

Quantum-Chemical Treatment of Cyclization and Recyclization Reactions: XXV.* Skeletal Rearrangements of Radicals, and Lowest Triplet-State Systems

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Abstract—The previously developed scheme for description of cyclization and recyclization reactions on the basis of the Fukui approach was extended to systems with open electron shell in terms of the unrestricted Hartree–Fock method. It was applied to odd-membered polyene radicals and even-membered polyenes in the lowest triplet state and trimethylenemethane derivatives. The obtained data were compared with the results of calculations of analogous systems and available experimental data.

We previously described thermal electrocyclic rearrangements of the series of five- and six-membered heterocycles (see, e.g., [2]), polyenes [3], fused hexatrienes [4], and benzyl- and naphthylcarbenes [5] and performed quantum-chemical analysis of the Kost–Sagitullin [6], Elbs [7], and other reactions in terms of the bounded version of the π -electron perturbation theory. The goal of the present study was to extend the approach developed on the basis of the unrestricted Hartree–Fock (UHF) procedure to systems with open electron shell, namely radicals, diradicals, and systems in the lowest triplet state, which in some cases require the second-order perturbation theory to be applied.

In terms of the π -electron approximation of the SCF MO LCAO procedure, transition states in electrocyclic ring closure, formed via interaction of two π -orbitals belonging to i th and k th atoms, are described by the following perturbation matrix:

$$(H_{ik})_{pq} = (\delta_{pi} \delta_{qk} + \delta_{pq} \delta_{gi}) \Delta\beta_{ik} \quad (1)$$

Accurate to second-order members of the perturbation theory, for variation of the π -electron energy we obtain

$$\Delta E = 2P_{ik}(0) \Delta\beta_{ik} + \pi_{i-k,i-k} \Delta\beta_{ik}^2, \quad (2)$$

where $\Delta\beta_{ik}$ is the change of the resonance integral for the i th and k th atoms, $\pi_{i-k,i-k}$ is the bond–bond self-

polarizability, and δ_{pq} are the Kronecker symbols. It is seen that in the first-order theory the absolute values of distant bond orders $R_{ik}(0)$, which were used to analyze electrocyclic reactions for the first time by Fukui [8], characterize the height of the potential barrier, and their sign, the stereospecificity of the process: When the change of the resonance integral $\Delta\beta_{ik}$ is positive, the reaction is conrotatory, and when $\Delta\beta_{ik}$ is negative, the reaction is disrotatory.

The second term in Eq. (2) is proportional to squared $\Delta\beta_{ik}$; insofar as the bond–bond self-polarizabilities $\pi_{i-k,i-k}$ are as a rule positive (in negative β values), when $P_{ik}(0) = 0$, regardless of the way of rotation of the corresponding orbitals (in either a syn- or antiphase mode), in all cases there is a gain in the π -electron energy, i.e., the reaction is allowed. This means in turn that cyclization of such systems should not be stereoselective. Let us emphasize once more that the use of $\pi_{i-k,i-k}$ as reactivity indices is justified only when the corresponding distant-bond orders are small or equal to zero [9].

Application of the procedure developed previously for description of substituent effects [10] gives expression (3) for the change in activation energy due to the presence of a substituent in the j th position:

$$\Delta\delta E_j = 2\pi_{j,i-k} \Delta\beta_{ik} \Delta a_{R_j} \quad (3)$$

Depending on the sign and value of the atom–bond polarizability $\pi_{j,i-k}$ and the parameter Δa_{R_j} which

* For communication XXIV, see [1].

Table 1. π -Electron orders of distant bonds $P_{i,i+5}(0)$ in polyene radicals

$i-k$	N									
	7	9	11	13	15	17	19	21	27	29
1-6	0.081	0.112	0.127	0.134	0.137	0.139	0.140	0.140	0.141	0.141
2-7		0.064	0.057	0.53	0.051	0.051	0.050	0.050	0.050	0.050
3-8			0.089	0.101	0.107	0.110	0.112	0.112	0.113	0.113
4-9				0.080	0.075	0.072	0.071	0.071	0.070	0.070
5-10					0.090	0.096	0.098	0.100	0.101	0.101
6-11						0.085	0.082	0.081	0.080	0.080
7-12							0.090	0.092	0.095	0.095
8-13								0.087	0.085	0.084
9-14									0.091	0.092
10-15									0.087	0.086
11-16									0.089	0.090

characterizes substituent in the j th position, not only the value but also the sign of the total energy gain and hence the stereospecificity of the given electrocyclic reaction may change. Weltin [11] noted the possibility in principle of describing nonsteric substituent effects in electrocyclic reactions by calculation of atom-bond mutual polarizabilities. It is known that polyenes having a long conjugated bond chain exhibit important optical and electric properties due to specific features of their electronic structure [12]. However, wide application of polyenes as dyes, fluorophores, photoconducting materials, etc., is limited because of difficulties in their preparation and stabilization. Therefore, apart from studies of the electronic and steric structure of such systems, analysis of their possible transformations is of specific interest (such analysis for unexcited even-membered polyenes was performed in [3]). Taking into account that radical, diradical, and carbene species are also formed under conditions of photochemical and thermal pyrolysis of polymers (e.g., polyvinyl chloride) and some coals, in the present work we examined electrocyclic ring closure in the doublet and triplet states of polyenes. We also tried to elucidate whether the general relations holding in skeletal rearrangements of even-membered polyenes are valid for radicals and systems in the lowest triplet state.

The most stable products formed by cyclization of polyenes and polyene radicals and subsequent dehydrogenation are aromatic hydrocarbons [13]; the same compounds are the most abundant among pyrolysis products of polymers and fossil fuels.

Taking this into account, electrocyclic closure of hexatriene fragments is the most interesting.

Table 1 contains the results of UHF calculations of the distant bond orders $P_{i,i+5}(0)$ for *trans*-polyene radicals of the general formula $C_{2n+1}H_{2n+3}$ (where $n = 1-29$). Just the same order of variation of $P_{i,k}(0)$ is observed for the *cis* isomers. Like uncharged even-membered polyenes [3], the corresponding radicals are characterized by different modes of bond order variation, depending on the evenness of the i th position (count off from the chain origin) at which the cyclization occurs. However, the alternation of the distant bond orders for even and odd positions i in polyenes decreases (though insignificantly) as the length of the carbon chain increases, while it increases for polyene radicals, i.e., $P_{i,i+5}(0)$ increases for odd i and decreases for even i . The absolute values of the corresponding bond orders are somewhat smaller for odd i and somewhat greater for even i , as compared to the respective polyenes. This should lead to some lowering of the selectivity of electrocyclic ring closure in going from polyenes to their radical forms.

The difference in $P_{i,i+5}(0)$ values for even and odd i rapidly disappears in going from peripheral to central carbon atoms at a fixed N value. Unlike even-membered polyenes [3], with rise in N the corresponding distant bond orders tend to a common $P_{i,i+5}(0)$ limit of 0.089. Thus thermal ring closure in both even- and odd-membered polyenes involves mainly the terminal carbon atoms.

We shall not discuss in detail the cyclization of butadiene fragments. It should only be noted that the

Table 2. π -Electron orders of distant bonds $P_{i,i+5}^{t1}(0)$ in polyenes in the lowest triplet excited state

$i-k$	N										
	6	8	10	12	14	16	18	20	26	36	60
1-6	0.134	0.109	0.024	0.020	0.053	0.078	0.095	0.107	0.128	0.138	0.141
2-7		0.086	0.098	0.095	0.088	0.079	0.072	0.067	0.056	0.051	0.050
3-8			0.056	0.031	0.004	0.022	0.044	0.061	0.093	0.109	0.113
4-9				0.127	0.133	0.128	0.120	0.110	0.088	0.074	0.070
5-10					0.023	0.010	0.007	0.025	0.067	0.094	0.101
6-11						0.146	0.148	0.143	0.115	0.088	0.080
7-12							-0.007	0.001	0.041	0.082	0.095
8-13								0.155	0.141	0.100	0.084
9-14									0.016	0.069	0.091
10-15									0.159	0.117	0.087
11-16									0.006	0.051	0.089
$(N/2-3)-(N/2+2)$										0.013	0.014
$(N/2-2)-(N/2+3)$										0.164	0.165

observed variation in the distant bond orders $P_{i,i+3}(0)$ are analogous to those given in Table 1 for $P_{i,i+5}(0)$, although the absolute values of $P_{i,i+3}(0)$ are approximately twice as high as $P_{i,i+5}(0)$: for example, at $N \rightarrow \infty$, $P_{1,4}(0) = -0.283$, $P_{2,5}(0) = -0.112$, ..., and $P_{(N-3)/(N+3)/2}(0) = -0.181$.

The probability of cyclization with formation of large $4n$ - and $4n+2$ -membered rings is close to zero because of increased distance between the atoms in polyene or polyene radical. The result is that the corresponding distant bond orders sharply decrease in absolute value with increase in n .

In going to quantum-chemical interpretation of photochemical rearrangements of polyenes, we should note that the particular form of expressions for photoelectrocyclization indices is determined by the method of calculation of excited states. The procedure for calculation of variation of excitation energy was described in [14]. It corresponds to the situation when singlet-singlet transitions are described on the basis of the stability frequencies of the Hartree-Fock ground state, and triplet transitions, in terms of the Tamm-Dancoff approximation. On the other hand, distant bond orders $P_{ik}^{t1}(0)$ can be used as photoelectrocyclization indices in the UHF calculations of systems in the first triplet state, as well as of those in the ground singlet state. Just the latter approach was utilized in the present study.

According to the Woodward-Hoffmann orbital symmetry rules, the stereospecificity of electrocyclic

ring closure should change in going from thermal to photoinduced isomerization [15]. With *cis*-butadiene, *cis*-hexatriene, and their analogs with a fused benzene ring as examples, it was shown in [14] that the above rule is valid only for the first allowed singlet-singlet and singlet-triplet transitions and that in the general case (excitation to higher energy levels) it is violated. Tables 2 and 3 contain distant bond orders responsible for formation, respectively, of 6-membered [$P_{i,i+5}^{t1}(0)$] and 4-membered rings [$P_{i,i+3}^{t1}(0)$]. These data indicate to what extent the above consequence of the Woodward-Hoffmann theory is applicable to polyenes having more than 6 carbon atoms in the lowest triplet state. It is seen that the bond order $P_{1,6}^{t1}(0)$ is negative only for hexatriene, octatetraene, and decapentaene. Therefore, the given photoelectrocyclization of only those compounds, unlike the dark reaction, should be conrotatory. On further increase of the chain length, negative $P_{i,i+5}^{t1}(0)$ (which appear exclusively for odd i) initially fall down and then change their sign: beginning with $N = 20$, all $P_{i,i+5}^{t1}(0) > 0$. In the framework of our approach, this should not result in change of the photoelectrocyclization stereospecificity with respect to the dark reaction (the reaction is disrotatory). The same is characteristic of cyclization of butadiene fragments (Table 3). Judging by the sign of the greatest (in absolute value) $P_{i,i+3}^{t1}(0)$, the formation of cyclobutene ring should be conrotatory.

We previously showed [3] that unexcited even-membered polyenes are characterized by sharp dif-

Table 3. π -Electron orders of distant bonds $P_{i,i+3}^{l1}(0)$ in polyenes in the lowest triplet excited state

$i-k$	N										
	4	6	8	10	12	14	16	20	26	36	60
1-4	0.197	0.051	-0.083	-0.135	-0.182	-0.212	-0.233	-0.257	-0.273	-0.281	-0.283
2-5		-0.206	-0.206	-0.197	-0.175	-0.158	-0.145	-0.129	-0.119	-0.113	-0.112
3-6			-0.007	-0.019	-0.069	-0.110	-0.141	-0.181	-0.208	-0.223	-0.226
4-7				-0.265	-0.263	-0.245	-0.225	-0.192	-0.166	-0.152	-0.149
5-8					-0.025	-0.048	-0.077	-0.128	-0.173	-0.197	-0.203
6-9						-0.282	-0.278	-0.245	-0.201	-0.173	-0.165
7-10							-0.049	-0.082	-0.140	-0.181	-0.192
8-11								-0.284	-0.238	-0.188	-0.174
9-12								-0.061	-0.103	-0.166	-0.186
10-13									-0.275	-0.206	-0.176
11-14									-0.074	-0.146	-0.183
12-15									-0.292	-0.231	-0.180
$(N/2-2)-(N/2+1)$										-0.289	-0.289
$(N/2-1)-(N/2+2)$										-0.074	-0.075

ferentiation of the distant bond orders $P_{i,i+5}(0)$ corresponding to cyclization at even- and odd-numbered carbon atoms. As follows from the data in Tables 2 and 3, such differentiation disappears in going to the lowest excited triplet state. Thus, if the probability of cyclization at odd-numbered carbon atoms appreciably decreases with rise in i and the reverse pattern is observed for even-numbered positions, the most favorable are internal cyclizations for which $P_{i,i+3(5)}^{l1}(0)$ are the largest in absolute value.

It is readily seen that the order of variation of $P_{i,i+3(5)}^{l1}(0)$ for excited polyenes with increase in the chain length resembles that observed for polyene radicals. However, in the first case, especially at large i , $P_{i,i+3(5)}^{l1}(0)$ slowly attains the limiting value, whereas in the second case the limit is reached even at $N = 21-25$. At small i , both quantities tend to a common limit, indicating the determining effect of the molecular topology on the properties under consideration.

In fact, the Hückel approximation gives the following expression (cf. [3]) for nonzero $P_{i,k}(0)$ [when the difference $i - k$ is even, all $P_{i,k}(0)$ are equal to zero]:

$$P_{ik}(0) = \frac{1}{n+1} \left\{ \frac{\sin[\pi(i-k)(n+l)/2(n+1)]}{\sin[\pi(i-k)/2(n+1)]} - \frac{\sin[\pi(i+k)(n+l)/2(n+1)]}{\sin[\pi(i+k)/2(n+1)]} \right\} \quad (4)$$

Here, $l = 1$ for even-membered polyenes, $l = 0$ for odd-membered polyenes, and $l = -1$ for polyenes in the lowest excited state. Obviously, regardless of the evenness and the degree of electron shell filling, the charges and bond orders of polyenes tend to the same limit as $n \rightarrow \infty$ {see Eqs. (3) and (4); cf. [3]}; this tendency becomes stronger as the sum $i+k$ decreases.

The most probable site of rupture of the polyene radical chain may be determined from the orders of bonds between chemically linked atoms; their analysis was given in [16]. The observed alternation of bond orders between directly linked carbon atoms resembles that considered above for distant bond orders in radicals. As the length of polyene chain increases, the alternation becomes more pronounced for terminal bonds, while the orders of nearby central bonds tend to level with one another. Therefore, the weakest bond is 2-3, and the decomposition is most likely to occur with rupture of that bond.

The above conclusions do not change when differences in bond lengths are taken into account according to the procedure reported in [17]; the only result is a slower convergence of the distant and nearby bond orders in going from periphery to center.

It should be emphasized that the orders of bonds between carbon atoms of the same alternant set in odd-membered alternant radicals are equal to zero. Therefore, the probability for formation of odd-membered rings from such systems should be low.

For example, benzyl cation and anion are characterized by large positive values of $P_{2,7}(0)$ (0.283) and $P_{4,7}(0)$ (0.294); correspondingly, in the first case tropylium cation is formed, and in the second, vinylcyclopentadienyl anion. However, the orders of distant bonds 2–7 and 4–7 in the radicals derived therefrom are equal to zero, and these radicals are stable and they do not undergo recyclization (neither ring expansion nor ring contraction occurs).

It should be noted that application of the second-order perturbation theory is limited to those simple systems for which the formation of even-membered rings is either impossible (as with allyl radical) or sterically hindered. Comparison of the available experimental data with our results indicating the absence of stereospecificity in electrocyclic reactions for such systems would be of undoubted interest, since even the simplest model of allyl radical gives rise to contradictions with predictions made on the basis of the Woodward–Hoffmann correlation diagrams [18, 19]. On the other hand, the frontier orbital approximation [18] also predicts the lack of stereospecificity in the allyl–cyclopropyl rearrangement. The available experimental data do not allow us to draw an unequivocal conclusion as to whether this or other electrocyclic reaction of odd-membered alternant radicals, involving atoms of the same alternant set, is disrotatory or conrotatory [18, 19].

It should also be noted that, according to Eq. (3), introduction of a substituent into a radical should increase the stereospecificity of electrocyclic reaction at the respective position. For example, the cyclization of 1,1'-dicyclohexenylmethyl radical gives product of conrotatory ring closure, though a small amount of the *cis* isomer is also formed [18]. This result is very consistent with the corresponding distant bond order $P_{1,5}(0) = -0.084$ calculated by Eq. (3) on the basis of mutual atom–bond polarizabilities ($\pi_{1,1-5} = -0.0087$, $\pi_{2,1-5} = 0.0207 \text{ eV}^{-1}$). The substituent parameters were assumed to be equal to those typical of methyl radical, $\Delta\alpha = -3.51 \text{ eV}$ [10].

In keeping with the twoness theorem, orders of distant bonds between atoms of the same alternant set change their sign when the charge of the system changes to the opposite. As a result, the reverse stereospecificity of electrocyclic ring closure for anions and cations of odd-membered alternant hydrocarbons should be observed. Therefore, the formation of odd-membered rings by thermolysis or photolysis of polyenes or their precursors is most likely to involve intermediate formation of singly charged ions, which is favored by low ionization potentials and

electron affinities of such systems, especially when the polyene chain is long.

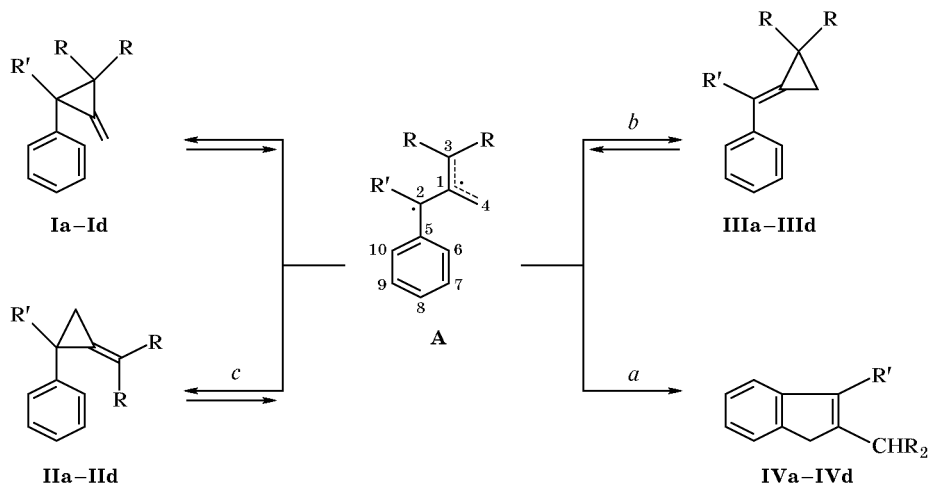
The positive sign of the order of the bond between the terminal carbon atoms in allyl cation, $P_{1,3} = 0.517$, suggests its preferential thermal disrotatory cyclization to cyclopropyl cation. This is confirmed by numerous experimental data (see, e.g., [20, 21], etc.). In the case of allyl anion, the most probable is conrotatory cyclization, in keeping with the experimental data [22] and the results of frontier orbital analysis.

Likewise, the sign of the order of the bond between the terminal carbon atoms of heptatrienyl cation, $P_{1,7}(0) = 0.251$, indicates that its disrotatory cyclization is possible. However, the large negative value of $P_{1,5}(0)$ (-0.264) does not exclude conrotatory ring closure at the 1,5-positions. The results of calculation of mutual atom–bond polarizabilities show that introduction of four methyl groups into positions 1 and 7 increases the absolute values of both $P_{1,7}(0)$ and $P_{1,5}(0)$; in fact, the 1,5-cyclization product is obtained for steric reasons [21].

According to the above stated, the 1,7-cyclization of heptatrienyl anion should be conrotatory ($P_{1,7}(0) = -0.251$) with formation of cycloheptadienyl anion (for experimental data, see [22]). In keeping with the Woodward–Hoffmann rules [23] and the negative sign of $P_{1,5}(0)$, the cyclization of pentadienyl cation is conrotatory. An experimental proof is the cyclization of diphenylmethyl cation at the 2,2' positions [21], which is in full agreement with the sign of the distant bond order $P_{2,2'}(0) = -0.099$. The corresponding anion should undergo electrocyclic ring closure in the disrotatory mode: $P_{2,2'}(0) = 0.099$.

The presence of an additional phenyl ring in triphenylmethyl cation increases its stability relative to diphenylmethyl cation. The bond order $P_{2,2'}(0)$ is smaller in absolute value (-0.076); therefore, the activation barrier should be higher, and the cyclization stereoselectivity should be lower. The potential of the developed model is not limited to concerted isomerization processes. As an example of reactions involving a diradical transition state, let us consider thermal rearrangements of methylenecyclopropane derivatives (Scheme 1). It should be emphasized that although this reaction has been studied as long as more than 30 years by experimental and theoretical methods, no final conclusion on the nature of its transition state has been drawn. *Ab initio* calculations with the minimal STO-3G basis set showed [24] that a probable path (along the reaction coordinate) involves singlet diradical $^1\mathbf{B}$ in which one of the methylene groups lies in a plane orthogonal to the

Scheme 1.



plane including all the other atoms. On the other hand, the planar triplet state of trimethylenemethane ($^3\mathbf{A}$, calculated with both STO-3G and extended SCF/3-21G basis set) has an energy lower by ~15–17 kcal/mol than that of the singlet state. Dowd and Chow [25] experimentally measured the difference between the $^3\mathbf{A}$ and $^2\mathbf{B}$ terms, which turned out to be considerably smaller, no more than 2.0–7.8 kcal/mol. These data suggest that the reaction involves the lowest triplet state of trimethylenemethane.

As cyclization indices in triplet diradical \mathbf{A} derived from (di)phenylmethylene-cyclopropane, we used mutual bond–bond polarizabilities $\pi_{i-k,j-k}$ and atom–bond polarizabilities $\pi_{j,i-k}$ (Table 4), for the distant bond orders corresponding to formation of 3- and 5-membered rings are equal to zero due to alternant symmetry. We considered only those rearrangements which involve rupture and formation of one σ -bond and do not lead to formation of strained bicyclic compounds (Scheme 1).

The data in Table 4 show that the lowest value is typical of the 3–4 bond, and the greatest value belongs to the 4–6 bond. Therefore, unsubstituted (di)phenylmethylene-cyclopropane should react mainly along pathway *a* rather than *b* (Scheme 1). This conclusion is confirmed by the experimental data [26]. Heating of compound \mathbf{Ib} for 9.5 h at 140°C leads to irreversible formation of 2-methyl-3-phenylindene (\mathbf{IVb}), while the yield of diphenylmethylene-cyclopropane (\mathbf{IIIb}) does not exceed 5%.

Obviously, on introduction of substituents into the cyclopropane ring, the most probable path is that to

which the greatest values of both indices, $\pi_{i-k,i-k}$ and ΔP_{ik} , correspond. The latter are calculated by the known formula $\Delta P_{ik} = \pi_{j,i-k} \Delta \alpha_{R_j}$. The contributions of these indices to the overall distant bond order may considerably differ in magnitude and even may have opposite signs. Therefore, description of the cyclization direction on the basis of only one of these is incorrect. Introduction of two methyl groups into position 3 of \mathbf{Ia} (compound \mathbf{Ic}), which are taken into account through $\pi_{j,i-k}$, increases the order of the 2–4 bond to a greater extent than $P_{3,6}$ (which has the maximal value in the unsubstituted molecule) and reduces the other distant bond orders ($P_{2,4} = 0.133$, $P_{3,6} = 0.070$, $P_{4,6} = -0.062$). The experimental result is that the thermal rearrangement of 1,1-dimethyl-2-methylene-3-phenylcyclopropane (\mathbf{Ic}) at 100°C gave mainly 1-isopropylidene-2-phenylcyclopropane (\mathbf{IIc}) [27] (pathway *c* in Scheme 1); no indene derivatives were detected in the reaction mixture.

The only thermolysis product of 2-vinylmethylene-cyclopropane was 3-methylenecyclopentene [28, 29], which is well consistent with cyclization indices in the corresponding vinyltrimethylenemethane diradical (Table 4). As follows from the data in Table 4, the presence of methyl groups (or, in the general case, donor substituents) in position 3 should not change the reaction direction, for the greatest increase in ΔP_{ik} corresponds to the 3–6 bond (in keeping with the experimental data [28]). Here, it is worth noting that the equilibrium between 1-methyl-2-methylene-3-vinylcyclopropane and 1-vinyl-2-ethylidene-cyclopropane [28], as well as between their dimethyl derivatives [29], is strongly displaced to the right.

Table 4. Cyclization indices for rearrangements of substituted methylenecyclopropanes

Precursor of triplet diradical	Index	Bond $i-k$					
		2-3	2-4	3-4	2-6	3-6	4-6
1-Methylene-2-phenyl-cyclopropane	$\pi_{i-k, i-k}$	0.078	0.078	0.056	0.145	0.140	0.153
	$\pi_{3, i-k}$	0.016	-0.017	0.028	0.005	-0.009	0.008
1-Methylene-2,2-diphenyl-cyclopropane	$\pi_{i-k, i-k}$	0.090	0.090	0.058	0.146	0.145	0.158
	$\pi_{3, i-k}$	0.009	-0.016	0.029	0.002	0.002	0.007
1-Methylene-2-vinyl-cyclopropane	$\pi_{i-k, i-k}$	0.089	0.089	0.057	0.087	0.118	0.118
	$\pi_{3, i-k}$	0.009	-0.015	0.028	0.010	-0.019	0.014

This is also consistent with the values and signs of the corresponding distant bond orders in the diradical.

The diradical reactions under consideration also include thermal rearrangement of 1-methylenespiro[2.4]hepta-4,6-diene. Insofar as the system is non-alternant, the reactivity indices are both distant bond orders and bond-bond polarizabilities of the corresponding diradical. Their absolute values are the largest for that bond ($P_{i-k} = -0.065$; $\pi_{i-k, i-k} = 0.208 \text{ eV}^{-1}$), the cyclization at which leads to formation of 7-methylenebicyclo[3.2.0]heptadiene, i.e., the product obtained experimentally [30].

Thus the index approach developed for estimation of reactivity of organic compounds and extended to systems having an open electron shell gives results which agree well with the available experimental data. It can be applied to quantum-chemical interpretation of both concerted and diradical reactions.

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