

# The electronic substituent influence on the thermally allowed electrocyclic interconversion cyclobutene/butadiene. A MNDO study

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The effects of donor/acceptor substitution on the conrotatory cyclobutene/butadiene interconversion have not yet been experimentally studied. MNDO Synchronous Transit/MINIMAX calculations for all possible combinations of  $\text{NH}_2/\text{NH}_3^+$  groups at the fissile single bond reveal very large substituent effects on the opening reactions and reverse cyclisations. Diamino- (*1b/2b*), diammonio- (*1c/2c*) and amino-ammonio-substitutions (*1d/2d*) change the activation energy of the reference ring opening reaction (*1a* → *2a*) from 49.9 kcal/mol to 34.7, 29.8 and 26.0 kcal/mol, respectively. This rate enhancement parallels the monotone shift of the transition state pathcoordinate towards the cyclobutenes. Relative to the electrocyclic reactions *1a/2a* – *1c/2c* the calculated result for *1d/2d* is in opposition to the Hammond postulate, but a detailed analysis of the reaction paths suggests a mechanistic deviation in this kind of reaction. The calculated data for the reference process (*1a/2a*) and the oxetene isomerisation (*3/4*) when compared with available experimental data indicate that the MNDO calculations accurately reflect the experimental trends.

**Key words:** Electrocyclic reactions—prediction of substituent effects—synchronous transit/MINIMAX method—semiempirical calculations

## 1. Introduction

The conservation of orbital symmetry has long been recognized [1] as a central principle in the field of pericyclic reactions, without taking into account any

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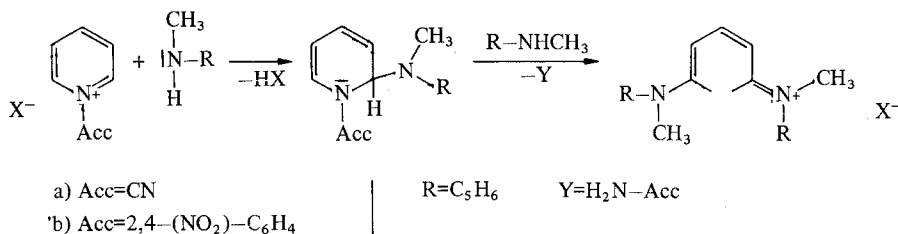
special electronic effects of substituents. Nevertheless, it is well-known that electron-withdrawing or -releasing groups influence both the reaction rates and the stereoselectivity of cyclo-addition processes [2]. Experimental results suggest similar effects for electrocyclic reactions. In the case of thermal conrotatory ring opening of cyclobutene the activation energy is reduced from 32.5 kcal/mole to 21.0 kcal/mole for the *trans* 1,2,3,4-tetraphenyl cyclobutene [3].

Methyl groups on the cyclobutene skeleton produce smaller-butregiospecific-effects: A methyl substituent at the 1- or 2-position of the ring increases the free enthalpy of activation ( $\Delta\Delta G^\ddagger = 1.2$  kcal/mole) but the opposite influence is found at the 3- or 4-position ( $\Delta\Delta G^\ddagger = -1.8$  kcal/mole), both effects obviously showing some additivity [4].

As expected, hetero-atoms in the ring/polyene-skeleton also strongly affect the reaction rates of the ring opening/closure. This is shown in a great variety of 1,5-electrocyclic reactions [5]; but in the interconversions of four-membered rings, only the tetramethyl oxetene isomerisation has been studied in comparison with *cis*-1,2,3,4-tetramethyl cyclobutene ring opening. The activation enthalpy for ring opening of the cyclobutene compound is lowered from 36.4 kcal/mole to 25.1 kcal/mole for the isoelectronic process of the oxetene corresponding to a ratio of  $1:10^7$  for the rate constants [6].

Apart from these results, there are several well-known reactions which are not yet discussed within the context of substituent effects on electrocyclic processes:

- (1) On nucleophilic addition of amines (nucleophiles) to N-acceptor-pyridinium salts, adducts are formed, which show extremely facile ring opening (1) to compounds of the "Koenig's salt"-type [7].
- (2) The reverse reaction, a fast 1,6-electrocyclisation, is found for polymethines terminally substituted with donor and acceptor groups [8]; unfortunately, subsequent aromatization renders the study of substituent effects more difficult.



**Scheme 1**

## 2. Models for predicting the effects of substituents

While a simple perturbational treatment is usually used to explain the effects of substituents on cycloadditions in a semi-quantitative way [2], the same methods may be less successful when applied to electrocyclic reactions [9].

Till now, all theoretical attempts to explain and predict the influence of substituents on these reactions have been based on the simple HMO method. Epiotis

[10a] calculated the stabilisation energies of an orbital interaction for the butadiene termini in a 1st order perturbational treatment, simulating the consequences of additional- $\pi$ -conjugation, electron release to and electron withdrawal from the  $\pi$ -system within the HMO-framework. The conclusion was reached that in every case (hetero-atomic substitution included the preference of the conrotatory ring closure versus the disrotatory electrocycloisatation is diminished.

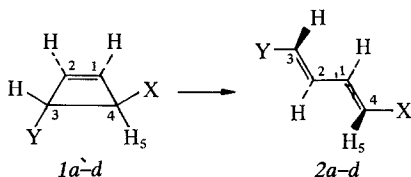
Similar results for cyclisation were calculated by Epiotis [10b] within the context of a model configuration interaction analysis. A different method was applied by Carpenter [11]: since transition states of pericyclic reactions are characterized (by definition) by a completely conjugated cycle of orbitals, changes in electron delocalisation are assumed to be the sole determining effect of a substituent on the reaction rate. Relative changes in activation energy upon substitution were estimated as changes in  $\pi$ -energy differences for the assumed planar  $\pi$ -skeletons of a model transition state and the reactant simulating  $\pi$ -electron donor (or acceptor) groups respectively by doubly occupied (or empty)  $p_{\pi}$ -orbitals at carbon. In the case of the cyclobutene ring opening, the following conclusions are found: Without exception, substitution on carbons of the breaking bond should accelerate ring opening, the opposite effect being true for substitution of the ring double bond. In both cases,  $\pi$ -donor-/acceptor groups (summarized as polar) will act more strongly than conjugated groups such as vinyl and phenyl.

Ignoring the deficiencies of the simple HMO-theory, agreement of calculated effects and experimental results must be regarded as somewhat fortuitous, since special electronic and/or geometric influences of substituents (and possible changes in reaction mechanism) are neglected. Some important information, such as geometric and thermodynamic data are not obtained using either of the methods described above, thus leaving the question of the reaction conditions unanswered.

### **3. Influence of donor-/acceptor-substituents on the electrocyclic isomerization of cyclobutane/butadiene: MNDO-calculations and results**

The interconversion cyclobutene/butadiene is a well studied process [12] at different theoretical levels. For this reason we chose this reaction as the reference to investigate the effects of model substituents on electrocyclic reactions of neutral molecules. In order to calculate accurate heats of reaction and molecular geometries, the semiempirical MNDO-method [13] was used to calculate transition states and reaction paths according to the Synchronous Transit/MINIMAX strategy [14].

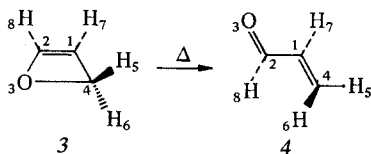
Being mainly interested in the electronic effects of substitution, we chose the model compounds given in Scheme 2, thus avoiding steric effects and possible differences in MNDO-parameterization associated with different heteroatoms.



Scheme 2

Compounds 1, 2. a)  $X = Y = H$  reference compound(-reaction); b)  $X = Y = NH_2$   $\pi$ -donor/ $\pi$ -donor; c)  $X = Y = NH_3^+$   $\sigma$ -acceptor/ $\sigma$ -acceptor; d)  $X = NH_3^+$ ,  $Y = NH_2$   $\sigma$ -acceptor/ $\pi$ -donor.

With the exception of the reference reaction  $1a/2a$  none of the compounds or interconversions have yet been studied, either experimentally or theoretically. For this reason, we decided to include the oxetene/acrolein isomerization (Scheme 3) in our investigation as an additional reference to experimental results described in chapter 1.



Scheme 3

For all calculations of (Schemes 2 and 3), the same procedures were applied as described elsewhere [14a]. First, MNDO-optimized path-limiting structures of reactant and product in Schemes 1–4 were calculated [15], and linear synchronous transit (LST) paths were constructed between these geometries. The transition states [16] were localized by the MINIMAX-optimization of the corresponding maxima. Finally, two structures [17] lying at opposite sides of the path maximum of that QST path were submitted to an exhaustive orthogonal optimization to yield an improved path between all optimized structures as a composite LST segment path (LST2...LST5).

The final multi-segment paths are displayed in Fig. 1, and the corresponding thermodynamic data for reactions (Schemes 2 and 3) are summarized in Table 1.

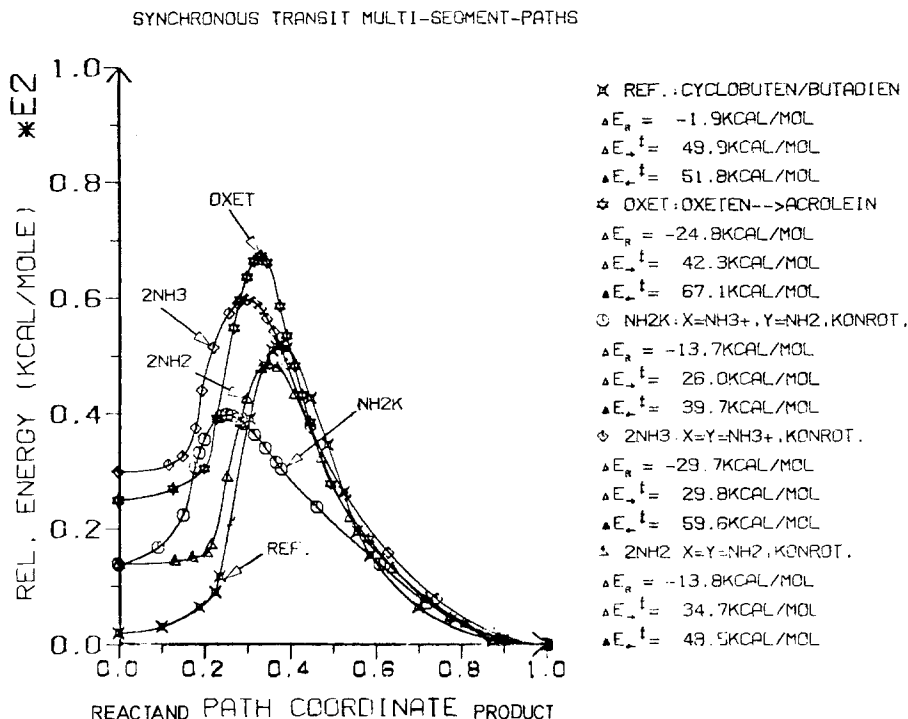
From the data given in Table 1 and from Fig. 1 the following analysis of the substituent effects is supported:

1) Both heteroatomic replacement (Scheme 3) as well as donor- and/or acceptor-substitution (Scheme 2) at the fissile bond make the ring opening processes more exothermic relative to the reference reaction. This is due to several effects:

a) Since all substituents act as  $\sigma$ -acceptors, ring strain is increased as a consequence of an enhanced core-core repulsion.

b)  $\pi$ -donors ( $NH_2$ ) and  $\pi$ -acceptors ( $NH_3^+$ , via degenerate pseudo  $\pi^*$ -orbitals [19]) may increase polyene resonance energy and induce direct interactions among the donor/acceptor groups, as in the case of  $2d$ .

c) The high cationic charges of  $NH_3^+$ -substituents cause strong polarization of the  $\pi$ -skeleton and, as a consequence, large geometric changes of the polyene



**Fig. 1.** Final multi-segment paths (LST2...LST5) for the conrotatory electrocyclic reactions of cyclobutenes trans substituted at the fissile bond with  $\text{NH}_2$  and/or  $\text{NH}_3^+$  groups (1b-d/2b-d). The corresponding processes of cyclobutene (ref.) and oxetene (OXET, 3/4) are given for comparison

**Table 1.** Calculated thermodynamic and kinetic data for reactions (2) and (3)

Inter-conversion	Heat of formation R	Heat of formation P	Heat of reaction	Activ. energy for ring opening <sup>a</sup>	Activ. energy for ring closure <sup>a</sup>	Pathcoord. for TS <sup>b</sup>
1a, 2a, [14a]	30.5	28.6	-1.9	49.9	51.8	0.376
1b, 2b	39.0	25.2	-13.8	34.7	48.5	0.349
1c, 2c	459.4	429.7	-29.7	29.8	59.6	0.301
1d, 2d	202.2	188.5	-13.7	26.0	39.7	0.253
3, 4	5.8	-19.1	-24.8	42.3	67.1	0.334

All energies in kcal/mole, R = reactant, P = product, TS = transition state.

<sup>a</sup> Calculated from the difference in heat of formation to TS and reactant.

<sup>b</sup> Values for the path coordinate PC refer to (2) and (3); PC=0 means reactant (ring), PS=1 corresponds to product (butadiene). For definition of PC refer to [14].

structure and conformation. The exceptionally high reaction enthalpy for the diammonio-compound 1c shows, that the effects of ring strain and Coulomb repulsion dominate over a gain of resonance energy (1d/2d).

2) Relative to the reference reaction (1a/2a) a continuous shift of the transit path maxima to lower values (to the reactant side) occurs. Due to the increased

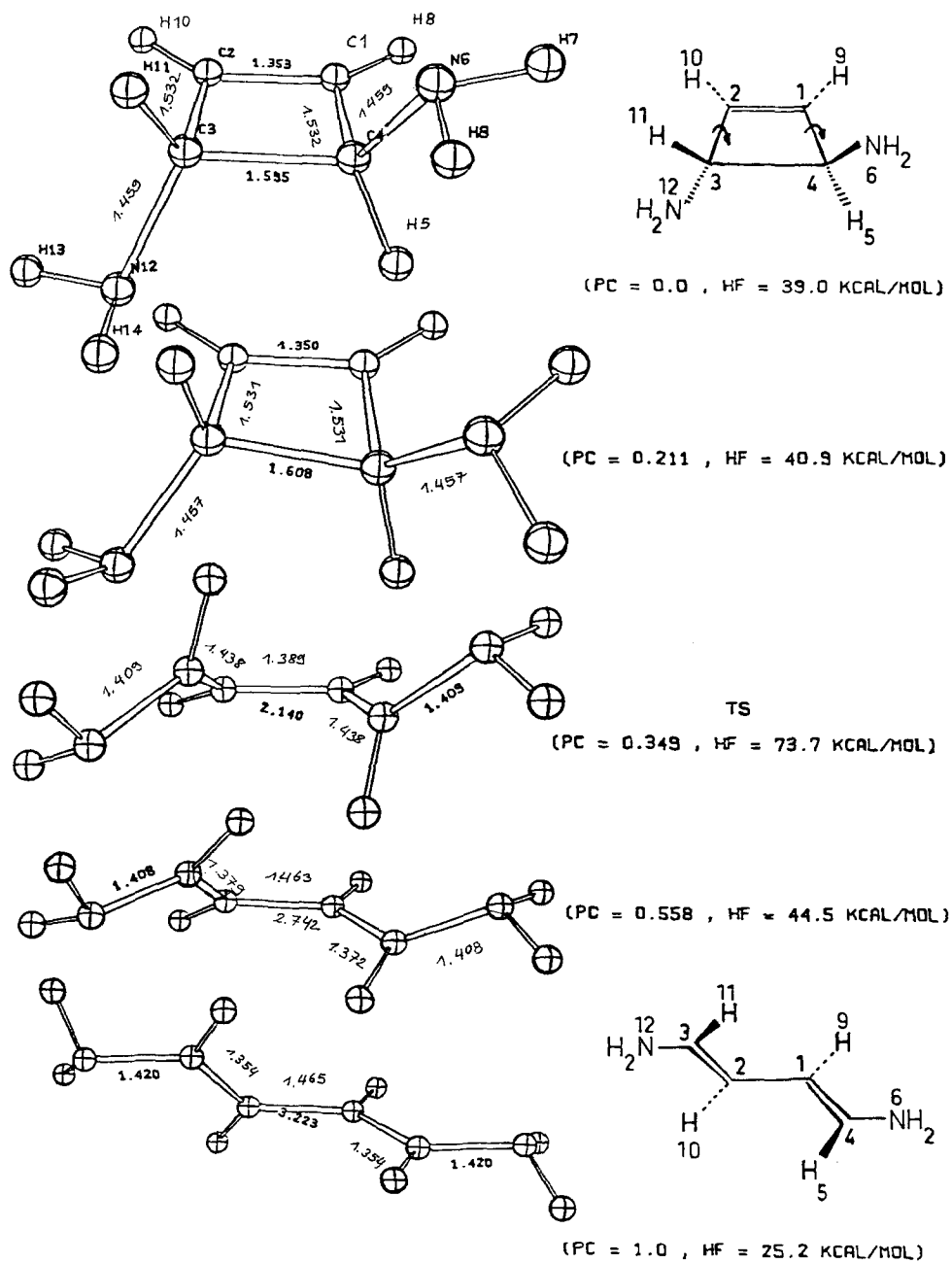
exothermicity (refer to 1) this is in agreement with the Hammond postulate except for the reaction  $1d/2d$ .

3) a) All ring opening processes are strongly accelerated by substitution at the fissile bond. Despite the fact that multiple substitution was not studied by Carpenter [11] one may concede agreement with his results. The calculated changes in activation energy for heteroatomic substitution at the reactive bond (oxetene ring opening  $3 \rightarrow 4$ ) confirm the large kinetic effects of the homologous tetramethyl compounds described in chapter 1. Even larger rate accelerations for donor and/or acceptor substituted cyclobutenes ( $1b-d \rightarrow 2b-d$ ) can be predicted by the MNDO results since the calculated degradation of the activation energies significantly exceeds that one of the oxetene isomerization. Again, an exceptional result is found for the donor/acceptor compound  $1d$ : while protonation of both amino groups in  $1b$  strongly facilitates ring opening ( $1c \rightarrow 2c$ ) a similar effect is found in contrast to this trend by deprotonation of one ammonio group in  $1c$ . Thus, the activation energy for  $1d \rightarrow 2d$  is almost halved by amino-ammonio substitution with respect to the model reaction ( $1a \rightarrow 2a$ ) with no substituents.

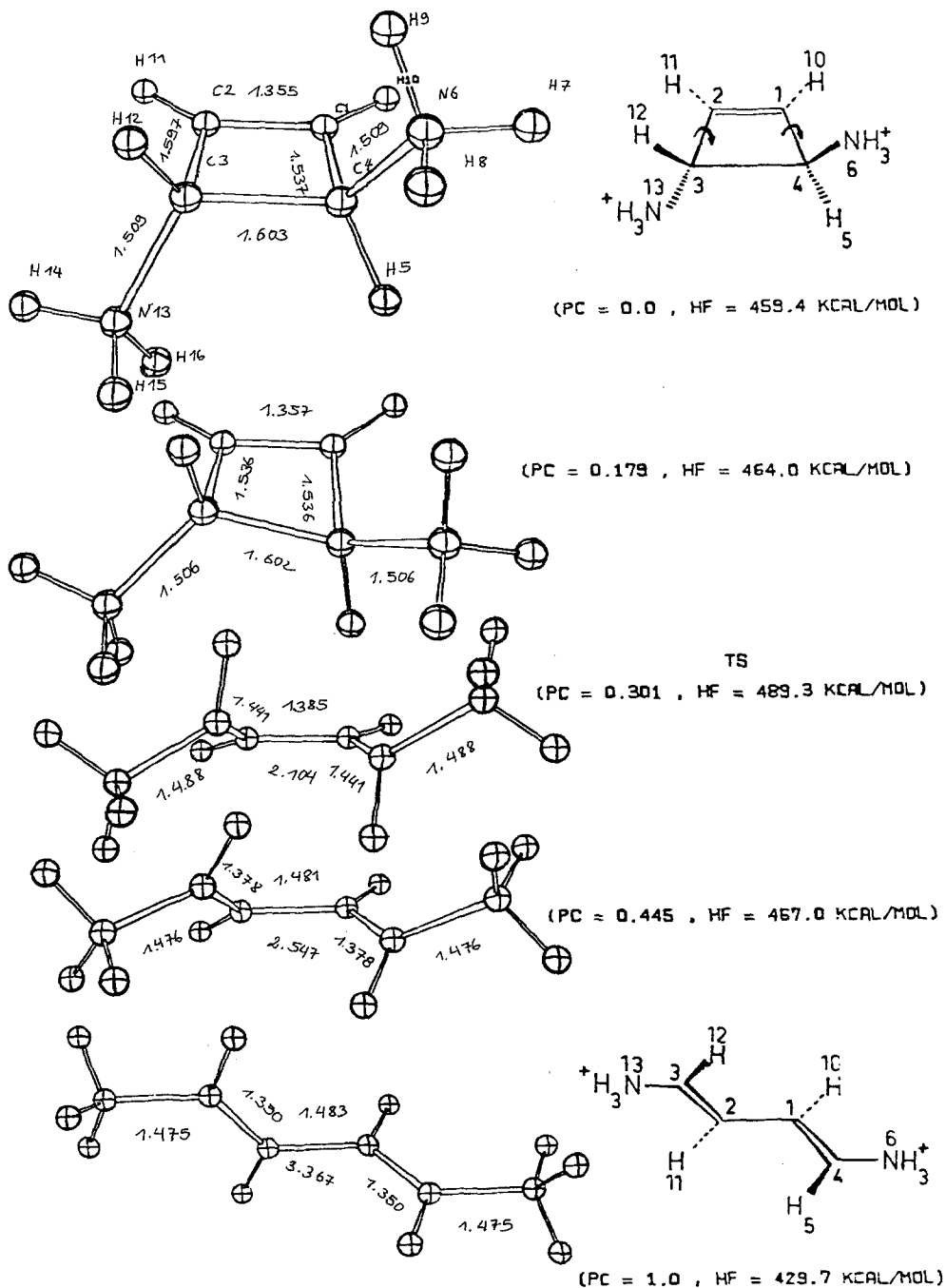
b) For the reverse reactions (ring closure to cyclobutenes) smaller but contradictory substituent effects may be recognized. Only for the cyclisations of  $2c$  and  $4$  rate retardation is found relative to the reference reaction and in agreement with the postulate of Epiotis. Again,  $2d \rightarrow 1d$  proves to be the fastest process among all cyclisations of this group.

Figs. 2-4 show the ORTEP-plots of all optimized geometries of the reaction paths for  $1b-d/2b-d$ . The geometric data allowing conclusions for special substituent effects are given in Table 2.

Our original hypothesis, that geometric substituent effects should predominantly occur in the linear polyene skeletons, is strongly supported (Table 2), although activation energies for ring closure ( $2 \rightarrow 1$ ) are strikingly less affected than those for the corresponding reverse processes (Table 1). For the ring compounds  $1a-d$ , above all the fissile bond C3C4 is significantly prolonged from 1.569 Å ( $1a$ ) to 1.610 Å ( $1d$ ); the longest bond, however, is surprisingly not found in the dication  $1c$ , but in the donor/acceptor compound  $1d$ . Perhaps this is due to the population of antibonding cyclobutene orbitals ( $\sigma^*$ ), which could result through orbital interaction with the  $\text{NH}_2$  lone pair and  $\text{NH}_3^+$   $\pi$ -orbitals [19]. Indeed, Kemister et al. [20] detected a minimal  $\pi$ -donor effect for  $\text{NH}_3^+$  groups to benzene but both  $\pi$ -acceptor and  $\pi$ -donor capabilities are not yet clarified. This is due to the insufficiencies [21] of the Mulliken charge analysis [22] and to the extraordinarily strong  $\sigma$ -withdrawal of the  $\text{NH}_3^+$  group. For the  $\text{NH}_3^+$  substituent, the smallest Mulliken group charge (+0.674) along the whole reaction path  $1d/2d$  is found in  $1d$ , hence the acceptor capabilities are maximal in this structure. Simultaneously, the Mulliken group charge for  $\text{NH}_2$  has a disappointingly small value of +0.002, but compared to  $1b$  (-0.071) the donor capacity is clearly demonstrated. Thus,  $\text{NH}_3^+$  possibly acts as a weak  $\pi$ -acceptor group via its degenerate  $\pi^*$ -orbitals.



**Fig. 2.** ORTEP plots of the optimized path limiting structures for the synchronous transit segments (LST2...LST5) of the conrotatory interconversion *1b/2b* with two NH<sub>2</sub> substituents



**Fig. 3.** ORTEP plots of the optimized path limiting structures for the synchronous transit segments of the conrotatory interconversion  $1c/2c$  with two  $\text{NH}_3^+$  substituents



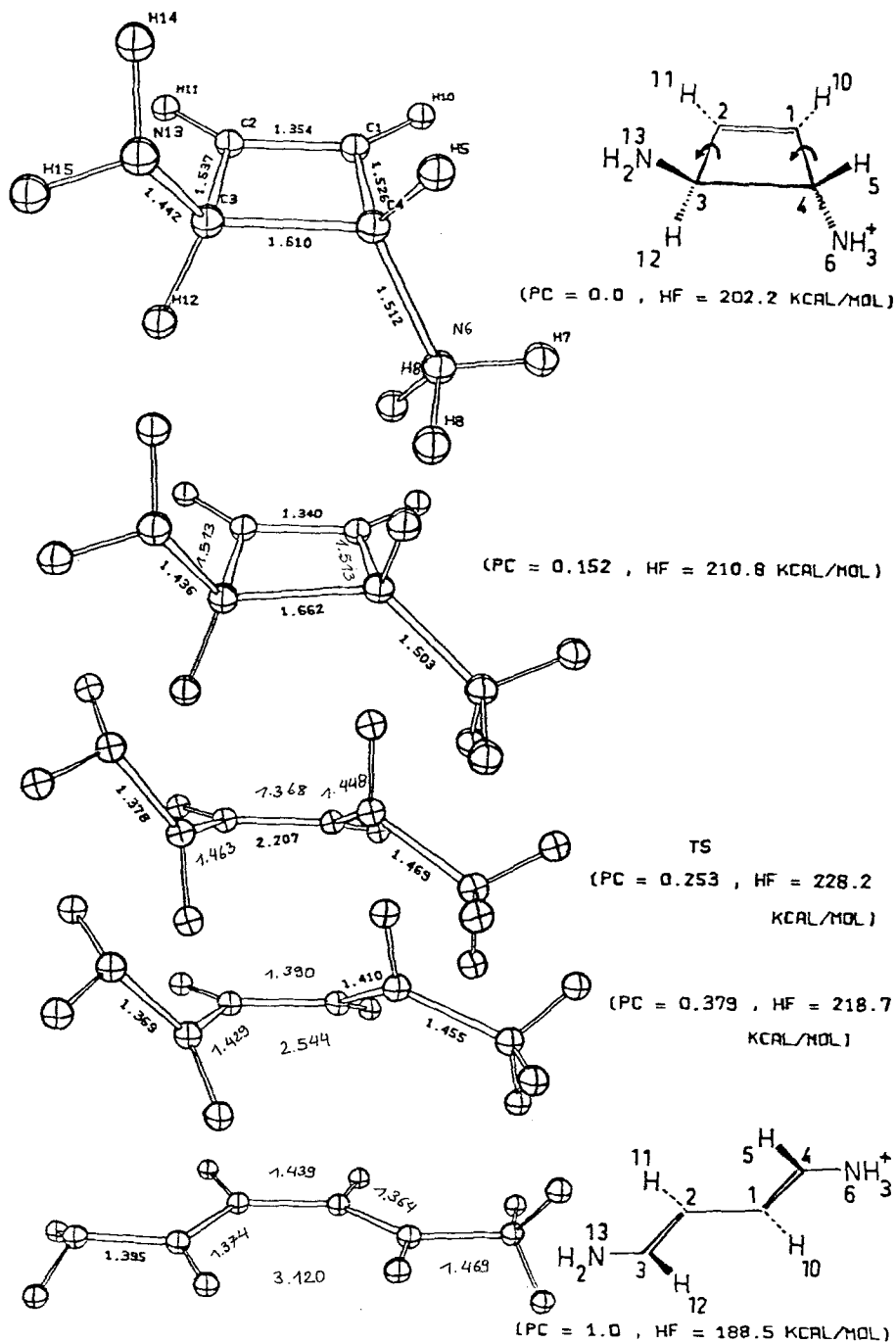


Fig. 4. ORTEP plots of the optimized path limiting structures for the synchronous transit segments of the conrotatory interconversion  $1d/2d$  with  $\text{NH}_2$  and  $\text{NH}_3^+$  substituents

**Table 2.** Key-geometric variables for reactants, transition states and products of reactions (2)

Bond	Ref. (1a/2a) [14a]			2NH <sub>2</sub> (1a/2b)			2NH <sub>3</sub> + (1c/2c)			NH <sub>2</sub> /NH <sub>3</sub> (1d/2d)		
	R	TS 0.376	P	R	TS 0.349	P	R	TS 0.301	P	R	TS 0.253	P
C1C2	1.354	1.408	1.470	1.353	1.389	1.465	1.355	1.385	1.483	1.254	1.368	1.439
C2C3	1.524	1.417	1.341	1.532	1.438	1.354	1.527	1.441	1.350	1.537	1.463	1.374
C1C4	1.524	1.417	1.341	1.532	1.438	1.354	1.527	1.441	1.350	1.528	1.448	1.364
C3C4	1.569	2.123	3.265	1.595	2.140	3.223	1.603	2.104	3.367	1.610	2.207	3.120
CNH <sub>2</sub>	—	—	—	1.459	1.409	1.420	—	—	—	1.442	1.378	1.395
CNH <sub>3</sub>	—	—	—	—	—	—	1.509	1.488	1.475	1.512	1.469	1.469

All bond length in angstrom, R = reactant, P = product, TS = transition state. Numbering refers to (2) and should not be confused with IUPAC conventions.

Geometric changes in *2b* may be explained with the  $\pi$ -donor capabilities of both amino groups: electron donation to the butadiene LUMO results in additional bonding effect between C1 and C2 (refer to (2)), while antibonding interactions are superposed to the double bonds.

Following perturbational arguments given above, this effect is pronounced in *2d*, suggesting an adequate description via the resonance form of the push-pull butadiene.

Mulliken charges of the substituent groups and of C4 seem to support this interpretation by a positive group charge at the amino group. Since calculations on planar push-pull-substituted butadienes have not been performed, the possible  $\pi$ -acceptor capabilities are still unclear. In *2c*, the extreme electron withdrawal of both NH<sub>3</sub><sup>+</sup> groups is reflected in an uniform lengthening of all bonds, despite the fact that Coulomb repulsion has forced the polyene to adopt an almost orthogonal conformation.

Since strong electronic differences of the substituents cause rather large geometric changes in the reacting species, it is justifiable to ask to what extent a common stereospecific [23] reaction route might be followed, corresponding to the Woodward-Hoffmann rules [1].

Analysis of the geometry path for the reference reaction (1a/2a) in Fig. 2 [and Fig. 14 of Ref. 14a] shows that the reaction may be subdivided into three reaction zones:

- (i) Preliminary conrotation of the methylene groups induces a conformational change of the ring to facilitate a subsequent bond stretch.
- (ii) The actual reaction zone is characterized by a concerted bond stretch, methylene rotation (conrotatory) and rehybridisation of the polyene termini.
- (iii) Relaxation of the polyene to a local energetic minimum mainly by a final methylene rotation.

The same features are retained for the reactions *1b-d/2b-d* and *3/4* (refer to Figs. 5 and 6).

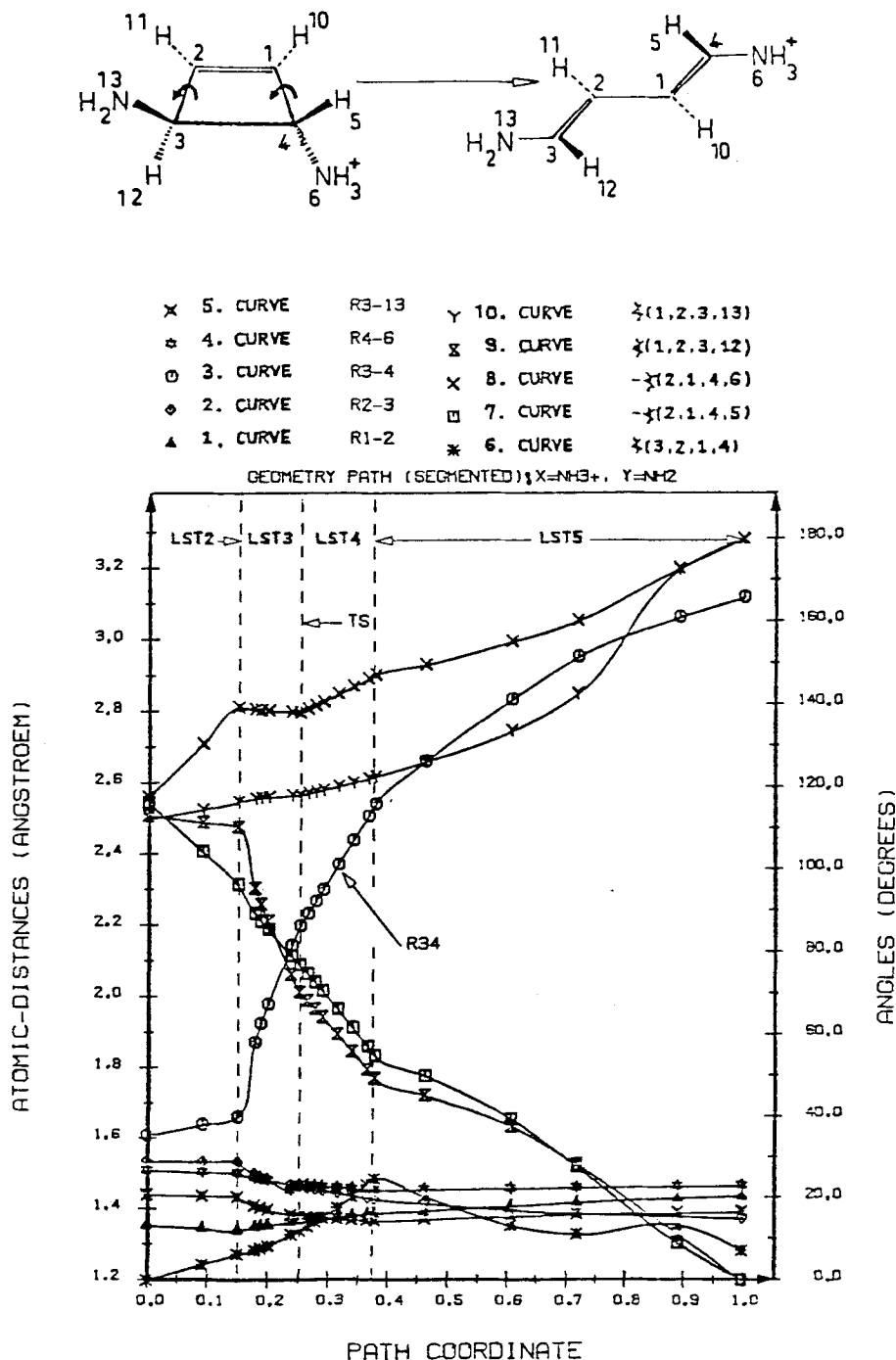
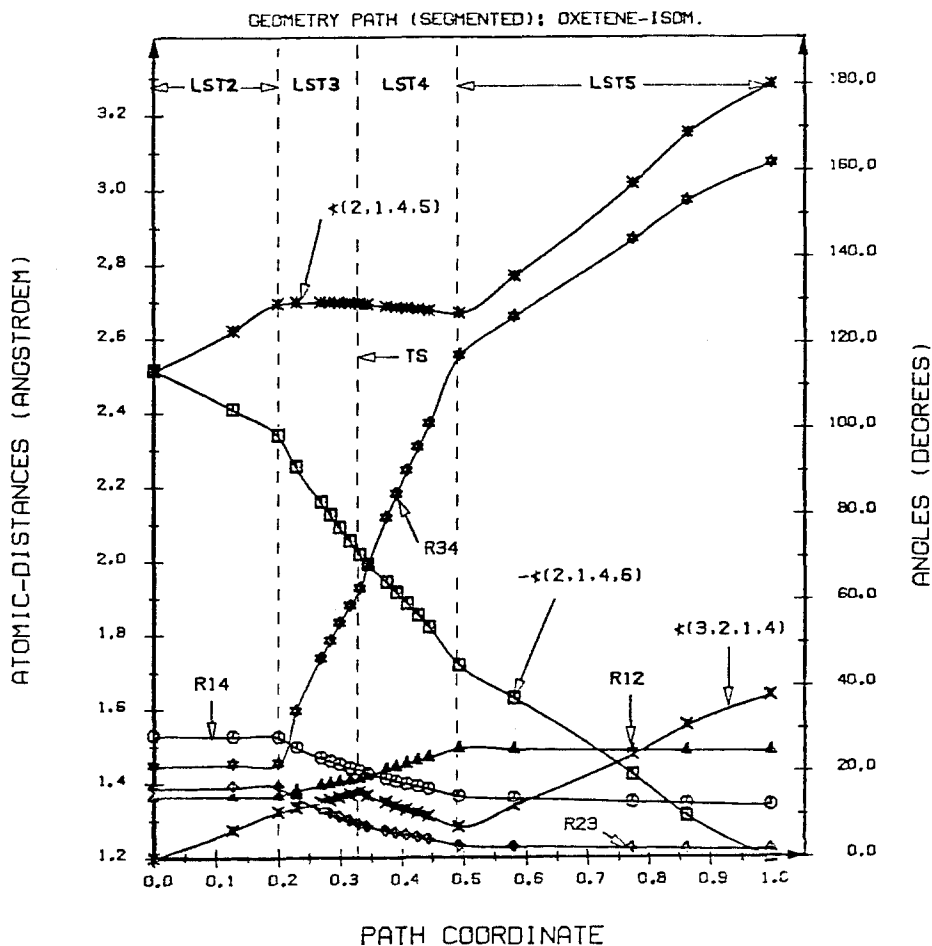


Fig. 5. Variation of key-geometric parameters for the conrotatory interconversion 1d/2d along the final multisegment path



**Fig. 6.** Variation of key-geometric parameters for the conrotatory interconversion 3/4 along the final multisegment path

As also may be seen from the ORTEP-plots (Figs. 2-4), strong visual similarities may be detected in all these reactions. However, a close geometric comparison based on the results of Table 2 reveals mechanistic peculiarities for the push-pull-system  $1d/2d$ .

It has been mentioned earlier that the transition state is placed at an abnormally small value of the path coordinate corresponding to approximately one fourth of the total reaction route. Consequently, geometric data of the transition state should most closely resemble those for the ring compound. From Table 2, however, it is found that this is true only for the bond length C1C2 (the double bond in cyclobutene). The development of the other bond lengths of the skeleton has proceeded to the same amount as in the symmetrically substituted transition states for  $1b/2b$  and  $1c/2c$ . Moreover, the breaking bond is prolonged, and the bond lengths of the  $\text{NH}_3^+$  and  $\text{NH}_2$  groups have already reached (or even exceeded)

their product values. Consequently, ring opening  $1d/2d$  must be regarded as an asynchronous mechanism. Additional peculiarities are revealed in Figs. 4 and 5: As in the other reactions  $1a-c/2a-c$ , the ring opening starts via conformational changes of the cyclobutene, but, in contrast to the other processes, the conrotatory movement of the  $\text{NH}_2$ -substituted methylene group is strongly retarded. As a consequence, a significantly enhanced heteropolar bond lengthening (C3C4) occurs, which is basically brought about by the strong  $\sigma$ -acceptor capacity of the  $\text{NH}_3^+$  group and the lack of molecular symmetry. Thus, a positive Mulliken charge is generated in the vicinity of the amino substituent and likewise a larger negative charge in the neighborhood of the  $\text{NH}_3^+$  group. The positive charge accelerates rehybridisation of the amino-methylene unit via pronounced rotation of the "inner" hydrogen atom, this being simultaneously aided by a  $\text{NH}_2$ -group rotation to yield a mesomeric stabilisation of the carbenium ion through the  $\text{NH}_2$  lone pair (Fig. 4). At this point the transition state is reached. The Mulliken group charge for  $\text{NH}_2$  is maximal, while the  $\text{NH}_3^+$  group keeps its minimum charge (+0.683) almost unchanged, due to maximal acceptance of electronic charge. The extremely high polarity of the transition state is schematically shown in Fig. 7.

On leaving the transition state in the direction to the product, the  $\text{NH}_2$ -methylene group compensates for the conrotatory movement of the  $\text{NH}_3^+$  (Fig. 5).

In summary, donor-/acceptor substitution causes marked changes in the electronic mechanism of the conrotatory interconversion of cyclobutene/butadiene which is here best described as a push-pull bond breaking/forming process. In its progress cationic charges of the fissile bond are stabilized through mesomeric electron donation of the  $\text{NH}_2$  lone pair and negative charges are reduced by the inductive electron withdrawal by the  $\text{NH}_3^+$  group. As a consequence, charge separation at the reacting bond (Mulliken group charges) shows a broad maximum along the reaction path in the vicinity of the transition state.

Correspondingly, the oxetene opening is found to occur in a heterolytic manner, involving geometric consequences (Fig. 6) similar to those described for  $1/2$ : In the reaction zone, rotation of the "outer"-hydrogen at the positive carbon C4 is significantly retarded, while the "inner" hydrogen is displaced faster. Once more, rehybridisation occurs rather than methylene rotation.

For the other reactions ( $1a-c/2a-c$ ), monotone and similar charge transfers at the fissile bond between the path-limiting structures occur, corresponding to a homolytic bond fission.

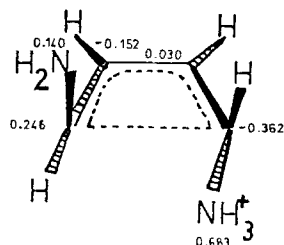


Fig. 7. Mulliken group charges at the transition state of the interconversion  $1d/2d$

Comparison of all key-geometric variables along the final reaction routes for (2) and (3) shows that the strongest effects of substitution are found for the critical bond length C3C4 and the dihedral angles of the outer methylene substituents (H, NH<sub>2</sub>, NH<sub>3</sub><sup>+</sup>); both are mechanistic pacemakers of the electrocyclic process. In consequence, these parameters should change most rapidly during the reaction. For the bond length C3C4 this may be immediately verified: At constant path coordinate, bond lengths increase on substitution in the same order as the decrement in the activation energy for ring opening. In the reaction zone differences of more than 0.4 Å are found for this parameter while bond lengths in the transition states fall within the narrow range from 2.123 Å (Ref.) to 2.207 Å (1*d*/2*d*). This may be explained by the fact that MNDO does not allow for changes in orbital sizes. On the other hand this may indicate that an upper limit for a bonding interaction is reached under these conditions.

In the dihedral angle for the outer methylene substituents the effects are less marked. This is a result of the heterolytic fission discussed above: The cationic methylene fragments favor rehybridisation through a retardation of the conrotatory movement of the outer substituents. Effects of 20 degrees may be estimated in the reaction zones from structural data and the diagrams of Figs. 5–6.

Despite all mechanistic differences due to the electronic effects the following common features should be pointed out:

- (i) With increasing rates of ring opening, the path coordinates for the transition states are shifted to the reactant side. In effect this means that a bond length pattern similar to that of the reactant is retained.
- (ii) The transition states are in all cases non planar, the dihedral angles for the carbon skeleton ranging from 10 to 22 degrees. Small changes of this parameter are sufficient to guarantee an optimal orbital interaction of the atoms C3 and C4.

As a consequence of (i), decreasing amounts of resonance energy will be gained in the transition states (1*a*/2*a*–1*d*/2*d*) on forming the butadiene double bonds. Since the activation energy is reduced on substitution in the same order as the bond length is increased, the force constant of the fissile cyclobuten bond C3C4 seems to be uniformly reduced upon substitution. In summary, the commonly neglected electronic effects of substituents on electrocyclic processes should influence the reactions markedly.

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13. For simplicity, in NH<sub>3</sub><sup>+</sup> and NH<sub>2</sub> groups the individual H-bond lengths were kept equal because the same assumption was made along the synchronous transit paths [16]. A *gauche* conformation was chosen as starting geometry for the butadienes
16. Along the reaction paths for *1a-c/2a-c*, C<sub>2</sub>-symmetry was assumed. As noted earlier [14a, c], H-bond lengths were excluded from MINIMAX optimization since the automatic parabolic variation along the QST-paths is adequate. For NH<sub>2</sub> and NH<sub>3</sub><sup>+</sup> groups the individual H bonds within each group were kept equal
17. The structures were determined such that their path coordinates form approximately equal ratios with the corresponding values for the path *maxima*
18. For *2d* the MNDO-result was an almost planar conformation (Fig. 5) but corresponding to the reflected images of the other polyenes. Since we had decided to accept the result of each optimization run despite other possible molecular conformations, the corresponding transit paths were calculated counter-clockwise for *1d/2d*
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23. Since the corresponding disrotatory reactions are not yet calculated this is not discussed further here