

Where is the Limit to which the Qualitative Theory of Chemical Reactivity can be Extended? Study of Dienophilic Activity of Cyanoethylenes

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A qualitative quantum-chemical approach, based on the stabilization energy method, is applied to discuss the mechanism and some kinetic regularities observed in Diels-Alder (DA) reactions of cyanoethylenes with cyclopentadiene and phencyclone. For the former reaction series the polar effect predominates over the localization effect and both the regular activity sequence and the great range of the rate constants can be understood as a result of the charge transfer from diene to dienophile in a synchronous transition state (TS). The inversion of the regular activity sequence observed for the latter reaction series seems to be caused by localization effects in asynchronous TS. The relative weakening of the charge transfer is associated with the increased role of electron correlation. Possible distortions of the TS structure within a reaction series are analyzed. The shift of the TS along the anti-symmetric mode appears to be significant and should be taken into account when considering the kinetic data. The TS shift along the symmetric coordinate is negligible. The influence of the pre-reaction complex formation on DA reaction kinetics is found to be inconsequential for the reactions under consideration.

INTRODUCTION

The Diels-Alder (DA) reaction has been known for about fifty years, but the problem of its mechanism is still under discussion. The first mechanism suggested by Evans¹ considered the reaction as a synchronous concerted process. Later, Woodward and Katz² after studying some DA reactions concluded that the synchronous mechanism does not account for their regioselectivity, and therefore, proposed an alternative two-step biradical mechanism. The latter, however, is in poor agreement with the observed high stereoselectivity of DA reactions. That is why the synchronous mechanism is so widely accepted. Nevertheless, the problem could hardly be considered as solved³⁻⁸.

DISCUSSION

1. Potential Energy Surfaces for Diels-Alder Reactions

A number of semiempirical and *ab initio* calculations of the potential energy surface (PES) was reported for the simplest DA reaction, the cycloaddition of ethylene to butadiene⁹⁻¹⁸



The results of *ab initio* computations¹²⁻¹⁵ revealed different reaction paths on this PES, corresponding to the synchronous and asynchronous* mechanisms, the synchronous transition state (TS) being by ~ 4 kcal/mol more favourable than the asynchronous one (cf. Figure 1). Semiempirical calculations^{10,11} predicted an asynchronous TS, the synchronous one being discarded. On the calculated PES a symmetric ridge separating asymmetric valleys was observed

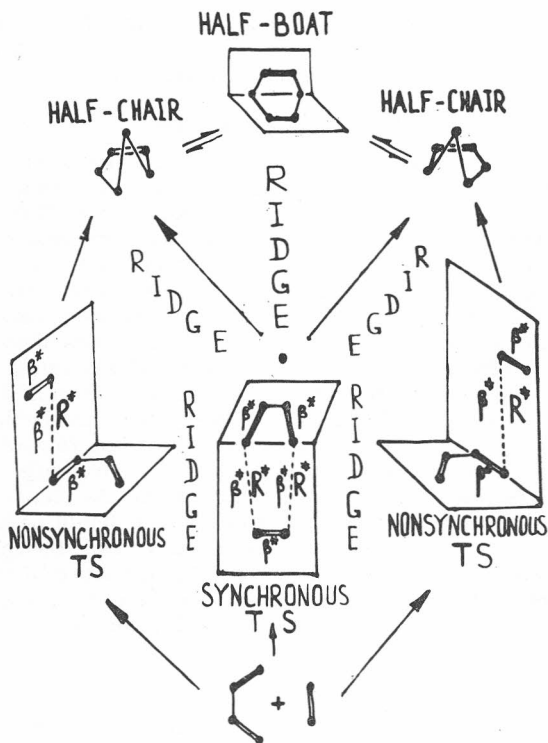


Figure 1. The principal scheme of a Diels-Alder reaction: Arrows stand for valleys on a potential energy surface; R_{\pm} represent the lengths of the bonds formed, β_{\pm} are corresponding resonance integrals of the bonds adjacent to the reaction center.

* Throughout the paper the terms *synchronous* and *asynchronous* are used in the following sense: *synchronous* means *one-stage concerted* (either symmetric or asymmetric), whereas *asynchronous* covers all other cases (both *concerted two-stage* and *nonconcerted two-step*). We did not distinguish between two-stage and two-step mechanisms because the stabilization energy method we followed did not allow such a distinction to be made.

in its place. This is due to the incorrect treatment of the intermolecular non-orthogonality effects in semiempirical methods based on the neglect of differential overlap (NDO) scheme¹⁷. A set of comparative computations¹⁹ showed that an asynchronous TS was invariably preferable only in the calculational methods using NDO approximation. Missing a valley corresponding to the synchronous mechanism seems to be the most serious defect of MINDO-type procedures.

Thus, the mechanism of DA reactions can be adequately treated only by a high-quality *ab initio* calculation involving very intensive geometry optimization (25 or even more internal degrees of freedom for the simplest reaction (1)). The situation is additionally complicated by the necessity of involving the electron correlation needed to describe the biradicaloid electronic structure of asynchronous TSs. That is why reaction (1) is the only DA reaction whose PES was calculated *ab initio*. A number of *ab initio* PESs is however available for the reactions related to 1,3-dipolar cycloaddition (cf. review²⁰ surveying 41 simplest reactions of this type). The computations indicate that a synchronous (although somewhat asymmetric for such asymmetric systems) TS is preferable in all cases. The same result was obtained in calculations using extended basis sets and partial configuration interaction (CI)^{21,22}. Recent computations involving complete CI in the framework of the second-order perturbation theory²² led to the opposite conclusion: asynchronous TS appeared energetically more favourable.

Whatever the case, the presence of two types of valleys and two types of TSs on the PES of the simplest reaction (1) can be considered as certainly established. This seems to be also true for the PESs of more intricate DA systems. However, there is still the question of which of the two TSs, synchronous or asynchronous, is more stable. Though the best recent calculation¹⁴ shows the symmetrical TS for reaction (1) to be more favourable, still, when passing to a more complicated case, one should not overlook the presence of the second valley on a PES. Introducing substituents in a diene or dienophile leads, in principle, to the following two effects. First, if the substituted system is asymmetrical, then the valley, completely symmetrical in an original non-substituted system, becomes more or less asymmetrical, corresponding to an asymmetrical synchronous mechanism. Second, even if substituents are introduced symmetrically, their introduction leads to lowering or rising the bottom of both synchronous and asynchronous biradicaloid valleys. And since the energies of the respective TSs in a nonsubstituted system are similar, a very delicate question arises which of the two TSs would be energetically more favourable in a substituted system. Generally, it is not impossible that all feasible mechanisms could be realized within a single reaction series: symmetric synchronous, asymmetric synchronous, and asynchronous biradical (or zwitter ionic, if the diene and dienophile differ significantly in their polarity).

Since high level *ab initio* calculations are hardly available for such complicated chemical systems, it is very desirable to have a simplified theory capable of providing information concerning the mechanism of DA reactions without a complete PES calculation. For this purpose the stabilization energy (SE) method^{1,23} seems appropriate. SE is defined as

$$SE = \left(\begin{array}{c} \text{energy of } \pi\text{-electrons} \\ \text{in a delocalized TS} \end{array} \right) - \left(\begin{array}{c} \text{energy of } \pi\text{-electrons} \\ \text{in initial reactants} \end{array} \right)$$

The efficiency of the SE method has been demonstrated for radical addition reactions²³. Moreover, both energetic and geometrical parameters of the TS of reaction (1), obtained in the SE calculation with additional consideration of nonorthogonality effects⁹, agree well with experimental data²⁴ and *ab initio* results¹²⁻¹⁶.

Therefore, there is hope of being able to discriminate the type of the TS structure in a DA reaction by comparing suitable experimental data with the results of SE calculations.

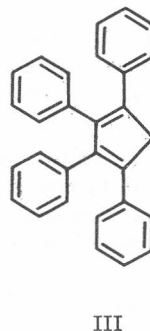
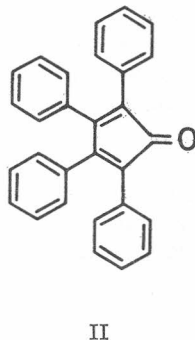
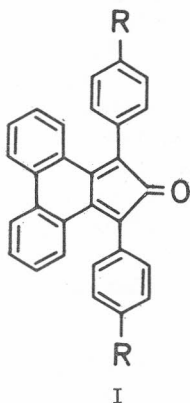
2. Kinetic Characteristics of Some Reaction Series of Cyanoethylenes

Kinetic data for the reaction series involving addition of cyanoethylenes (CNE) to cyclopentadiene (CPD) and 9,10-dimethylantracene²⁵ are listed in Table I (series A and B). These series stand out (cf. *e. g.* Refs. 26-29) in that they combine simplicity with completeness, and exhibit a wide range of reactivities. Therefore, they represent an excellent object for testing different theoretical models.

TABLE I
Rate Constants, k , and Activation Free Energies, ΔF^\ddagger , for CNE Cycloaddition to CPD (Series A) and 9,10-Dimethylantracene (Series B) in Dioxane at 20 °C²⁵

Dienophile	Series A		Series B	
	$10^6 \cdot k/l \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta F^\ddagger/\text{kcal mol}^{-1}$	$10^6 \cdot k/l \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta F^\ddagger/\text{kcal mol}^{-1}$
1 TCNE	430 000 000	-3.52	13 000 000 000	-5.49
2 3-CNE	4 830 000	-0.91	5 880 000	-1.03
3 DCNE	450 000	0.46	127 000	1.20
4 MDN	910	4.06	139	5.15
5 FDN	810	4.13	131	5.19
6 AN	10.4	6.66	0.89	8.08

There is a regular decrease of rate constants in the sequence: tetra-CNE (TCNE), tri-CNE (3-CNE), 1,1-di-CNE (DCNE), maleodinitrile (MDN), fumaro-dinitrile (FDN), acrylonitrile (AN). This, 'regular', dienophilic activity series was also observed for other hydrocarbon dienes^{5,26,30}. However, for polar dienes with electron-withdrawing substituents this is often not the case: the activity sequences are inverted as compared to the regular ones³¹⁻³⁴. The decisive role of electron-acceptor groups was demonstrated in comparative studies of the



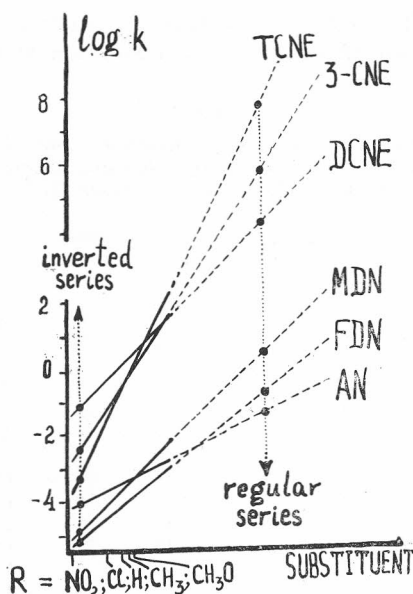


Figure 2. Dependence of the reactivities of phencyclones (structure I) on the donor-acceptor properties of substituent R. Solid lines represent experimental correlations³². Their extrapolation (dashed lines) shows the trend to restore the regular structure of the series with increasing the donor strength of a diene.

CNE cycloaddition to phencyclones I ($R = \text{NO}_2, \text{Cl}, \text{H}, \text{CH}_3, \text{CH}_3\text{O}$), tetracyclone II and tetraphenyl-CPD III^{32,33}. The first two series are inverted, whereas the last sequence is regular (like series A and B). Exhaustive studies of inverted sequences of substituted phencyclones I³² have revealed that the electron-acceptor strength of substituent R controls the qualitative structure of the activity sequence (cf. Figure 2). Table II presents a typical inverted series C: CNE + phencyclone (I; $R = \text{H}$).

TABLE II

Kinetic Parameters for CNE Cycloaddition to Phencyclone (Series C) in Dioxane at 25°C³¹

Dienophile	$10^6 \cdot k/1 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta F^\ddagger/\text{kcal mol}^{-1}$	$\log A$	$E_a/\text{kcal mol}^{-1}$
1 TCNE	1 531	4.45	5.7	12.2
2 3-CNE	12 500	2.59	5.0	9.4
3 DCNE	233 000	0.86	4.8	7.5
4 MDN	44	5.92	9.7	19.1
5 FDN	188	5.06	7.2	14.9
6 AN	301	4.78	7.5	15.0

A comparison of kinetic parameters for related reactions in different solutions^{25,30} shows that solvent effects can be neglected in the analysis, at least at a primary stage. There are some indications^{5,35-8} that the mechanism of these reactions is complicated by the association of the reactants into π -complexes. However, the results of our calculations, using the earlier re-

ported method³⁹, (cf. Table III) show that prereaction complexes under consideration are weak and therefore their formation should not influence the kinetics.

TABLE III

Intermolecular Distances, Equilibrium Constants, and Formation Energies for π -Complexes of Cyanoethylenes with Cyclopentadiene (Series A), Anthracene (Series B) and Phencyclone (Series C)^{a,b}

CNE	Series A			Series B			Series C		
	$r/\text{\AA}$	$10^3 \cdot K/1 \text{ mol}^{-1}$	$\Delta U/\text{kcal mol}^{-1}$	$r/\text{\AA}$	$10^3 \cdot K/1 \text{ mol}^{-1}$	$\Delta U/\text{kcal mol}^{-1}$	$r/\text{\AA}$	$10^3 \cdot K/1 \text{ mol}^{-1}$	$\Delta U/\text{kcal mol}^{-1}$
1 TCNE	3.63	6	2.4	3.38	89	4.9	3.47	18	3.8
2 3-CNE	3.52	2	2.7	3.42	29	4.2	3.47	3	3.3
3 DCNE	3.48	3	2.1	3.50	12	3.1	3.50	14	3.9
4 MDN	3.40	9	2.2	3.43	32	3.6	3.50	16	4.0
5 FDN	3.54	1	2.0	3.43	4	4.8	3.50	2	3.2
6 AN	3.63	1	1.6	3.50	3	2.6	3.50	3	2.9

^a Parameters $W_N = -16.3$ eV, $\beta_{CN} = -3.25$ eV ($R_{CN} = 1.16$ \AA) were used (cf. Appendix 1).

^b 25 °C.

Unfortunately, for the most interesting reaction series A and B the activation energies are unknown. We have used activation free energies $\Delta F^\ddagger = -RT \ln k$ as an experimental measure of reactivity, based on the experimental data for the related reaction series^{26,30}, which show that the preexponent factor only slightly varies within the series.

3. Quantum-Chemical Study of the Reaction of Cyanoethylenes. Preliminary Discussion

We attempted to treat the above reaction series in terms of a simple SE model at PPP-CI-3 \times 3, complete Hückel (HMO), perturbational Hückel (PMO) and frontier orbitals (FMO) levels. However, it appeared that the SEs, as calculated both by using HMO and taking into account π -electron interaction, were practically equal for all the reactions of series A. Typical results are listed in Tables IV and V. Still, one could try to make use of the minor changes in SEs. Then, the results of calculations become more surprising because, as seen from Table IV, in the sequence HMO-PMO-FMO only the last, the most primitive method, correctly reproduces the real tendency in reactivities of CNEs.

The possibility of such a disagreement between the predictions of PMO and FMO on the regioselectivity of DA reactions has already been emphasized⁴¹. The simple reason is that FMO in different cases gives different (and not always determining) relative contributions into PMO. The complete mismatch between the PMO and FMO predictions, as obtained here for series A, makes the applicability of FMO to chemical reactivity problems rather questionable.

TABLE IV

Estimation of the SEs (in β_0 Units^a) for the TSs of the Reaction Series A (HMO, PMO, and FMO Calculations^b)

Dienophile		Synchronous TS ^c			Asynchronous TS ^c	
		$\beta^\ddagger=0.8 \beta_0$	$\beta^\ddagger=1.0 \beta_0$		$\beta^\ddagger=1.5 \beta_0$	
			HMO	PMO	FMO	HMO
1	TCNE	1.03	1.51	1.18	0.25	1.18
2	3-CNE	1.04	1.52	1.17	0.23	1.25
3	DCNE	1.04	1.53	1.16	0.23	1.32
4, 5	MDN, FDN	1.05	1.54	1.17	0.19	1.14
6	AN	1.06	1.56	1.18	0.17	1.12

^a $\beta_0 \approx 1$ eV ≈ 23 kcal/mol is the standard Hückel thermochemical value of the resonance integral corresponding to the internuclear distance in benzene (1.4 Å).

^b HMO parameters from Ref. 40 were used.

^c β^\ddagger denotes resonance integrals of the bonds formed in TS (cf. Figure 1).

In nonperturbational treatment we computed SEs for series A with and without consideration of π -electron interaction. The length R^\ddagger of the bonds formed in synchronous or asynchronous TSs (cf. Figure 1) and respective resonance integrals β^\ddagger were widely varied, starting from the TS structures taken from the *ab initio* PES of standard reaction (1)¹⁴. The molecules of reactants were arranged one over another in parallel planes at a distance corresponding to a specified value of R^\ddagger . In the asynchronous TS the molecules were oriented so as to minimize the nonvalent interactions of reactants at a given R^\ddagger . The structure of reactants in TSs did not vary, as usually accepted in the standard practice of SE computations. We employed PPP parameters commonly used in reactivity calculations⁴².

Tables IV and V show that no computation was successful. We shall discuss below some possible origins on the failure in order to reveal the real causes governing the reactivity in the reactions considered.

4. The Validity Range of the Stabilization Energy Method

A discussion on the SE level is useful if a TS represents the delocalized 'quasi- π -electron system'²³. It means that resonance integrals β^\ddagger for the formed bonds should not greatly exceed in magnitude the intramolecular resonance integrals of π -bonds:

$$|\beta^\ddagger| \lesssim 2-3 \text{ eV} \quad (2)$$

If the absolute values of β^\ddagger are considerably higher, then essentially σ -bonded system is obtained which cannot be discussed in terms of the ' π -electron' ('quasi- π -electron') model.

When estimating β^\ddagger , one has to bear in mind possible changes in hybridization of AOs belonging to the reaction center⁹. These AOs are linear combinations of 2s and 2p AOs:

$$|\text{AO}\rangle = a|2s\rangle + \sqrt{1-a^2}|2p\rangle$$

$$0 \leq a \leq 0.5$$

The hybridization parameter, a , is zero for the planar geometry of the reaction center. It should be optimized in a consistent treatment. In present computations we varied its value more or less arbitrarily, on the basis of the experience of the complete PES calculation for reaction (1): ethylene + butadiene⁹.

In the synchronous TS of this simplest reaction the value of R^\ddagger is about 2.2–2.3 Å^{12–14,16}. With proper hybridization taken into account, according to (7), we obtain $\beta^\ddagger \approx -2$ eV for $R^\ddagger = 2.3$ Å ($a \approx 0.2$) and $\beta^\ddagger \approx -2.5$ eV for $R^\ddagger = 2.2$ Å ($a \approx 0.3$). The reactions under consideration proceed more rapidly than reaction (1), so one might anticipate (in accordance with the Hammond postulate) that β^\ddagger should not exceed estimate (2). This reasoning justifies the application of the SE method to the synchronous TSs of the considered systems.

For the asynchronous TS of reaction (1) $R^\ddagger \approx 2$ Å¹⁴. At this distance $|\beta^\ddagger| \sim 3\text{--}4$ eV, depending on hybridization ($a \sim 0.3\text{--}0.4$). We suppose that qualitative estimations of the SE theory are valid in this case as well, although high values of a restrict the range of their reliability.

The PES calculations for reaction (1) have shown that the initial structure of reactants is strongly distorted in the TS. The bonds adjacent to the reaction center are changed most. When the TS is formed, the possibility of conjugation through these bonds is decreased. This is manifested as a decrease (in absolute values) of the respective resonance integrals β^* (cf. Figure 1). The following three factors diminishing $|\beta^*|$ should be mentioned:

- Respective C—C bonds may be stretched from 1.34 Å to 1.5 Å.
- The variation of hybridization decreases the contribution of 2p AO in hybrid AO. In extreme cases, the weight of 2p AO falls from 1 ($a = 0$) to $\sqrt{3}/2$ ($a = 0.5$).
- The angle between hybrid AO and other AOs of the π -system increases, deflecting from its optimal value of 0°. Its maximal value is 19° 30' for tetrahedral hybridization ($a = 0.5$).

The lowering of $|\beta^*|$ originating from all these three factors can reach 40% (at $a = 0.5$). These changes should be especially important for a dienophile in a synchronous TS, since both AOs forming the same intramolecular π -bond alter simultaneously. In this case, $|\beta^*|$ may drop to 50% of its initial value, β_0^* , in reactants.

A consistent consideration of the β^* changes requires again some variational calculations of hybridization in the TS. We did not carry out such calculations, assuming that the corresponding changes are the same for all TSs of a reaction series. A comparison with experimental data allows us to check the validity of this assumption.

5. Preliminary SE Calculations: Comparison with the Experiment

SE calculations for reaction series with hydrocarbon dienes described in Section 3 are compared with the experiment in Table V. In discussing them, it is convenient to distinguish the following three substituent effects.

Effect of extension of the conjugated system. — It operates *e. g.* when passing from AN to DCNE.

Localization effect. — This effect is typical of the asynchronous TSs and is less perceptible in synchronous TSs. It is due to the addition to the terminal (primary) AO of a conjugated system being energetically preferable to an

TABLE V
Relative SE Values for the Reaction Series A (Preliminary Calculations)

Dienophile	SE/kcal mol ⁻¹ Asynchronous TS		$\Delta \Delta F^\ddagger$ ^a kcal mol ⁻¹	SE/kcal mol ⁻¹ Synchronous TS	
	HMO ^b	PPP+CI-3×3 ^c		HMO ^d	PPP+CI-3×3 ^e
1 TCNE	-1.38	+0.25	-10.18	+1.15	-1.20
2 3-CNE	-2.99	-0.28	-7.57	+0.91	-1.10
3 DCNE	-4.60	-1.45	-6.20	+0.69	-0.35
4 MDN	-0.46	+1.15	-2.60	+0.45	-0.97
5 FDN	-0.46	+1.24	-2.53	+0.45	-0.76
6 AN	0	0	0	0	0

^a Differences of experimental activation free energies taken from Table I.

^b $\beta^\ddagger = 1.5 \beta_0$.

^c $R^\ddagger = 2.0 \text{ \AA}$; $\beta^\ddagger = -3.73 \text{ eV}$.

^d $\beta^\ddagger = 1.0 \beta_0$.

^e $R^\ddagger = 2.2 \text{ \AA}$; $\beta^\ddagger = -2.23 \text{ eV}$.

inner (secondary or tertiary) AO. The introduction of a conjugated substituent converts a primary AO of a reaction center into a secondary one, and the introduction of two substituents makes it tertiary. The localization effect in an asynchronous TS suppresses considerably the reactivity of dienophile, as seen from the comparison of FDN and MDN with AN and DCNE. The nature of the effect can be easily comprehended by considering a complete localization of a π -electron at a reaction center AO. The localization of a σ -bond cuts off from the conjugated system one, two or three conjugated fragments in the case of a primary, secondary or tertiary AO, respectively. This effect, as well as the effect of extension of the conjugated system, is well known from the SE and localization energy computations for the radical addition reactions^{21,43,44}. Both effects can be easily deduced in a general way from the Hückel SE⁴⁵.

The importance of the localization effects in the DA reactions considered here was emphasized³²⁻³⁴. It was found that two-parametrical correlations of the rate constants with both $(IP-EA)^{-1}$ * and localization energies provide a better description of experimental reaction sets than one-parametrical correlations with only $(IP-EA)^{-1}$ (the latter reproduce only the polar effect).

Polar effect. — It is mainly caused by the charge transfer from diene to dienophile and consists in that the TS becomes more stabilized as the number of electron-withdrawing substituents increases in dienophile. In a pure form this effect may be seen in the FMO computations for synchronous TSs (Table IV). At the complete HMO level it is masked by the localization effect. When passing to PPP the relative role of the polar effect increases. Nevertheless, the localization effect is so great in an asynchronous TS that the sequence of the calculated SEs is opposite to the polarity sequence of dienophiles. For synchronous TSs the SE sequence agrees more or less with dienophile polarities.

Experimental rate constants in the reaction series A and B behave as if the reactivity of dienophiles were determined by the polar effect. One might conclude that this fact suggests a synchronous TS. However, this is merely an

* IP and EA mean ionization potential and electron affinity, respectively.

illusion: SEs of synchronous TSs range over only 1.2 kcal/mol (from AN to TCNE), whereas the experimental activation free energies vary within 10 kcal/mol. So wide range of activation free energies represents a special effect, no less important and interesting than traditional reactivity sequences. It should be explained by any theory claiming to interpret the regularities of reactivity in series A and B. The HMO and preliminary PPP (cf. Tables IV and V) calculations which give such a small range of SE variations are completely inadequate on this point.

At first sight, the SE variation range could be extended by increasing the interactions in a TS by increasing $|\beta^\ddagger|$. It is really the case for the asynchronous TS with its incorrect activity sequence. For the synchronous TS, an increase of $|\beta^\ddagger|$ results in a very little extension of the SE range. Therefore, although unsuccessful, the results presented in Table V appear optimal for the given PPP parametrization and given TS model.

6. Reparametrization of PPP Method and Variation of the Reactant Structure in TS

In the above computations the degree of the charge transfer in a TS was underestimated. Two ways of eliminating this drawback are considered below.

Reparametrization of the PPP method. — In order to be convincing, the reparametrization should be motivated not only by the explanation of the effect considered. An additional evidence should be provided by comparing some independent experimental data with the results of computations using new parameters.

Until recently the canonical PPP parametrization⁴⁶ has been in common use. We have found this parametrization to be invalid for the description of ionization potentials and electron affinities of CNEs. To correct it we lowered the conventional energy value for 2p AO of N-atom in CN-group: $W_N = -14.12$ eV^{42,46} was substituted by $W_N = -16.3$ eV. It resulted in an increase of the effective electronegativity of CN-groups. The resonance integral $\beta_{CN} = -3.25$ eV ($R_{CN} = 1.16$ Å)⁴⁷ was used instead of $\beta_{CN} = -2.85$ eV ($R_{CN} = 1.2$) Å⁴², since it better reproduced experimental energies of the lowest singlet transitions. The conventional values⁴² of other parameters were kept. As a result, we were able to reproduce satisfactorily the relative values of experimental ionization potentials of CNEs with respect to those of cis-butadiene (the model for CPD in the PPP calculations), as well as the relative values of experimental electron affinities of CNEs with respect to nonsubstituted ethylene (cf. Appendix 1). The computed energies of the lowest singlet transitions of CNEs agree well with spectral data.

Variation of resonance integrals β^ of C—C bonds adjacent to the reaction center.* — The increase of the charge transfer due to parametrical increase of the electronegativity of electron-withdrawing groups is an obvious result. The fact that charge transfer is sensitive to resonance integrals β^* (for their characteristics see Section 4) is much more unexpected. But just the variation of β^* within reasonable limits allowed us to extend significantly the SE range in the reaction series A and to obtain a correct sequence of dienophilic activities (cf. Section 7).

Let us discuss why the β^* variation influences the charge transfer so markedly. This is easy to understand for an asynchronous TS if one uses a valence

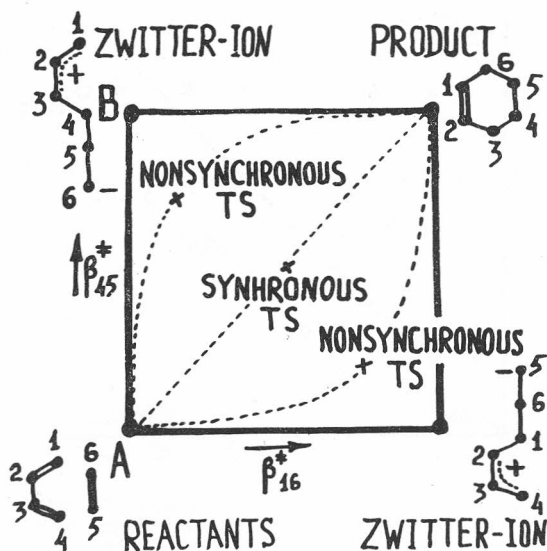


Figure 3. Scheme of cycloaddition of electron-acceptor dienophile to electron-donor diene (substituents are not shown).

bond instead of MO treatment and considers the electronic structure of a TS as a superposition of covalent and ionic structures. The state of separated reactants (point A in Figure 3) corresponds to a purely covalent structure. Point B in Figure 3 represents a purely ionic structure (one electron is transferred from the diene to the dienophile, forming a zwitter ion), which can be obtained if one of the new bonds of a TS is completely formed, whereas the formation of the other has not yet started. The charge transfer in a TS can be facilitated by increasing the weight of the ionic structure, *i.e.* by shifting the TS closer to point B. It could be attained by the following two mechanisms: either by increasing $|\beta^{\ddagger}|$, or by decreasing $|\beta^*|$. The first mechanism appears inefficient, because the description of a TS using a limited number of structures is imperfect. The ionic and covalent structures strongly interact, and the intensity of their interaction is proportional to $|\beta^{\ddagger}|$. Increasing $|\beta^{\ddagger}|$ shifts the TS structure towards B, but it diminishes the validity of its description in terms of only two structures. By increasing the electron delocalization, the role of the ignored structures with the back charge transfer is increased. On the other hand, decreasing $|\beta^*|$ allows one to decrease the electron delocalization in a TS. Thus, only the two-parametric description of a TS in terms of both β^{\ddagger} and β^* appears to be sufficiently versatile to bring the electronic structure of a delocalized TS closer to the localized zwitter ionic structure B.

7. SE Calculations: Regular Activity Sequences (Series A)

The most representative results of the new calculations for the reactions of CNEs with CPD are presented in Figure 4. Parameters β^{\ddagger} and β^* were varied over a wide (but reasonable) range so as to provide a closer fit to the exper-

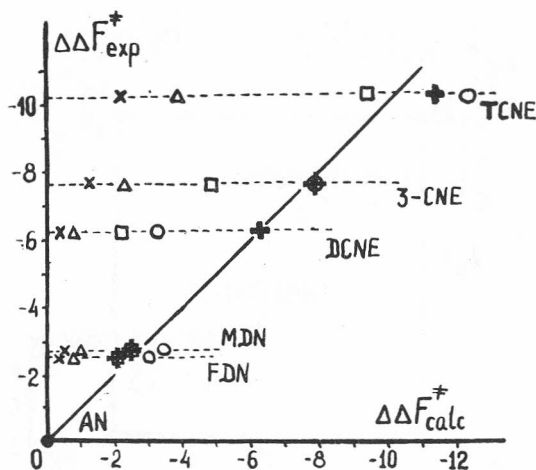


Figure 4. Relative activation free energies (calculated vs. experimental; kcal/mol) in the DA series of cyclopentadiene with cyanoethylenes (AN is taken as a zero reference point): x — synchronous TS ($R^\ddagger = 2.2$ Å, $\beta^\ddagger = -1.39$ eV, $\beta^*/\beta_0^* = 1.0$); Δ — synchronous TS ($R^\ddagger = 2.2$ Å, $\beta^\ddagger = -2.23$ eV, $\beta^*/\beta_0^* = 0.6$); \circ — synchronous TS ($R^\ddagger = 2.2$ Å, $\beta^\ddagger = -2.23$ eV, $\beta^*/\beta_0^* = 0.6$ + TS geometry correction); $+$ — synchronous TS ($R^\ddagger = 2.2$ Å, $\beta^\ddagger = -2.23$ eV, $\beta^*/\beta_0^* = 0.6$ + TS geometry correction); \square — asynchronous TS ($R^\ddagger = 2.0$ Å, $\beta^\ddagger = -3.73$ eV, $\beta^*/\beta_0^* = 0.6$). Diagonal solid line represents the ideal correlation (*i. e.* identity). Horizontal dashed lines represent experimental activation free energy levels.

perimental data. As seen, single reparametrization of the PPP method appears insufficient: a considerable reduction of β^* is required.

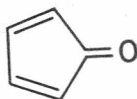
Correct activity sequences and the range of the activation free energy variations were reproduced both for synchronous (Figure 4 — circles) and asynchronous (Figure 4 — squares) TS models. Nevertheless, even the best SE results do not provide sufficiently good correlation with the experiment. The points most deviating from the ideal correlation (solid line in Figure 4) are 3-CNE (asynchronous model) and DCNE (both synchronous and asynchronous models). We supposed that the main principle of the SE method implying exactly the same TS geometry for all reactions of a series is too restrictive. Actually, the explicit consideration of possible distortions of symmetric configuration for a synchronous TS in the case of asymmetrically substituted dienophiles, 3-CNE, DCNE and AN, (see Appendix 2 for details) allows one to improve substantially the quality of the correlation. The slope of the correlation line for the whole synchronous set is close to the ideal value of 1. Similar corrections of the TS geometry are negligible in the asynchronous TS (*cf.* Appendix 2).

Thus, the results for the synchronous TS model provide a considerably better fit to the experimental data. The asynchronous mechanism, however, cannot be completely rejected. As seen from Figure 4, the results for the asynchronous model fall on two straight lines: AN-FDN-MDN and DCNE-3-CNE-TCNE. It is not unlikely that reaction series A consists of two subseries with different reaction mechanisms — synchronous (AN, FDN, MDN) and

asynchronous (DCNE, 3-CNE, TCNE). Nevertheless, the hypothesis of a single synchronous mechanism seems more attractive since it allows us to reproduce the kinetic data with minimal assumptions. In addition, the constancy of the observed preexponent factors³⁰ indicates indirectly that the reaction mechanism is likely to be unique.

8. SE Calculations: Inverted Activity Sequences (Series C)

The above computations indicate that the main factor determining the qualitative structure of the regular dienophilic sequences for hydrocarbon dienes (e. g. series A and B) is the polar effect predominating over the localization effect. The introduction of electron-withdrawing groups in a diene suppresses this polar effect, which may result in the inversion of the regular series. The experiment (Refs. 32—34; cf. discussion in Section 2 and Figure 2) points to the clear correlation between the electron-acceptor strength of a diene and the degree of inversion of activity sequences: even dienes as similar in their structure as II and III (cf. page 1426) generate totally distinct sequences. The carbonyl oxygen distinguishing II from III operates far stronger than a large system of π -electron substituents distinguishing tetraphenyl-CPD III from nonsubstituted CPD. Taking this into account, we replaced phencyclone I by



IV

simplified model structure IV (cyclopentadienone) when studying the inverted series C.

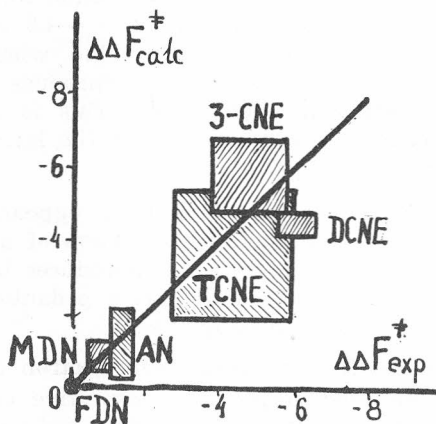


Figure 5. Relative activation free energies (calculated vs. experimental; kcal/mol) in the DA series of phencyclones I (cyclopentadienone IV was used as model structure in computations) with cyanoethylenes. FDN is taken as zero reference point. Shaded rectangles represent the uncertainty limits, the vertical bounds coming from the experimental data on variously substituted phencyclone series [32], the horizontal bounds being the results of computations for asynchronous TSs with different structures ($\beta^{\ddagger} = -3.7$ and -4.8 eV, respectively; $\beta^{\ddagger}/\beta_0^{\ddagger} = 0.6$). Diagonal solid line represents the ideal correlation.

The results of computations presented in Figure 5 for the asynchronous TS model correlate satisfactorily with the experiment, reproducing both the range of the activation free energy variation and the qualitative structure of the inverted series C. The synchronous TS is a poor model (cf. Table VI).

TABLE VI
Relative Experimental and Calculated Activation Free Energies for the C-Type Reaction Series

Dienophile	$\Delta F^\ddagger/\text{kcal mol}^{-1}$					
	Experiment ^{a, 32}			Calculation		
	R = CH ₃ O	H	NO ₂	Asynchronous TS		Synchro- nous TS ^d
			Earlier ^b	Later ^c		
1 TCNE	-5.31	-4.63	-2.72	-5.36	-1.77	-3.75
2 3-CNE	-5.68	-4.95	-3.69	-6.74	-4.92	-0.46
3 DCNE	-6.43	-5.91	-5.63	-4.12	-4.83	+1.33
4 MDN	-0.96	-0.78	-0.34	-0.69	-0.46	-1.24
5 FDN	0	0	0	0	0	0
6 AN	-0.96	-1.12	-1.63	-0.23	-2.14	+0.94

^a Structure I, page 1426.

^b $R^\ddagger = 2.0 \text{ \AA}$; $\beta^\ddagger = -3.73 \text{ eV}$; $\beta^*/\beta_0^* = 0.6$.

^c $R^\ddagger = 1.7 \text{ \AA}$; $\beta^\ddagger = -4.80 \text{ eV}$; $\beta^*/\beta_0^* = 0.6$.

^d $R^\ddagger = 2.2 \text{ \AA}$; $\beta^\ddagger = -2.23 \text{ eV}$; $\beta^*/\beta_0^* = 0.6$.

It is also seen from Table VI that the calculation for the later (and consequently more localized) TS ($R^\ddagger = 1.7 \text{ \AA}$, $\beta^\ddagger = -4.8 \text{ eV}$) is closer to the experimental data on nitro-substituted phenylcyclohexene, whereas the results for the earlier TS ($R^\ddagger = 2.0 \text{ \AA}$, $\beta^\ddagger = -3.7 \text{ eV}$) reproduce better the activity sequence of methoxy-substituted phenylcyclohexene. This is in accord with the Hammond postulate because the condensation of the latter diene with CNEs proceeds more rapidly³².

Thus, both the experiment and calculations appeared sensitive to the particular structure of diene and to the parameters of a TS. This indicates, on the one hand, that the model in general reproduces the main features of the phenomenon and, on the other hand, that a pedantic adjustment of the calculations to the experiment is unreasonable.

It should be mentioned in conclusion that electron correlation plays an important role in the inverted series. The respective contributions to SEs of asynchronous TSs ($\sim 0.5\text{--}1 \text{ eV}$) are especially important in the case of inactive dienophiles FDN, MDN, AN. This considerably narrows the range of the reactivity variations in inverted series, as compared to the regular ones (the calculated effect due to electron correlation attains 4–8 kcal/mol depending on the value of β^\ddagger ; the experiment predicts a narrowing of the range of the activation free energies by 4–7 kcal/mol when passing from series A and B²⁵ to C-type series³²).

To clarify the specific role of CI, we are continuing the qualitative discussion of the charge transfer presented in Section 6. Consider a hypothetical limiting case of complete localization of the diene and dienophile fragments ($|\beta^\ddagger|$ is large, $\beta^* = 0$). Both fragments involve an odd number of π -AOs. The arrangement of the frontier MOs is altered as compared to their initial arrangement in reactants: now HOMO belongs to dienophile and LUMO is localized on diene. In the case of a negligible interaction between the fragments, the electron pair is transferred from diene to dienophile providing the regular Hartree-Fock (HF) occupation of the electron levels of the considered system. It is convenient to use the double-charged zwitter ion thus obtained as a reference system when considering the charge transfer in some weak (but finite) coupling between the fragments. This coupling partially returns the charge back from the dienophile to diene, and therefore the system becomes more or less biradicaloid. At small $|\beta^*|$ this back electron transfer is almost completely caused by electron correlation. However, the role of CI readily decreases as the coupling increases. The boundary, at which the correlation mechanism of the back charge transfer is replaced by HF mechanism, appears sharp and depends strongly on the structure of fragments, primarily on the mutual arrangement of the frontier MOs. In its main features this effect is similar to the well known sudden polarization phenomenon^{48,49}. Conditions of its occurrence are discussed in Appendix 3.

CONCLUSION

The SE calculations reproduced the experimental sequences of the dienophilic activity of CNEs in the diene condensation with CPD (reaction series A) and phencyclone (reaction series C), and gave a satisfactory estimation of the activation free energy variations in these reaction sets. More or less unambiguously the computation results indicate that regular and inverted series are characterized, respectively, by synchronous and asynchronous TSs. This conclusion is in agreement with the experimental observation that the 'cis-principle' can be violated in DA reactions of acceptor dienes^{5,50-53}, whereas it strictly obeys for donor dienes^{5,54,55}.

Our computations became successful only after some additional corrections were introduced into the traditional SE scheme. Firstly, the consideration of late asynchronous TSs required an explicit treatment of electron correlation determining, under certain conditions (cf. Appendix 3), the degree of charge transfer in such systems. Secondly, the modification of the resonance parameters β^\ddagger and β^* imitated the variation and optimization of the TS geometry in PES calculations. The structure of reactants is distorted in TSs of DA reactions so drastically that it appears impossible to explain experimental kinetic regularities without explicit consideration of the respective changes. Moreover, these changes should be varied for different members of synchronous series. Our estimation of the structure variations is valid only if they are small, since the procedure applied⁵⁶ is practically nothing more than the first iteration of the Newton-Raphson extremum search method⁵⁷ (cf. also discussion in Ref. 56). However, it is quite sufficient to predict whether the variation is essential or not. We can certainly state that the TS shift along the reaction coordinate is negligible for all reaction series under consideration (as in the case of radical addition reactions²³). The result that the only considerable

distortion of TS geometry is the twist of symmetrical configuration of a synchronous TS in the case of asymmetric reactants is due to the fact that force constants of antisymmetrical modes are, as a rule, notably lower in absolute values than those of symmetrical modes. (In the radical hydrogen abstraction reactions, where the reaction coordinate embodied an antisymmetrical mode, distortions of the TS structure along this mode were also considerable⁵⁶.)

The reported tentative calculations cannot, of course, replace complete PES calculations. However, as long as PES computations are unavailable, simple SE calculations in combination with experimental kinetic data provide some useful preliminary information on a TS structure and different factors determining its variations. A necessary comment is: in order to become a source of useful information, the SE computations should be perfected. Being carried out at a level lower than a certain standard (different for different reactions), these computations give only illusion of an explanation. With these precautions and reservations the SE method retains its importance as a practical tool for the theoretical study of chemical reactivity.

APPENDIX 1. THE PPP+CI-3×3 CALCULATIONS

In the PPP calculations of molecules containing CN-groups, the value of $W_N = -14.12$ eV for the energy of $2p$ AO of N-atom in CN-group is usually adopted^{42,46}. As for β_{CN} , different authors recommend different values varying from -2.675 to -4.75 eV. We accepted the value $\beta_{CN} = -3.25$ eV which gives a good correlation between the computed experimental spectral characteristics of CNEs⁴⁷ (cf. Table VII).

TABLE VII

Ionization Potentials (IP), Electron Affinities (EA) and Energies of the Lowest Singlet Transitions for CNE Series

CNE	$IP_{CNE} - IP_{\text{butadiene}}$ eV				$EA_{CNE} - EA_{\text{ethylene}}$ eV				$S_0 \rightarrow S_1$ Transition energy eV			
	Experiment		Calculation		Experiment		Calculation		Exp.		Calculation	
	Ref. 58	Ref. 59	a	b	Ref. 58	Ref. 59	a	b	Ref. 47	Ref. 47	a	b
TCNE	2.97	3.09	1.18	3.17	5.04	4.18	4.09	5.31	5.02	4.61	4.27	4.76
3-CNE	—	2.85	1.18	2.87	—	3.40 ^c	3.48	4.45	—	5.02	4.65	5.02
DCNE	—	2.68	1.22	2.51	—	2.84 ^c	2.56	3.21	—	5.87	5.48	5.80
MDN	—	2.45	1.13	2.44	—	2.08	2.80	3.48	5.63	5.38	4.90	5.41
FDN	2.46	2.45	1.15	2.48	2.95	2.08	2.83	3.53	5.63	5.45	4.87	5.20
AN	2.21	2.22	1.16	1.96	—	1.32 ^c	1.76	2.12	6.42	6.24	5.77	6.02

^a Parameters $W_N = -14.12$ eV, $\beta_{CN} = -2.85$ eV ($R_{CN} = 1.20$ Å) were used.

^b Parameters $W_N = -16.3$ eV, $\beta_{CN} = -3.25$ eV ($R_{CN} = 1.16$ Å) were used.

^c Extrapolation.

The calculation of the relative values of ionization potentials of CNEs with respect to those of cis-butadiene with $W_N = -14.12$ eV indicated that this parameterization gave rather poor agreement with experimental data (cf. Table VII). This led to underestimation of the polar effect in the CNE reaction series. In final computations the value $W_N = -16.3$ eV was used, giving better fit to experimental ionization potentials and electron affinities (cf. Table VII). Energies of the lowest singlet transitions computed with $W_N = -16.3$ eV agree well with experimental data.

Other atomic and bond parameters were taken from Ref. 42. The SE calculations described in the main text were carried out by a standard technique. As in the PES computations for reaction ethylene + butadiene⁹, reacting systems were treated as supermolecules in which all intermolecular resonance integrals, except for β^\ddagger , were assumed to be zero. Electron correlation was treated by means of the regular CI-3×3 procedure, taking into account HOMO→LUMO transitions.

APPENDIX 2. VARIATION OF THE TS GEOMETRY IN A REACTION SERIES

A study of the TS geometry variation in the reaction series of radical hydrogen abstraction reactions provided an explanation of some observed kinetic regularities⁵⁶. In this connection it is reasonable to perform a similar analysis in order to estimate possible variations of TS structure within series A and C and their influence on the calculated activation energies.

Let us choose some reaction of the series as a standard. In the vicinity of its TS (with $\beta^\ddagger = \beta_0^\ddagger$), the interaction energy of reactants, E_0 , can be presented as

$$E_0(\Delta\beta) = E_0^\ddagger + \frac{1}{2} \kappa [\Delta\beta]^2 \quad (3)$$

where $E_0^\ddagger = E(\Delta\beta = 0)$ is the activation energy of the standard reaction, κ is the force constant, and $\Delta\beta$ is a parameter describing variations of the TS structure. This parameter will be specified below.

Within the limits of the SE method (cf. Section 4) the difference between the interaction energy of reactants for some reaction, $E(\Delta\beta)$, and the quantity $E_0(\Delta\beta)$ will be described by the difference of the respective SEs:

$$E(\Delta\beta) - E_0(\Delta\beta) = SE(\Delta\beta) - SE_0(\Delta\beta)$$

$$E(\Delta\beta) = SE(\Delta\beta) - SE_0(\Delta\beta) + E_0^\ddagger + \frac{1}{2} \kappa [\Delta\beta]^2 \quad (4)$$

Expansion of the SE in the Taylor series to second order in parameter $\Delta\beta$ gives

$$SE(\Delta\beta) = SE^\ddagger + l \cdot \Delta\beta + \lambda \cdot [\Delta\beta]^2 \quad (5)$$

where $SE^\ddagger = SE(\Delta\beta = 0)$, and l and λ are some coefficients expressed in terms of corresponding bond orders and polarizabilities (see below). We search for an extremum of quantity (4), and use the stationary condition. The result is

$$\Delta\beta^\ddagger = -\frac{\Delta l}{\kappa + 2\Delta\lambda}$$

$$E^\ddagger = E_0^\ddagger + SE^\ddagger - \frac{1}{2} \frac{[\Delta l]^2}{\kappa + 2\Delta\lambda} = E_0^\ddagger + \Delta SE^\ddagger + \frac{1}{2} \Delta l \cdot \Delta\beta^\ddagger \quad (6)$$

Here $E^\ddagger = E(\Delta\beta^\ddagger)$ is the activation energy of the considered reaction, $\Delta\beta^\ddagger$ is the parameter describing the difference between TS structures of a discussed and standard reactions, $\Delta SE^\ddagger = SE^\ddagger - SE_0^\ddagger$, $\Delta l = l - l_0$ and $\Delta\lambda = \lambda - \lambda_0$ represent differences of respective coefficients entering the series (5).

The following three specific cases should be considered:

All TSs of a reaction series are symmetric synchronous. — In this case both bonds formed have equal parameters $\beta_{ir'} = \beta_{ss'}$, and it is natural to stand for $\Delta\beta$

the quantity $\Delta\beta = \beta_{rr'} - \beta_{0\ddagger}$ (here $\beta_{0\ddagger}$ is the value of the resonance integral in the TS of the standard reaction). For Δl and $\Delta\lambda$ we get

$$\Delta l = 2 \sum_{rr'} (p_{rr'} - p_{rr'}^0); \quad \Delta\lambda = \sum_{rr', ss'} (\pi_{rr', ss'} - \pi_{rr', ss'}^0)$$

where $p_{rr'}$ and $\pi_{rr', ss'}$ are bond orders and polarizabilities (the SCF ones in the case of PPP calculations), and superscript '0' indicates the standard reaction.

In estimating the force constant κ of the symmetric mode (negative), the corresponding value for reaction (1) was used. According to Ref. 9 it is about -10 eV^{-1} . Our calculations show that $\Delta\lambda \sim 10^{-1} - 10^{-2} \text{ eV}^{-1}$ and $\Delta l \sim 10^{-2} - 10^{-3}$. Therefore, both $\Delta\beta\ddagger$ and respective correction to $\Delta SE\ddagger$ in (6) appear negligible.

All TSs of a reaction series are synchronous, but not necessarily symmetric. — As shown above, the TS shift along the symmetric coordinate appears negligible. So one can choose $\frac{1}{2}(\beta_{rr'} - \beta_{ss'})$ as $\Delta\beta$. In this case the force constant κ (positive) is about $0.1 - 1 \text{ eV}^{-1}$. As in the preceding case, the quantity $\Delta\lambda = \sum_{rr', ss'} (\pi_{rr', rr'} - \pi_{rr', ss'} - \pi_{rr', rr'}^0 + \pi_{rr', ss'}^0) \approx 10^{-2} - 10^{-3} \text{ eV}^{-1}$ can be neglected, but $\Delta p = p_{rr'} - p_{ss'}$ for asymmetric CNEs is about 0.1. If one takes for κ the lowest limit $\kappa \approx 0.1 \text{ eV}^{-1}$, then $|\Delta\beta\ddagger|$ will be about 1 eV and $\frac{1}{2}\Delta l \cdot \Delta\beta\ddagger \approx 1 \text{ kcal/mol}$. Respective corrections for asymmetric dienophiles are: 3.9 kcal/mol for DCNE, 1.0 kcal/mol for 3-CNE and 0.9 kcal/mol for AN. In the case of DCNE $\Delta\beta\ddagger = -1.8 \text{ eV}$. That is to say, one of the bonds formed is strengthened to $\beta_{rr'} \approx -4.3 \text{ eV}$, whereas another is weakened to $\beta_{ss'} \approx -0.7 \text{ eV}$. The TS of such a structure should be classified as asynchronous rather than asymmetric synchronous. At so great geometry distortion both the harmonic approximation (3) and the expansion (5) become invalid. Nevertheless, even in the case of DCNE it is useful to make this crude estimation, since it shows that the twist of the symmetric configuration of a synchronous TS may represent an important factor lowering its energy.

All TSs of a reaction series are asynchronous. — As in the first case, we stand for $\Delta\beta$ the quantity $\Delta\beta = \beta_{rr'} - \beta_{0\ddagger}$. For Δl and $\Delta\lambda$ we get: $\Delta l = 2(p_{rr'} - p_{rr'}^0)$ and $\Delta\lambda = \pi_{rr', rr'} - \pi_{rr', rr'}^0$. The force constant κ (negative) should be of the same order as in the case of symmetric synchronous TSs, i. e. $\kappa \approx -10 \text{ eV}^{-1}$. That is why, although $\Delta l \sim 10^{-1}$, the shift of a TS along the reaction coordinate is negligible, like in the first case.

Thus, the analysis of three most probable directions of the distortion of the TS structure shows that the SE method is fit for describing DA reactions with asynchronous or symmetric synchronous TSs. However, some caution is needed when it is applied to treat the series with synchronous TSs, including both symmetric and asymmetric reaction systems because of possible structure distortions of some TSs with respect to the antisymmetrical coordinate.

APPENDIX 3. CORRELATION-INDUCED CHARGE TRANSFER

Electron correlation effects are rather weak in synchronous TSs of DA reactions of CNEs with hydrocarbon dienes. They become, however, considerable for asynchronous TSs, which reveals their partially biradicaloid nature. The contribution of the correlation energy to SE usually increases monotonously as an asynchronous TS shifts along the reaction coordinate towards the intermediate (or quasi-intermediate) product of primary addition involving single bond formation. This effect is especially pronounced in the case of electron-acceptor dienes where a sharp increase of correlation energy was observed in the late asynchronous TSs. This effect was quite sensitive to the structure of a diene-dienophile system. The similar structure-dependent strong correlation effect was first discussed for cis-trans isomerisation of conjugated systems (sudden polarization^{48,49}). The effect of the same origin seems to occur at the initial stage of some electrophilic substitution reactions⁶⁰. In all the cases, a strong charge transfer (direct or back) takes place. The qualitative treatment of these effects is presented below.

Consider a conjugated system consisting of two fragments. For sudden polarization to occur, it is necessary for the two fragments to be *weakly* coupled:

$$g = \left| \frac{h\ddagger}{\Delta \varepsilon_0} \right| \ll 1 \quad (7)$$

Here $h\ddagger$ is the matrix element of one-particle (HF) interaction between completely localized MOs of the fragments. The denominator $\Delta \varepsilon_0 = \varepsilon_{\text{HOMO}}^{(0)} - \varepsilon_{\text{LUMO}}^{(0)}$ represents the difference of the respective MO energies of isolated fragments.

Condition (12) provides a strong localization of MOs of the combined system on separate fragments, the frontier MOs (HOMO and LUMO) being localized on different fragments. Two particular cases, depending on where these MOs are localized, are illustrated by Figure 6.

The effect considered arises due to the delocalization of electrons promoted by CI in a weakly coupled system (condition (7) obeys) with localized MOs. The CI contribution is determined by the dimensionless parameter G ,

$$G = \left| \frac{V\ddagger}{\Delta E} \right| \quad (8)$$

$$V\ddagger = (AA' | AA')$$

$$\Delta E = 2 \Delta \varepsilon + (AA | AA) + (A'A' | A'A') - [2(AA | A'A') - (AA' | AA')]$$

Here V is the interaction matrix element between the ground state configuration and two-particle charge transfer configuration $\text{HOMO} | A \rangle \rightleftharpoons \text{LUMO} | A' \rangle$; ΔE is the energy difference of these configurations.

In the NDO approximation, all the quantities entered (8) can be expressed in terms of respective characteristics of the system with completely noninteracting fragments (the latter being labelled '0')

$$\begin{aligned} |A\rangle &= |A_0\rangle + g |A_0'\rangle \\ |A'\rangle &= |A_0'\rangle - g |A_0\rangle \\ \Delta \varepsilon &= \Delta \varepsilon_0 (1 + 2g^2) \\ (AA | AA) &= \Gamma_{AA} + 2g^2 \Gamma_{AA'} \\ (A'A' | A'A') &= \Gamma_{A'A'} + 2g^2 \Gamma_{AA'} \\ (AA | A'A') &= \Gamma_{AA'} + g^2 (\Gamma_{AA} + \Gamma_{A'A'}) \\ (AA' | AA') &= g^2 (\Gamma_{AA} + \Gamma_{A'A'} - 2\Gamma_{AA'}) \end{aligned} \quad (9)$$

Here Γ_{AA} , $\Gamma_{A'A'}$, $\Gamma_{AA'}$ are respective Coulomb integrals for completely localized MOs; the terms of orders higher than g^2 are neglected.

HF delocalization of MOs results in resonance stabilization and charge transfer, this effect being proportional to g^2 . The correlation effect is proportional to G^2 . Under usual conditions it follows from (9) that $G^2 \sim g^4$, i. e. the resonance HF charge transfer, predominates over the correlational one.

Sudden polarization occurs when denominator ΔE in Eq. (8) becomes of the order of g^2 due to the mutual compensation of its zero-order constituents (quasi-intersection of HF terms). Then the weight of doubly excited configuration becomes high ($G \approx 1$), and the CI contribution to SE , equal to $-G^2 \Delta E_0$, becomes proportional to g^2 and quite comparable to the HF contribution. This is the case of

$$g^2 \approx \Theta^2 \quad (10a)$$

$$\Theta^2 = \left| \frac{2 \Delta \varepsilon_0 + \Gamma_{AA} + \Gamma_{A'A'} - 4 \Gamma_{AA'}}{3 (\Gamma_{AA} + \Gamma_{A'A'}) - 2 \Gamma_{AA'} - 2 \Delta \varepsilon_0} \right| \ll 1 \quad (10b)$$

These relations can be obtained by substituting (9) into (8) with $G \approx 1$.

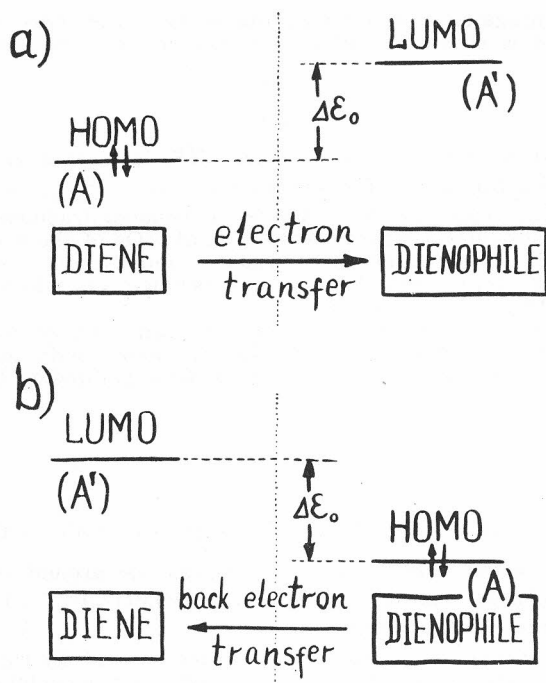


Figure 6. Assignment of frontier MOs to the localized fragments of the system 'diene-donor + dienophile-acceptor'. Symbols A and A' label unperturbed MOs of different fragments. (a) An early charge-transfer-complex-type TS (synchronous or asynchronous). (b) A late zwitter-ionic-type asynchronous TS: π -systems of residual fragments of diene and dienophile both involve an odd number of AOs.

Eq. (10a) represents the condition of the quasi-intersection of the HF terms. It must be consistent with localization condition (7). This gives inequality (10b). Otherwise, the description of the system in terms of localized MOs becomes invalid: MOs are the delocalized and sudden polarization is therefore impossible.

Parameter g varies continuously along the reaction coordinate. For early TSs (Figure 6a) it increases from 0 to $g \approx 1$. For a late asynchronous TS it decreases from $g \approx 1$ to 0. Therefore, if inequality (10b) obeys, then sudden polarization will occur somewhere on the reaction path. If, otherwise, inequality (10b) is violated, then condition $G \approx 1$ cannot be realized for a given system in the regions where MOs are localized. Thus, correlation effects vary monotonously over the whole reaction path.

Specific properties of a particular system are of key importance in determining whether inequality (10b) will apply or not. Just this circumstance accounts for the high specificity of sudden polarization. A situation corresponding to Figure 6b takes place in the *cis-trans* isomerization^{48,49}, whereas the description of the type of Figure 6a is relevant for the early stages of electrophilic substitution reactions⁵⁰. For the reactions studied here parameter Θ (10b) is such that sudden polarization appears impossible at their early stage. For reactions of CNEs with electron-acceptor dienes it may occur at the late stages of the asynchronous process (cf. Figure 6b).

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SAŽETAK

Do koje se granice može proširiti kvalitativna teorija kemijske reaktivnosti? Studij dienofilne aktivnosti cijanoetilena

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Kvalitativan kvantno-kemijski pristup utemeljen na metodi stabilizacijske energije iskorišten je za proučavanje mehanizama i opaženih kinetičkih pravilnosti Diels-Alderovih (DA) reakcija cijanoetilena s ciklopentadienom i fenilciklonom. U prvoj reakciji polarni su efekti daleko važniji od lokalizacijskog efekta. Velik raspon konstanti brzina reakcija može se protumačiti prijenosom naboja s diena na dienofil u sinkronoj prijelaznoj strukturi (TS). Obrnuto ponašanje druge reakcije prouzrokovano je lokalizacijskim efektom u asinkronoj prijelaznoj strukturi. Razmatrane su i moguće deformacije TS.