while the X-ray spectrometer and the first crystal structure studies were done by the father and the son together who jointly shared the Nobel Prize for their work. Moving next to the names of the scientists, the formula for the relativistic contraction of apparent length (pp. 26–27, 53) is due to Lorentz and to Fitzgerald. The reciprocal of the fine structure constant being very close to 137 has been the basis for the suggestions by Eddington (p. 69). Pauli is misspelt as Paul on p. 73 and Mie as Mei on p. 119. Irene Curie and Frederick Joliot (p. 264) are the more usual names. Murray Gell-Mann (p. 281) is one person. Richardson derived the thermionic emission formula on the basis of the classical electron gas kinetic theory with a $T^{1/2}$ term, Dushman obtained the T^2 term on thermodynamic considerations and Sommerfeld completed the full derivation on the basis of the degenerate electron gas model using Fermi–Dirac statistics (p. 299). On p. 307, one has the Lorenz number. The nearest star is proxima centauri (p. 350). The H-R diagram (p. 354) is the Hertzsprung–Russel diagram. Worked examples and problems, which have been attempted as the unusual features of the book, are not given in Chapters 4, 5, 11, 14, 17 and 18, i.e. in about 33% of the chapters. This is unfortunate. Not only the students but also the teachers—(as question-paper setters)—would have welcomed the numerical or the analytical problems in these topics. The author has also occasionally introduced some concepts without adequate background, which can be pardoned in a book for supplementary reading. For example, the quantum hypothesis of Planck and the quantisation of the angular momentum are implied in the discussion of the earlier chapters, especially Chapter 3 onwards. The Van de Graaf accelerator is introduced on p. 255 without indicating its special

Chapter 9 which deals with vacuum science and technology contains very useful introductory information on vacuum pumps and measuring gauges which are normally not included in traditional textbooks on physics.

Chapter 10 takes the reader to the revision of the elementary theory of atomic structure. However, electronic structure cannot be considered to be complete without the introduction of the four quantum numbers n, l, m_l and m_s which are essential for the complete description of an electronic state.

Chapter 11 gives a good introduction to semiconductor devices particularly diodes and transistors. However, the variation of conductivity with temperature and a discussion on the Fermi level for intrinsic and extrinsic semiconductors is essential for completeness of the topic. Physical interpretations of Fig. 11.16 has not been given. The symbol of the zener diode in Fig. 11.19 is wrong.

Chapter 12 on dielectrics should be a little more elaborate on the types of polarization. The absence of the topic on ferroelectrics is conspicuous as they are a very important class of dielectrics having many engineering applications.

Chapter 13 on magnetic materials is very concise but adequate. However, to understand Fig. 13.13, an introduction to crystallography will be a good addition.

Chapter 14 gives a fairly good introductory idea on superconductivity but a brief description with examples of the modern High T_c ceramic superconductors is a must on any present-day book on physics for engineers.

Chapter 15 on magnetism and electricity should be introduced before dielectrics and magnetism. Also, the basic aim should be to develop Maxwell's equations and wave equation and its solution. Section 15.15.2 has been misprinted as 15.5.2. Section 15.9 to 15.20 should form an Appendix. The boundary conditions on electric and magnetic fields will be an appropriate and useful addition.

Chapter 16 on heat and thermodynamics is well written to suit the needs of engineering students. However, mechanical equivalent of heat and its determination is very fundamental to appreciate first law of thermodynamics. Similarly, black-body radiation up to Planck's distribution law is very fundamental to many areas in physics which are relevant to engineering.

The book is otherwise very well planned and the author has included many problems relevant to the text which will help the students in understanding the subject. If the additions mentioned are incorporated the book will serve not only as the textbook for engineering students in Karnataka but also as a textbook of physics for first and second semester courses of many other technical institutions in India.

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Modern physics through problems by B. V. Narayana Rao, New Age International Publishers Ltd, 4835/24, Ansari Road, Daryaganj, New Delhi 110 002, 1998, pp. 372 + v, Rs 165.

The book is aimed at B.Sc. degree-level students of Indian universities. In an unconventional way, the presentation of the subject is through questions and answers. Thus the book will appeal to students who are oriented towards success in examinations. However, it has other features which commend it to trolled ecological life support system (CELSS) in space is another activity which is being promoted by NASDA and Space Technological Agency (STA).

Articles related to beneficial applications of space systems include studies on crystal growth in compound semiconductors in micro-gravity and also a description of solution/protein crystal growth experimental facility being built by JEM for the ISS. Apparently, certain crystals grown in micro-g nearly have nearly 50 times lower levels of a key defect. Micro-gravity enables scientists to create physical models of important processes such as combustion, fluid flows, aging, etc. and make observations that would be impossible on earth. Also, diamond synthesis experiments in space reveal the superior quality of diamond thin films produced in micro-gravity condition.

A progress report of the 1996 missions to Mars, the Pathfinder and the Global Surveyor is included in the Space Science and Mission section. Both these highly successful missions are now a part of history. The lunar exploration project, SELENE (SELenologycal and ENgineering Explorer), which is presently under conceptual study in Japan, is planned to be launched by H-IIA rocket around 2003. An account of its objectives, launch schedule and sub-systems is also included in this section.

Papers on Space Transportation and Propulsion focus on the development of the Japanese H-IIA rocket, evaluation of the McDonnel Douglas Aerospace's Delta III system for launching commercial communications satellite, description of newly developed 5 Newton hydrazine thruster, etc. It is apparent that a majority of the world's propulsion systems are utilizing 25- to 40-yr old main engine technology. Significant advancements in propulsion systems are hindered by high initial development cost and low reliability from new systems.

Capturing of unwanted space objects, such as damaged satellites by using a tether, has been a topic of several investigations. New approaches seem to make the method feasible. HOPE-X, the Japanese unmanned winged space transportation system, is planned to be launched in the early 21st century by H-IIA rocket. An analysis of the flight control system gives a glimpse of the various technologies necessary to realize a reusable space transportation system. Another interesting article listed in this section describes the dynamic behaviour of tumble orbit transfer, a method of orbit transfer fully utilizing momentum exchange between two bodies.

Space debris, defined as any non-functioning man-made object orbiting the Earth, could cause damage to an operating satellite or spacecraft by colliding with it. At present, there are over 8,000 such objects in orbit and with this number increasing in time, the probability of collision is real. Several papers devoted to this topic discuss various aspects, not just seeking to minimize the creation of space debris but to analyze the situation by modeling and simulation, collision probability analysis, etc. The results of hydrocode simulations for JEM, the Japanese contribution to the ISS and shield design evaluation against the strikes of debris are presented.

The papers presented in this rather large collection (over 1,000 pages), give an overview of the recent projects in the consortium countries. Impressive involvement of Japan in space research and rocketry is evident from the collection. Equally impressive is the very high standard of papers presented. The volume will undoubtedly be a valuable addition to space research libraries. It is particularly recommended to researchers and students interested in recent developments in space science and technology. Bound in hard cover, it has an illustration of the 'Oura Catholic church' built by French missionaries in Japan.

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feature. The discovery of nuclear fission is too advanced for the level of students. The description of superconductivity, especially of the developments in high-temperature superconductors in the past decade (p. 235), is quite inaccurate and would surely mislead the students. The SI system is based on the 1960 version (p. 264 at seq.) and the later improvements are not mentioned. A few other mistakes would be noticed quickly by the readers. The path difference is not the glancing angle (p. 135). The Bose–Einstein distribution law (p. 293) is wrongly printed. The reviewer did not have time to scrutinise all the other questions; hopefully, the errors would be discovered by those who go through the text carefully.

In today's context of staff and students putting premium on the examination results, a book of this type is likely to become popular. If the mistakes are weeded out in the next edition, it would do a good service. In answering the various questions, the students would inevitably get some understanding of the subject.

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Space cooperation in the 21st century by Peter M. Bainum *et al.* Published for American Astronautical Society by Univelt, Inc., P. O. Box 28130, San Diego, California 92198, USA, 1997, pp. 1098, $ 145.

The volume is a collection of the available papers (over 90) presented at the Seventh International Space Conference of the Pacific-basin Societies (ISCOPS, formerly PISSTA), July 1997, Nagasaki, Japan. The ISCOPS consortium consists of astronautical professionals from Japan, China and USA. The papers presented cover a wide range of topics classified as space communication, space transportation and propulsion, space science and missions, beneficial applications of space systems (including remote sensing and micro-gravity), manned space flights, space station and Pacific space port, astrodynamics, guidance and control, space structure and space debris and environment.

Most of the papers are sort of status reports on a particular project/subject. Some are covered as brief abstracts only. For example, NASA—a look into the future gives an interesting account of the future space programs but is covered only by presentation charts. The contribution of the member nations in building the international space station (ISS), which is being built currently, has been charted out.

The Japanese Rocket Society has been carrying out detailed studies to determine how to establish commercial service providing visits to low-Earth orbit for fare-paying passengers using the indigenously designed 'Kankoh-maru', SSTO (single-stage-to-orbit), VTOVL (vertical take-off verticle landing), fully reusable rocket. Kankoh-maru is designed to carry 50 fare-paying passengers to a 200-km latitude orbit, and may cost around $20,000 per head, using the HIIA rocket which is currently under development. Even the feasibility of an orbiting hotel to rendezvous and dock the Kankoh-maru has been explored. Apparently, space tourism is soon going to be a reality.

The Japanese experimental module (JEM), being developed by National Space Development Agency (NASDA), Japan, for the IIS, lists four candidate experiments which include, all-sky X-ray monitoring, optical communications experiment, space environment monitoring and observation of atmosphere. Conthrough steam turbines. Project 'Horizon' (1959) at Alabama was a study of manned LRV designed to run on electric batteries, and would have a range of 80 to 240 km. Finally, NASA–Marshall in 1969, designed, developed and manufactured the LRV within a span of 17 months only, which worked as specified upon the Moon.

A history of the Viking engine designed and developed by the Société Européene de Propulsion, which powers the mighty Ariane 1 to 4 rockets, reveals the impressive number of stage tests made for qualification. All Viking engines run on nitrogen tetroxide—unsymmetrical dimethylhydrazine (UDMH) hypergolic propellants. The Viking is believed to be the cheapest liquid rocket engine and an extremely reliable one. The French Space Agency, Centre National d'Etudes Spatiales (CNES), set up in 1962, which manages the Ariane program, has a creditable history. Besides the Ariane, it initiated the Meteosat and SPOT programs and is a prime contractor of the European Space Agency (ESA). This section also includes two short Russian articles on the history of the first stage of spacecraft control systems developed in the USSR and on the history of space navigation development.

Section 4 includes an interesting article on the development of space station objectives. The idea of a space station appeared as early as in 1869, but the first mission objective—to observe Earth and heavens from orbit was laid out by the famous Russian scientist Tsiolkovsky in 1903. Ideas such as putting a huge sunlight reflector on the space station to direct light to warm cold regions, melting icebergs and use as a strategic weapon; using manned space station to relay radio signals to all parts of the world, and maintaining an arsenal of atomic bombs onboard a military space station were suggested by Hermann Oberth (1923), Arthur Clarke (1945) and Wernher von Braun (1952), respectively. Of course, many of these concepts became obsolete by the time NASA debated this issue seriously. The Skylabs' missions, for example, included validating space station design theories, studying the effect of micro-gravity on humans, and providing scientific goals, such as Earth, celestial and solar observations, and micro-gravity research. A culmination of these concepts resulted in listing only three objectives for the space station 'Freedom', in 1993, namely, general space science research, remote Earth sensing and micro-gravity research. The US national objectives include enhancing US technological leadership and competitiveness, establishing international cooperative science and technology ventures, stimulating interest in science, maths and engineering education and providing a source of national pride and inspiration.

A history of the 50 years of the Rocket Research Institute, Inc. (1943–93) of the USA should rather have been listed under the previous section. Involved in experimental programs in rocketry for students and adults, the RRI has contributed significantly in developing various ideas and converting them to working technologies. Its achievements are numerous covering all types of propellants—solid, liquid and hybrid.

As is usual with this series, the articles listed are well-chosen historical documents of various concepts and issues with their chronology. The volume would provide a pleasant and stimulating reading to the space science students and working scientists. It is recommended to libraries and collectors who can afford purchasing it. Bound in blue hard cover, it has a portrait of Max Valier (1895–1930)—a designer of rockets and advocate of space flights. Valier died while experimenting with LOx–gasoline-fuelled rocket.

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Fluid electrolyte regulation in space flight by C. S. Leach Huntoon *et al.*, Published for the American Astronautical Society by Univelt, Inc., P. O. Box 28130, San Diego, California 92198, USA, 1998, pp. 238, $60.

History of rocketry and astronautics, AAS History Series, Vol. 22, edited by Philippe Jung, Series editor: D.C.Elder, published for the American Astronautical Society by Univelt Inc, P. O. Box 28130, San Diego, California, USA, 1998, pp. 406, $60.

The volume presents the papers presented at the 27th History Symposium of the International Academy of Astronautics held in Graz, Austria, in 1993. It includes a total of 16 papers grouped into four sections: Rocketry and astronautics: the pioneers, The march to space, The space age and Planning for the future.

Section 1 starts with a history of the rocket designed for the film company, UFA, for filming its movie, 'Frau im mond'. The company contracted the famous expert Hermann Oberth in 1929 to build a liquid rocket. However, from the very start UFA had neither the right kind of funding nor the willingness to invest in rocketry. The rocket never flew and gave a lot of bad reputation to Oberth, but the film was a great success. The next article which cites the personal memories of the rocket centre at Peenemunde by two German rocket engineers directly involved in its activities reveals the zeal and perseverance of Wernher von Braun in developing rocketry from its infancy to the famous A-4 (V-2) rocket. Hitler first ignored and then ridiculed the rocket project when he knew about it. Only in 1942 when the Germans were losing ground rapidly, Hitler turned to Peenemunde and ordered a rapid build up of A-4s. Since von Braun was not interested in mass production of A-4s, Himmler put him into a Gastapo jail accusing him that he had only the space flights in mind, and not the support to Germany's war effort. Another paper deals with the contributions of Klaus Riedel who was one of the driving forces behind the rocket research and development at Peenemunde in the 1920s.

Highlights of 50 years of an American pioneering company, Aerojet, started in 1942, lists its vast number of achievements. It was perhaps the second private company dealing in rocketry, the first being the Reaction Motors, Inc. which started in 1941. It was a direct outgrowth of Guggenheim Aeronautical Laboratory, California Institute of Technology (GALCIT) founded by its director, Theodore von Karman and his students, Frank Malina, John Parsons, Edward Forman and Martin Summerfield, who contributed $200 each towards the capital of the company. By 1950, it was the world's largest engine manufacturer and a leading researcher and developer of rocket technology. Among the several achievements of the company are: solid and hypergolic (self-igniting) liquid fuel-based JATOs, castable solid propellants based on ammonium perchlorate, and polyurethanes and polybutadienes, propellants for the submarine-launched Polaris missile, and all solid-fuel ICBM-Minuteman, hypergolic fuel-based engines for Titan ICBM, Able Star and Delta vehicles and finally, the atomic rocket propulsion engines.

The story of the French SE4200 series, believed to be the first ramjet missile, is narrated by the editor of this volume himself in Section 2. Several versions of the missile were built; 567 vehicles were launched out, which provided a formidable base of knowledge in various areas of missile technology.

The contribution of German engineers to the British rocket technology after World War II was minimal unlike of those migrated to USA. Only about 35-40 rocket specialists came to Britain. Of these, none was of the calibre of von Braun. Also, because of the enormous debt Britain had incurred during the war, it could not afford a massive rocket program. However, Germans' experience in handling hydrogen peroxide (H_2O_2) and liquid oxygen (LOx) was perhaps utilized in developing the early British liquid propellant rocket engines, Alpha, Beta and RTV-1. Both the Alpha and Beta used hypergolic propellants having H_2O_2 oxidizer. The rocket test vehicle (RTV-1) used LOx and methanol propellants and was developed at Westcott, where German engineers were also employed. A brief survey of rocketry for space science in Japan is also included in this section.

The 'Space age' section has an article on historical origin, development and deployment of the lunar roving vehicle (LRV) that would transport man on the surface of the Moon. Although described in several scientific fictions since 1901, von Braun in 1953 suggested a tracked lunar rover driven by H_2O_2 exhausted

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TITLE PAGE should contain the following: (i) a brief title with suitable words for indexing; (ii) the names of the authors and the institution(s) where the work was carried out; (iii) a footnote with the present address of the authors, if different from (ii); (iv) a 75-word Abstract which summarizes the significant results of the communicated paper; (v) keywords for indexing and information retrieval; (vi) major discipline; and (vii) a running/short title.

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8. HINGDON, A.	*Engineering mechanics*, Vol. 1. Ch. 3, pp 79–104, 1968, Prentice-Hall.
9. RAMA MURTHY, K.	*Convergence of state distributions in multi-type Bellman-Harris and Crump-Mode-Jagers branching processes*, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1978.

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The volume under review covers indepth the factors affecting humans in hypogravity as well as mechanisms through which their physiological systems react to these factors, i.e. to study the interrelationship of the *milieu interior* and the *milieu exterior*. An understanding of the physiology of fluid and electrolyte metabolism during the process of adaptation to hypogravity can give a proper perspective of the physiological process particularly to those associated with cardiovascular and renal systems and provide a basis to understand the true nature of the processes actually occurring in human body in space. The authors have brought out a comprehensive volume on their three decades of experience on the intricate mechanisms of homeostasis of fluid and electrolyte balance in humans and animals in space flight environment. The importance of nitric oxide and endothilin in the control of circulation and other processes has been referred to as important pieces of future studies.

This volume is addressed to doctors and scientists practicing space physiology and medicine. One of the most noted developments of the 20th century is the exploration of space by humans. Space physiologists are keen to learn more about the effects of weightlessness on humans. By now, flight durations have been markedly increased, and space technology has become more sophisticated. In parallel, the physiological parameters that can be evaluated both in simulated and actual flights have also grown exponentially. This volume covers technical capabilities of instrumental and biological method as well as provocative and loading tests to assess the functional reserves of the body in this extreme environment, the cost of adaptation and the physiological mechanism underlying adaptation.

This hard-bound volume has six informative chapters in 218 pages. The first one is a review of the physiological effects of weightlessness, landing and readaptation to Earth's gravity putting into perspective the overall human adaptation process. The next two chapters deal with regulatory mechanisms of body fluids and electrolytes during short and long flights. Chapters four and five focus on Earth-bound space simulations and animal experimentations which took place in Kosmos biosatellities. The last chapter reviews the principles underlying the counter-measures to alleviate the deleterious effects of spaceflight conditions. The book concludes with a brief overview of the current understanding of the subject with some very good suggestions for future research in the field of space medicine. All chapters are supported by extensive references. The comprehensive summary of human space flight experience provided at the end of the book is very interesting and an informative piece of human history.

The presentation is lucid and the book is easy to read with logical sequencing and adequate charts and tables. Some more stress could have been laid on fundamentals of fluid and electrolyte balance. Recent concepts have been adequately covered. The lack of an index is felt very much. This eminently readable book is recommended to libraries of medical colleges as well as to laboratories dealing with space physiology and medicine. It will also be a very useful reference guide to research scholars in the field of physiology, biochemistry, life sciences and medicine. The volume will remain a source of intellectual pleasure and knowledge to post-graduates, specialists and teachers of space physiology and medicine for many years to come.

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Contents