J. Org. Chem. **1994**, 59, 4887–4894

Theoretical Investigations on the Regio- and Stereochemistry of the Photochemical [2 + 2] Cycloaddition of Propene

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Received March 30, 1994®

Energy hypersurfaces for the lowest singlet states of the [2 + 2] cycloaddition of two ethylene molecules and of two propene molecules in all possible face-to-face orientations were calculated by the semiempirical MNDOC-CI method. A rhomboidal distortion of the pericyclic geometries results in conical intersections. Geometries and energies of the conical intersections were determined and show that for the propene dimerization the head-to-tail approach is favored over the head-to-head approach. Two different ground-state reaction paths emanate from the conical intersections leading to a cyclobutane structure and to a 1,4-biradical, respectively. The larger the rhomboidal distortion at the conical intersection the more pronounced is the 1,3-interaction that yields the 1,4-biradical. Electronic effects on the geometry at the conical intersection are discussed on the basis of the 2-electron−2-orbital model and suggest the rhomboidal distortion to be less pronounced for more electronegative substituents, yielding 1,3-disubstituted cyclobutanes via a concerted pathway.

Introduction

Considerable progress has been made in recent years in the field of stereoselective synthesis.[1] If a valid model exists for the "reactive conformation", stereospecifity can be explained and predicted in many cases on the basis of steric, stereoelectronic, and substituent effects.[1c] A representative example for the reactive conformation is provided by the Felkin−Anh model[2] for nucleophilic additions to the carbonyl group.

While it might be fairly straightforward to develop models for the reactive conformation of ground-state reactions with early transition states, the situation is somewhat more difficult for photochemical reactions,[3] because (i) excited-state species differ considerably in their bonding properties from the corresponding ground-state species, and minima and barriers in excited-state potential energy hypersurfaces are therefore more difficult to predict, (ii) the mechanism of the photochemical reaction may not be known in sufficient detail, and (iii) the different reactivity of singlet and triplet species has to be explained.

A typical singlet photoreaction is the [2 + 2] cycloaddition. Until recently it has been assumed that the regio- and stereochemistry of this type of reaction is determined by the pericyclic minimum, the exciplex (or excimer) minimum, and the barrier between these two minima.[4,5] HOMO−HOMO and LUMO−LUMO interactions always favor the head-to-head regiochemistry and syn or cis stereochemistry in an excimer, while the analogy to isoconjugate perturbed cyclobutadienes suggests that the head-to-tail geometry is favored by the pericyclic intermediate.[6]

However, recent calculations for the [2 + 2] photoadditions of two ethylene molecules demonstrated[7] that the pericyclic structure on the excited-state surface is not a minimum but rather a transition structure with a downhill direction leading to a real conical intersection,[7,8] at which the decay to the ground-state surface occurs within a single vibrational period[9] and thus follows a concerted pathway. The mechanism is thus not controlled by the avoided surface crossing and the resulting S_1−S_0 gap, but rather by the presence of minima and transition states on S_0 and S_1 themselves. Furthermore, the existence of a conical intersection region provides access to a number of ground-state pathways that can lead to different photoproducts.[8,10]

As a consequence of these findings, the established picture for the stereocontrol of singlet photoreactions has to be modified in order to take into account the special role of the conical intersection, which may be considered the reactive conformation. As a first step toward a revised model of stereoselectivity we present in this paper our results for the [2 + 2] photoaddition of two propene molecules. In order to study substituent effects we used the semiempirical MNDOC-CI method[11] to calculate ground- and excited-state potential energy hypersurfaces for the four possible arrangements **1**−**4** of the two propene molecules, which correspond to the syn and anti position of the substituents in a head-to-head and in a head-to-tail approach.

® Abstract published in *Advance ACS Abstracts,* July 1, 1994.

[1] (a) Nógrádi, M. *Stereoselective Synthesis*; VCH: Weinheim, 1987. (b) Rosini, C.; Franzini, L.; Raffaeli, A.; Salvadori, P. *Synthesis* **1992**, 503, and literature cited therein. (c) Winterfeld, E. *Prinzipien und Methoden der stereoselektiven Synthese*; Vieweg: Braunschweig, 1988.

[2] (a) Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.

[3] Klessinger, M.; Michl, J. *Lichtabsorption und Photochemie organischer Moleküle*; VCH: Weinheim, 1989.

[4] van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042.

[5] Michl, J. *J. Photochem. Photobiol.* **1977**, *25*, 141.

[6] Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 170.

[7] Bernadi, F.; De, S.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 1737.

[8] Olivucci, M.; Ragazos, I. N.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 3710, and literature cited therein.

[9] Manthe, U.; Köppel, H. *J. Chem. Phys.* **1990**, *93*, 1658.

[10] Bernardi, F.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 8211.

[11] (a) Reinsch, M.; Höweler, U.; Klessinger, M. *J. Mol. Struct. (Theochem)* **1988**, *167*, 301. (b) Reinsch, M.; Klessinger, M. *J. Phys. Org. Chem.* **1990**, *3*, 81. (c) Klessinger, M. *Kem. Ind.* **1991**, *40*, 503.

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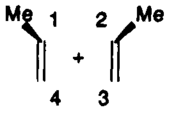

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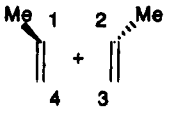

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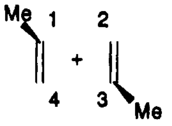

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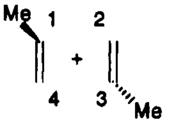

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Computational Method

All calculations were performed using the semiempirical MNDOC-CI method.[11] For each state under consideration, one or a few reference configurations were used and from these reference configurations single and double excitations within a properly chosen active space were constructed. In order to specify the active space and the reference configurations, the occupied ground state orbitals are numbered 1, 2, ... starting at the HOMO, while the virtual orbitals are numbered 1′, 2′, ... starting at the LUMO. In general, configuration interaction was taken into account between some 50−200 spin-adapted configurational functions. If the active space had to be chosen such that not all singly and doubly excited configurations could be included, the CI was further truncated by the use of excitation indices *m*/*n*, which specify the largest single and double excitations to be retained in the calcuation; for singly and doubly excited configurations $\Phi_{i\to k}$ and $\Phi_{i\to k}^{j\to l}$ the excitation indices are $(k - i)$ and $[(k - i) + (l - j)]$, respectively.[11c] All stationary points were characterized as minima or saddle points by calculating the vibrational frequencies.[12]

The truncation of the CI leads to inaccuracies in the calculated heats of formation, but yields reliable geometries and, most importantly, comparable accuracies for the ground state and the various excited states. The method is therefore particularly suited for discussing excited state potential energy surfaces and photochemical reaction mechanisms. For the ethylene dimerization a comparison with ab initio results[7] emphasizes the reliability of the MNDOC-CI results.

Results

The planar ethylene and propene dimerization reactions can be described by the intermolecular distance R and the angle α defined in Figure 1. For $\alpha = 0$ rectangular geometries are obtained along the reaction path, while for $\alpha \neq 0$ these geometries are rhomboidal. Thus we may refer to rectangular and rhomboidal reaction paths. In Figure 2 a global overview of the ground state (G), the singly excited (S), and the doubly excited state (D) singlet potential energy surfaces for the rectangular face-to-face [2 + 2] cycloaddition of two ethylene molecules are shown as function of R and (a) of the pyramidalization angle ω and (b) of the intramolecular CC distance r (cf. Figure 1). The angle ω and the CC distance r are those geometry parameters which (except for R) undergo the largest changes during the reaction. In generating these surfaces all other parameters were fixed to intermediate values (cf. Table 1). Very similar surfaces were obtained for the rectangular approach of two propene molecules with the two methyl groups in a cis-1,2 (**1**), trans-1,2 (**2**), cis-1,3 (**3**), and trans-1,3 (**4**) arrangement. Reactant-like geometries are on the rear right corner and product geometries on the left front corner.

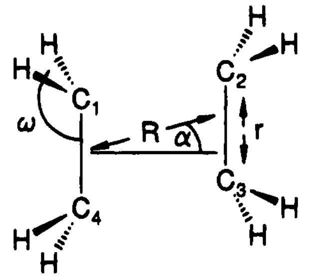

Figure 1. Definition of geometry parameters.

Table 1. Geometries and Heats of Formation of Some Points on the Potential Energy Hypersurfaces of the Rectangular [2 + 2] Cycloaddition of Two Ethylene Molecules and of Two Propene Molecules (r = 143.5 pm, r(CH) = 109.5 pm, ∠HCH = 111.0° and $r(CCH_3)$ = 148.5 pm kept fixed)[a]

	ethylene + ethylene	propene + propene			
		cis-1,2	cis-1,3	trans-1,2	trans-1,3
		Reactants[b]			
ΔH_f [kcal/mol]	67.1	60.1	58.0	58.2	58.0
		Product			
R [pm]	156.8	160.0	158.4	158.6	158.6
ω [deg]	140.3	136.6	138.2	138.0	138.0
ΔH_f [kcal/mol]	22.2	37.5	29.6	29.2	28.1
		Transition State on the G Surface			
R [pm]	217.9	219.6	218.2	215.5	216.3
ω [deg]	156.5	151.6	154.3	157.1	155.9
ΔH_f [kcal/mol]	113.3	122.9	118.1	117.6	117.9
		Minimum on the S Surface			
R [pm]	186.5	193.7	192.0	191.4	190.8
ω [deg]	153.8	147.1	151.8	151.5	151.4
ΔH_f [kcal/mol]	152.7	162.5	154.5	154.6	154.7
		Pericyclic Geometry			
R [pm]	217.1	219.0	216.7	216.7	214.4
ω [deg]	156.5	152.2	156.6	156.5	158.4
ΔH_f [kcal/mol]	143.9	147.9	142.4	142.2	142.3

[a] In all calculations the active space is 4−4′, and excitation indices are 6/8. In order to cover the whole range of distances R from the separated reactants to the products, reference configurations where chosen as follows: Φ_0 for G, $\Phi_{1\to 1'}$, and $\Phi_{2\to 2'}$ for S, and $\Phi_{1\to 1'}^{1\to 1'}$, $\Phi_{1\to 1'}^{2\to 2'}$, $\Phi_{1\to 2'}^{1\to 2'}$, and $\Phi_{2\to 1'}^{2\to 1'}$ for D. [b] Heats of formation of the reactants were calculated for R = 380 pm rather than for $R = \infty$.

The excited state surfaces exhibit two minima, one in the D state and one in the S state, as is to be expected from the Oosterhoff model.[4] The D-state minimum, in fact, results from an avoided crossing of the G and D states and thus represents the pericyclic geometry. The S-state minimum, however, is not an excimer minimum, which is expected to occur at larger distances R than the avoided crossing;[5] instead, it is found at rather short R and could be interpreted as spectroscopic minimum of the excited product. The S surface shown in the figures is that which is considered in the Oosterhoff−Michl model;[4,5] the true spectroscopic minimum, however, will involve a considerable amount of Rydberg character and cannot be calculated by semiempirical methods. The similarity of the ethylene and propene photoadditions becomes apparent from the data collected in Table 1,

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(12) Klessinger, M.; Pötter, T.; v. Wüllen, Ch. *Theor. Chim. Acta* **1991**, *80*, 1.

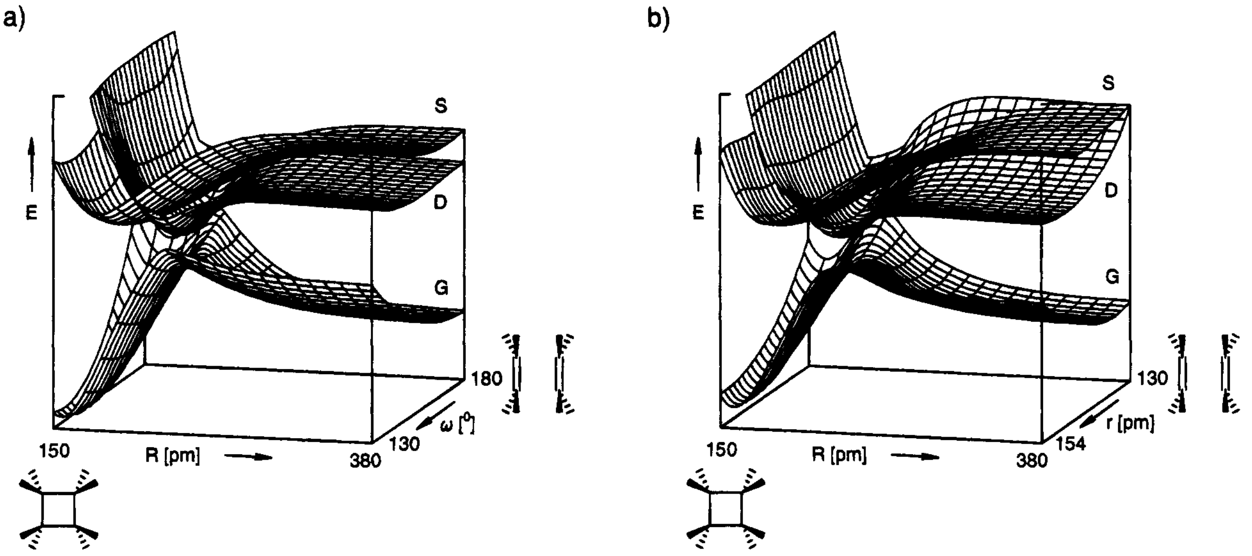

Figure 2. Energy hypersurfaces of the G, S, and D singlet states of the rectangular face-to-face [2 + 2] cycloaddition of two ethylene molecules (a) as a function of intermolecular distance R and the pyramidalization angle ω, and (b) as a function of R and the intramolecular CC distance r. All other geometry parameters are fixed at intermediate values (cf. Table 1). The full energy scale is 250 kcal/mol.

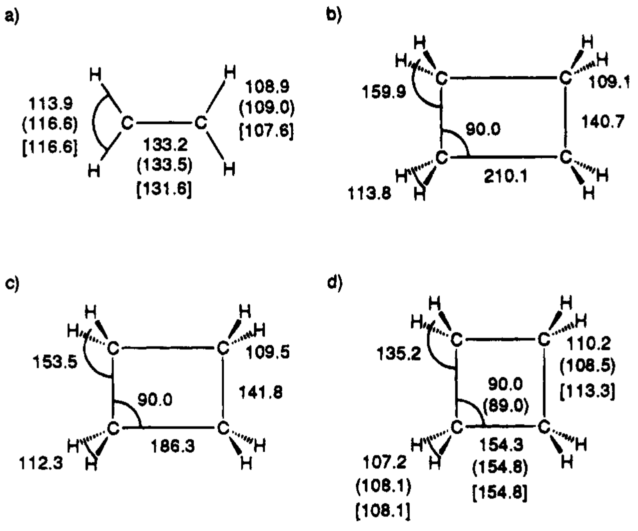

Figure 3. MNDOC-CI geometries optimized for the stationary points of the rectangular [2 + 2] cycloaddition of two ethylene molecules: (a) the reactant ethylene, (b) the pericyclic geometry, (c) the minimum on the S hypersurface, and (d) the product cyclobutane. Distances in pm, angles in degrees; experimental values (ethylene: Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906; cyclobutane: Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52*, 3857) in parenthesis, ab initio data (ethylene: Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679; cyclobutane: Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227) in brackets.

which were obtained from the surfaces corresponding to Figure 2a (E as function of R and ω) and therefore do not correspond to optimized geometries.

Fully optimized geometries of the stationary points for the rectangular [2 + 2] photoaddition of ethylene are shown in Figure 3; heats of formation and wave functions are collected in Table 2. Optimized geometries, heats of formation, and wave functions for propene and the four dimethylcyclobutanes are shown in Figure 4 and Table 3, respectively. The vibrational analysis proved all these points to be true minima except for the pericyclic structure of the ethylene dimerization reaction, for which one imaginary frequency was obtained which describes

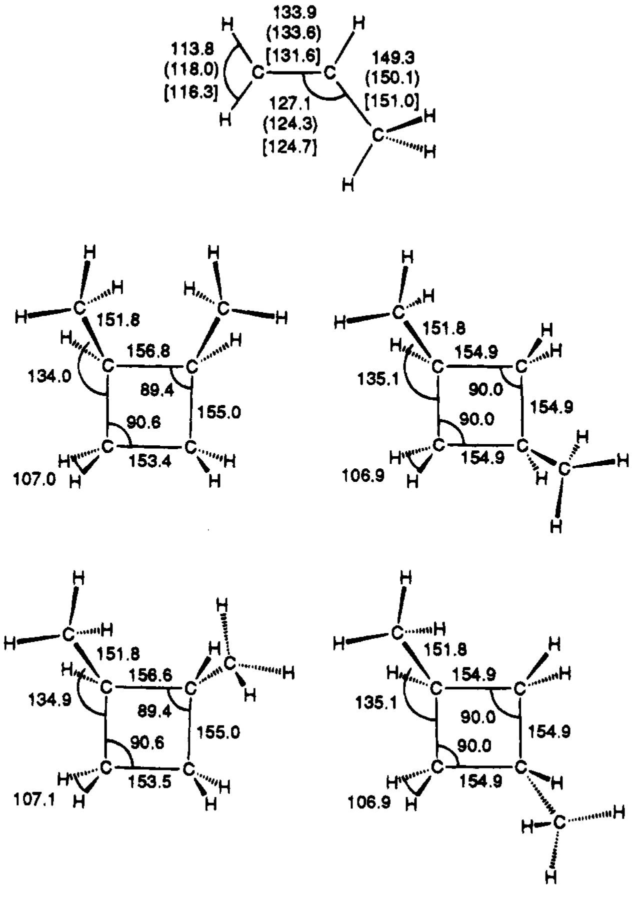

Figure 4. Optimized MNDOC-CI geometries of propene and of the four possible products of the [2 + 2] cycloaddition of two propene molecules. Distances in pm, angles in degrees; experimental values (Lide, D. R.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374) in parenthesis, ab initio data (Dorigo, A. E.; Pratt, D. W.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6591) in brackets.

a rhomboidal distortion. The rectangular pericyclic structure is thus a transition structure between two equivalent rhomboidal structures. No rectangular minima could be located for the dimerization of propene. Opti-

Table 2. Heats of Formation and Wavefunctions at MNDOC-CI Optimized Geometries of Stationary Points for the [2 + 2] Cycloaddition of Two Ethylene Molecules[a]

	ethylene	cyclobutane	pericyclic geometry	minimum in the S-State
ΔH_f [kcal/mol]	23.9	7.2	140.4	153.7
no. of configurations	101	153	199	172
reference configurations	Φ_0	Φ_0	Φ_0, $\Phi_{1-1'}^{1-1'}$	$\Phi_{1-1'}$
Φ_0 [%]	96.7	99.7	51.7	–
$\Phi_{1-1'}$ [%]	–	–	–	99.3
$\Phi_{1-1'}^{1-1'}$ [%]	–	–	40.8	–

[a] In all calculations the active space is 4–4′, and the excitation indices are 4/8. Geometries were optimized using a smaller CI.

Table 3. Heats of Formation and Wavefunctions at MNDOC-CI Optimized Geometries of the Reactant and Products for the [2 + 2] Cycloaddition of Two Propene Molecules[a]

	propene	*cis*-1,2-dimethylcyclobutane	*cis*-1,3-dimethylcyclobutane	*trans*-1,2-dimethylcyclobutane	*trans*-1,3-dimethylcyclobutane
ΔH_f [kcal/mol]	18.4	8.8	7.5	7.5	7.4
no. of configurations	153	153	153	153	153
Φ_0 [%]	96.8	99.8	99.8	99.8	99.8

[a] In all calculations the reference configuration is Φ_0, the active space is 4–4′, and the excitation indices are 4/8. Geometries were optimized using a smaller CI.

Table 4. Heats of Formation, S_1/S_0 Energy Gap, Mean Distortion Angle $\bar{\alpha}$, and Wavefunction at the Conical Intersections for the [2 + 2] Cycloaddition of Two Ethylene and Two Propene Molecules[a]

		propene + propene			
	ethylene + ethylene	*cis*-1,2	*cis*-1,3	*trans*-1,2	*trans*-1,3
ΔH_f [kcal/mol]	133.6	131.5	126.8	130.8	126.9
S_1/S_0 energy gap [kcal/mol]	<0.1	0.2	0.1	<0.1	<0.1
$\bar{\alpha}$ [deg]	22.4	24.8	21.8	23.1	21.5
no. of configurations	185	181	198	200	200
Φ_0 [%]	84.1	73.1	85.5	81.2	76.2
$\Phi_{1-1'}$ [%]	0.1	5.1	0.2	0.1	12.2
$\Phi_{1-1'}^{1-1'}$ [%]	11.4	5.1	9.5	7.5	7.9

[a] In all calculations the active space is 4–4′, and the excitation indices are 4/8. Geometries were optimized using a smaller CI.

mization of both the S-state minimum and the pericyclic structure led to the same rhomboidal geometry. This may be due to the lower symmetry as compared to the ethylene reaction, and to the steric interaction of the substituents.

These results demonstrate the necessity to investigate the rhomboidal structures in more detail. In Figure 5 singlet state potential energy surfaces for the ethylene and propene dimerization are shown as function of the intermolecular distance R and the distortion angle α (cf. Figure 1). These diagrams show the S_0, S_1, and S_2 surfaces, i.e. all crossings are avoided and the designation by G, S, and D is valid only for large values of R that correspond to separated molecules and are shown on the right-hand side of the diagrams. On the left-hand side a well-developed minimum in the S_0 surface can be recognized. It lies on the line $\alpha = 0$ corresponding to rectangular geometries and represents the reaction product. The surfaces for ethylene and for the head-to-head arrangements **1** and **2** of two propenes are symmetrical with respect to the line $\alpha = 0$, whereas for the head-to-tail arrangements **3** and **4** distortions along $+\alpha$, which move the methyl groups away from each other, are more favorable than distortions along $-\alpha$, which bring the methyl groups closer together.

As expected from the investigation of the rectangular approach, the rectangular pericyclic geometry situated just above the transition structure of the ground state reaction does not correspond to a minimum on the S_1 surface but rather to a transition structure. A rhomboidal distortion of this structure lowers the energy by 5–8 kcal/mol and leads to conical intersections of the S_0 and S_1 surfaces. Geometries of these conical intersections were optimized on the MNDOC-CI level in the usual way by means of the BFGS algorithm.[13] Since the gradient criterion cannot be satisfied at a surface crossing point, the optimization was terminated when no point of lower energy could be found. The geometries obtained in this way are shown in Figure 6, and energies and wave functions are given in Table 4, together with the mean values $\bar{\alpha} = \sum |\angle CCC - 90|/4$ for the distortion angle. The geometries at all conical intersections are more or less rhomboidal, with those for the head-to-head arrangement of the two propenes being more distorted due to the steric interaction of the two methyl groups. The heats of formation given in Table 4 show that the conical intersections are remarkably more stable for the 1,3 orientation (**3** and **4**) than for the 1,2 orientation (**1** and **2**) of the methyl groups.

Finally, in Figure 7 atomic and overlap populations in the two lowest singlet states are shown for the rhomboidal distortion of the rectangular pericyclic structure of two ethylene and of two propenes in the trans-1,2 (**2**) and trans-1,3 arrangement (**4**). The values were obtained by means of a Mulliken-type population analysis[14] of the CI wavefunction, using a deorthogonalized basis[15] obtained by the symmetrical Löwdin procedure.[16] They show that with increasing distortion angle α a considerable 1,3 interaction develops in the S_1 state, which is comparable with the 1,2 interaction at the conical intersection and which increases and by far exceeds the 1,2 interaction if one proceeds on the S_0 surface to larger α values.

Discussion

The results presented in the previous section have important consequences for the mechanism of the photochemical [2 + 2] addition. No excimer minimum could be detected, and the pericyclic structure does not correspond to a minimum but rather to a transition state between two minima or conical intersections, which,

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(13) (a) Broyden, C. G. *Math. Comput.* **1967**, *21*, 368. (b) Fletcher, R. *Comput. J.* **1970**, *13*, 317. (c) Goldfarb, D. *Math. Comput.* **1970**, *24*, 23. (d) Shanno, D. F. *Math. Comput.* **1970**, *24*, 647.

(14) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 2343.

(15) Pötter, T. Ph.D. Thesis, Universität Münster, 1990.

(16) Löwdin, P.-O. *J. Chem. Phys.* **1950**, *18*, 365.

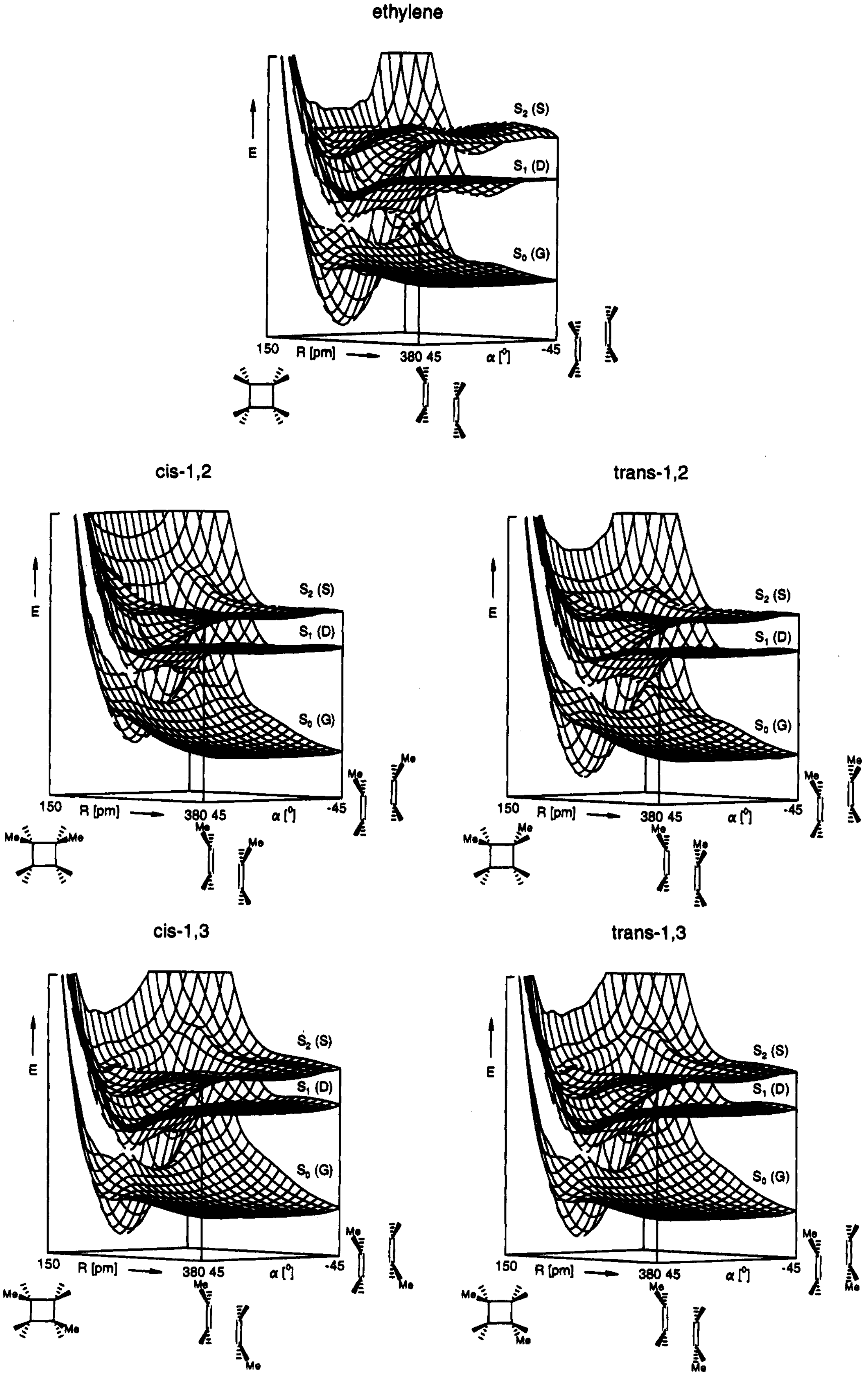

Figure 5. Energy hypersurfaces of the lowest singlet states of the rhomboidal face-to-face [2 + 2] cycloaddition of two ethylene molecules and of two propene molecules in all four possible arrangements as a function of the intermolecular distance R and the angle α of distortion from the rectangular approach. All other geometry parameters are fixed at intermediate values (cf. Table 1). The full energy scale is 250 kcal/mol, the cyclobutane structures shown below the diagrams correspond to the minimum in the S_0 surface.

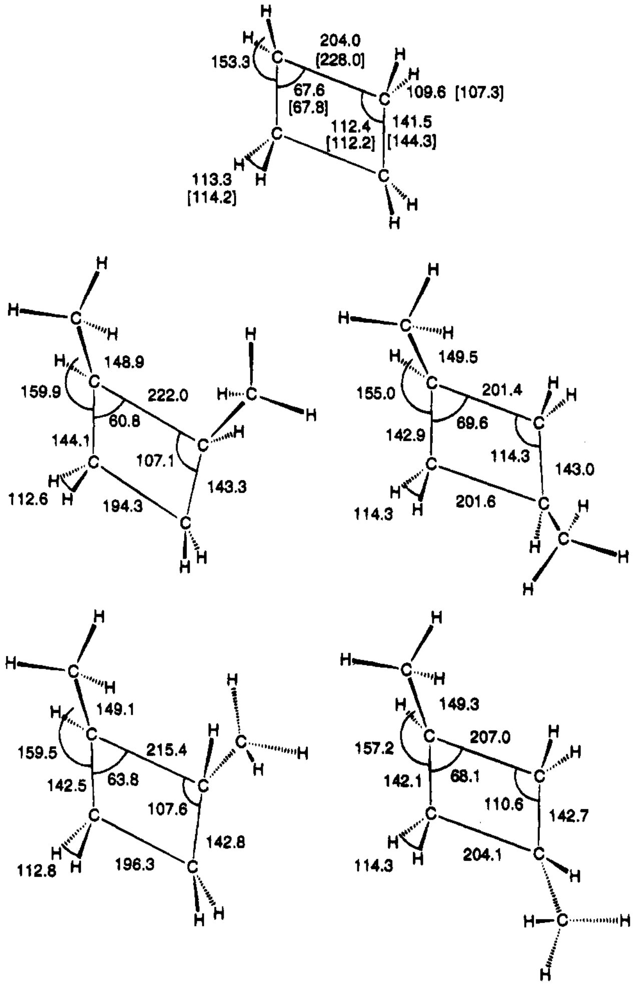

Figure 6. MNDOC-CI geometries optimized for the conical intersections of the face-to-face [2 + 2] cycloaddition of two ethylene molecules and of two propene molecules in all four possible arrangements. Ab initio data (ref 7) in brackets.

depending on the symmetry, will be equivalent. It has been known for a long time that for polyatomic molecules the crossings between states that belong to the same irreducible representation are possible in principle,[17] but it was supposed that a good part of the $(n - 2)$-dimensional hyperline of intersection between surfaces of the same symmetry may be at infinity or even in the imaginary plane. The conical intersections determined in this study have an analogy in a crossing that is allowed by symmetry in H_4 and has been carefully studied by Gerhartz, Poshusta, and Michl.[18] Bernardi and coworkers were the first to demonstrate that conical intersections occur in many photochemical reactions and are vital for the mechanisms of the reaction.[7,8,10,19] In fact, our results for the ethylene dimerization agree quite well with the ab initio data of Bernardi et al.,[7] whose geometry parameters at the conical intersection (R = 228 pm, α = 22.2°) are very similar to those given in Figure 5 (R = 204 pm, α = 22.4°). For the energy difference between the pericyclic structure and the conical intersection they find ~15 kcal/mol as compared to our value of 6.8 kcal/mol.[20]

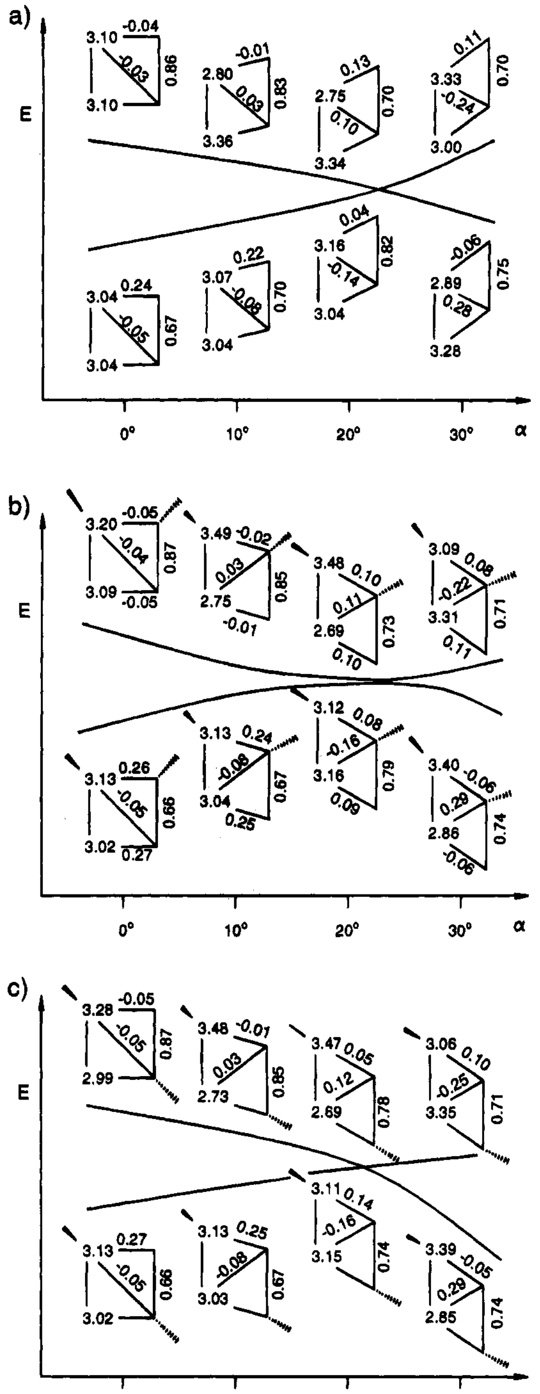

Figure 7. Atomic and overlap populations in the two lowest singlet states for various values of the distortion angle α for the face-to-face [2 + 2] cycloaddition (a) of two ethylene molecules, (b) and (c) of two propene molecules with trans-1,2 and trans-1,3 arrangement of the two methyl groups, respectively.

Thus, the role of conical intersections in the mechanism of the photochemical [2 + 2] cycloaddition is well established. The question now arises, how can the regio- and stereochemistry of this reaction be explained on the basis of this new mechanism in which neither an excimer minimum nor a pericyclic minimum is involved? The

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[17] Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982.

[18] Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263.

[19] Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc.* **1992**, *114*, 5805.

[20] Ragazos, I. N.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* **1992**, *197*, 217.

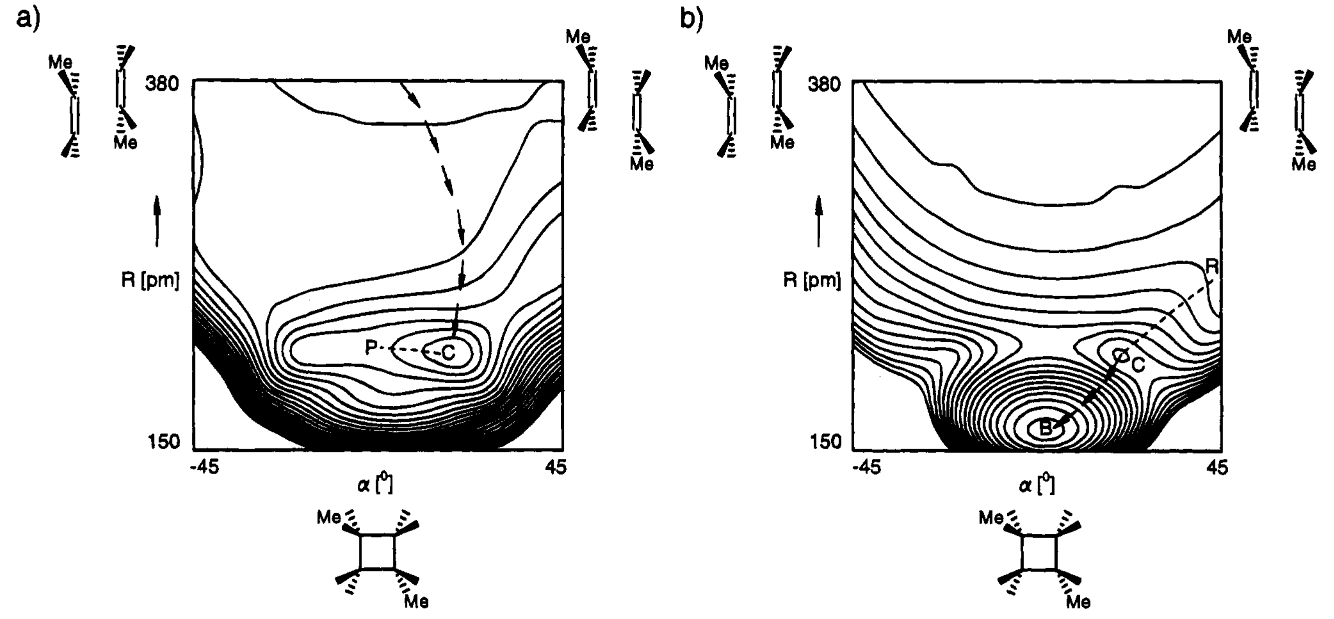

Figure 8. Energy contour maps for the face-to-face [2 + 2] cycloaddition of two propene molecules in the trans-1,3 arrangement, (a) lowest excited state S_1, (b) ground state S_0. P: pericyclic geometry, C: conical intersection, B: dimethylcyclobutane, R: 1,4-biradical intermediate. The separation of contour lines is 6 kcal/mol.

results in Table 4 indicate the influence of the substituents: for the head-to-tail arrangement (**3** and **4**) of the methyl groups the conical intersection is more stable by ~5 kcal/mol than for the head-to-head arrangement (**1** and **2**). This energy difference is small but significant and can be rationalized on the basis of a simple qualitative model (see below). But the favorable energetics of the head-to-tail arrangement does not necessarily imply that 1,3-substituted cyclobutanes will be formed. As Bernardi et al.[8] showed in the case of the photochemistry of butadiene, a number of different ground state trajectories leading to one or the other of the possible photoproducts may emanate from the apex of the cone. This is illustrated in Figure 8, which shows energy contour maps for the S_1 and S_0 state of the trans-1,3 approach (**3**) of two propene molecules. Two valleys starting at the conical intersection are seen on the ground state surface (Figure 8b), one leading to the cyclobutane minimum (B), the other one to the 1,4-biradical (R). The trans-1,3 approach of two propenes can thus yield either *trans*-1,3-dimethylcyclobutane or via the 1,4-biradical either *trans*-1,2- or *cis*-1,2-dimethylcyclobutane, depending on the ring closure reaction which can be achieved either by an in-plane rotation or an out-of-plane rotation of one of the radical centers. From the overlap populations shown in Figure 7 it may be concluded that the 1,3 interaction leading to the 1,4-biradical will be the more pronounced the larger the angle α, i.e. the more pronounced the rhomboidal distortion is at the conical intersection. Another factor that may influence the sterical outcome of the reaction is the way on which the system enters the conical intersection region (Figure 8a): A trajectory along the minimal energy path indicated in Figure 8 by arrows will lead in a concerted reaction to the cyclobutane structure (B), while a trajectory via the pericyclic geometry (P) could again favor the formation of the 1,4-biradical (R). The excited state branch of the reaction pathway enters the conical intersection in the direction of the gradient difference, which normally points to the apex of the cone. While, adiabatically, the system will follow this same direction on the ground-state surface, a specific ground-state trajectory will deflect depending on the direction and magnitude of the nonadiabatic coupling vector.[8] In this way substituents and environment will control the way in which the system enters and exits the conical intersection region.

Although more detailed calculations will be needed to characterize the $(n - 2)$-dimensional hyperline of the conical intersection in order to establish the importance of the various factors that determine the stereochemistry of the reaction, some general results may be derived from the 2-electron–2-orbital model of Michl and Bonačić-Koutecký.[6,21] In this model the pericyclic geometry corresponds to a perfect biradical and the distortion of the rectangular geometry to a rhomboidal one may be considered as a transition from the perfect biradical to a heterosymmetric biradicaloid, as may be inferred from the atomic populations shown in Figure 7, which indicate different electronegativity of the localized orbitals A and B (cf. **5**) centered on carbons 1,3 and 2,4, respectively. With increasing electronegativity difference δ, i.e. with increasing α, S_1 is lowered in energy relative to S_0 (or T), and the crossing of S_1 and S_0 for the critical value δ_0 of δ (or α) corresponds to the conical intersection. The fact that the conical intersection for the head-to-tail approach (**3** and **4**) of two propenes is energetically favored and occurs at a smaller value of α than that for two ethylenes can thus be explained by the effect that the substituents already introduce a perturbation δ, so that a smaller distortion is required for reaching the critical value δ_0 at which the crossing occurs. This argument allows for the prediction, that highly electronegative substituents like CN or NO_2 will produce a much larger perturbation δ and will lead to a conical intersection at considerably less distorted geometries with smaller 1,3 interactions as may be inferred from the overlap

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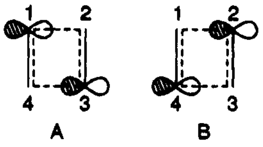
[21] Michl, J.; Bonačić-Koutecký, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990.

population shown in Figure 7. Such substituents should therefore favor the formation of trans-1,3-substituted cyclobutanes.



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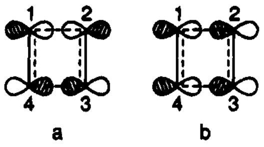

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In the case of 1,2 substitution, on the other hand, the localized orbitals A and B remain degenerate, while the delocalized orbitals a and b (cf. **6**) are no longer degenerate but split due to the effect of the substituents. Since an electronegativity difference δ_{ab} in the basis of delocalized orbitals is equivalent to a covalent interaction γ_{AB} in the basis of localized orbitals ($\delta_{ab} = \gamma_{AB}$), the pericyclic geometry no longer corresponds to a perfect biradical, but rather to a nonsymmetric biradicaloid. The S_1/S_0 crossing is avoided in this case, and no conical intersection is to be expected. This effect, which from the data in Table 4 is seen to be too small to be conclusive for methyl substitution, should be appreciable for more electronegative substituents and should make the head-to-head approach (**1** and **2**) even less favorable.

Conclusion

Calculations for the [2 + 2] photoaddition of two propenes provide a simple model for discussing the influence of substituents on the regio- and stereochemistry of this reaction. The results show clearly that the stereochemical outcome of the reaction cannot be interpreted in terms of a pericyclic minimum and an excimer minimum and the barrier between them. Instead, the main feature of the mechanism of this reaction is the existence of a real conical intersection, which may be considered the "reactive conformation" in discussing substituent effects. This is in contrast to thermal reactions, where the transition state is the reactive conformation, and to triplet photoreactions, in which the point of favorable intersystem crossing determines the reactive conformation.[22]

Electronic effects on the geometry at the conical intersection may be discussed on the basis of the 2-electron−2-orbital model and show that for substituted ethylenes the head-to-tail approach is favored over the head-to-head approach, in agreement with the results of the calculations. The rhomboidal distortion of the pericyclic geometry leading to the conical intersection is predicted to be less pronounced for electronegative substituents, suggesting a concerted pathway which yields 1,3-substituted cyclobutanes. Increasing rhomboidal distortion increases the 1,3 interaction and may yield cis-1,2- or trans-1,2-substituted cyclobutanes via a 1,4-biradical intermediate.

In summary, the reported results and their interpretation on the basis of the 2-electron−2-orbital model reveal the various factors that determine the regio- and stereochemistry of photochemical [2 + 2] cycloaddition reactions: Electronic effects will primarily influence the geometry of the conical intersections, while steric effects will control the way in which the system enters and exits the conical intersection region. However, detailed investigations of this region on the semiempirical and on the ab initio level, as well as studies of the dynamics of the system, are required for specific examples in order to produce quantitative results for the various reaction pathways. Such investigations are presently under way.

Acknowledgment. This work was partially supported by the Deutsche Forschungsgemeinschaft, Stiftung Volkswagenwerk, and Fonds der Chemischen Industrie.

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[22] Klessinger, M.; Böckmann, M.; Mählmann, J. *J. Inf. Rec. Mat.* **1994**, *21*, in press.