pyridyl-CH_2), 7.0–7.6 (11 H, m, aromatic-H and NH), 8.14 (1 H, dd, J = 1 and 8 Hz, Q-H^4), 8.48 (1 H, d, J = 5 Hz, Py-H^6), 8.74 (1 H, dd, J = 4 and 4 Hz, Q-H^7), 8.86 (1 H, dd, J = 1 and 4 Hz, Q-H^2), and 10.74 (1 H, s, NH) ppm; precise mass found 410.172, calcd for $C_{25}H_{22}N_4O_2$ 410.174; IR (KBr) 3310 (NH), 1690 and 1645 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} = 318 nm, $\epsilon \times 10^{-3}$ = 6.7. Anal. Calcd for $C_{25}H_{22}N_4O_2$: C, 73.15; H, 5.40; N, 13.65. Found: C, 72.83; H, 5.28; N, 13.55.

Transport of Metal Ions through Liquid Membranes. The transport experiments were carried out by using a U-type glass cell across the chloroform liquid membrane from the buffered aqueous source phase (pH 6.2) containing one or several kinds of metal ions of Cu(II), Ni(II), Co(II), and Zn(II) to the receiving phase containing 0.05 M sulfuric acid. The cell was kept at 25.0 ± 0.2 °C, and each phase was mechanically agitated at 200 rpm.[11] The amount of both metal ions transported into the receiving phase and metal ions remaining in the source phase was determined by atomic absorption spectroscopy.

General Procedure of Solvent Extraction. The following was poured into a 20-mL sample tube with screw cap: 5 mL of an aqueous solution containing 1 mM transition-metal ions (Cu(II), Ni(II), Co(II), or Zn(II)) and 5 mL of chloroform solution containing 1 mM malonamide derivative. The aqueous solution ranged from pH 6.2 to 1.4 and was adjusted by using both 1 M sodium acetate and 0.2 M acetic acid (or 1 N hydrochloric acid). The mixture was shaken vigorously for 24 h at 25 °C. The concentration of the remaining metal ions in aqueous solution was determined by atomic absorption spectroscopy. The concentration of the extracted metal ions was calculated from these values.

Registry No. 1, 123038-39-1; 3, 144436-25-9; 4, 131356-13-3; 5, 131356-14-4; 6, 144436-26-0; 7, 131356-15-5; 8, 131356-16-6; 9, 139424-08-1; $Bu_2C(CO_2H)_2$, 2283-16-1; $PhCH_2CH(CO_2H)_2$, 616-75-1; 8-aminoquinoline, 578-66-5; 2-aminopyridine, 504-29-0; 2-(aminomethyl)pyridine, 3731-51-9; 2-(aminoethyl)pyridine, 2706-56-1.

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Conrotatory and Disrotatory Reaction Paths for Thermal and Photoinduced Ring-Closing Reactions of 1,3,5-Hexatriene and Its Isoelectronic Analogs

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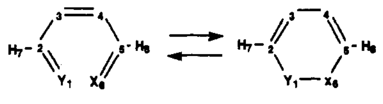
Received June 29, 1992

The reaction pathways for the thermal and photocyclizations of 1,3,5-hexatriene and its isoelectronic analogs **1** into 1,3-cyclohexadiene and respective heterocyclic dienes **2** have been investigated by use of the semiempirical MINDO/3 method. The main conclusions are as follows: (1) The transition-state structure of the symmetry-forbidden thermal reaction **1a** ↔ **2a** corresponding to the conrotatory reaction path has been located and found to be asymmetric. (2) The photocyclizations of 1,3,5-hexatriene (**1a**) and its isoelectronic analogs **1b–d** proceed as diabatic reactions that include internal conversion from the first excited singlet state (S_1) to the ground-state (S_0) potential energy surface (PES). (3) The photocyclizations of 1,3,5-hexatriene (**1a**) and 2,4-pentadienal imine (**1b**) may occur as "hot state" reactions through population of the vibrationally excited levels on the S_0 energy surfaces. The photoreaction **1d** ↔ **2d** is expected to be susceptible to triplet sensitization. (4) For the cyclizations of π-heteroanalogs of 1,3,5-hexatriene, containing terminal carbonyl, thiocarbonyl, or aldimine groups, two reaction channels similar to the dis- and conrotatory reaction paths of the **1a** ↔ **2a** reaction were revealed by calculations of both the ground and singlet excited electron states. The energy-preferred pathways correspond to the symmetry-allowed reaction modes, although the energy difference between the "allowed" and "forbidden" transition-state structures is smaller relative to 1,3,5-hexatriene. The orientation of the C2–H and C5–H bonds relative to the C1–X6–C5 plane serves as the structural criterion for assignment of the reaction channel to either dis- or conrotatory type. (5) Monoheterosubstitution in **1a** decreases the energy difference between the cyclic and polyene forms, although the ring-closed form remains more stable. Heteroatom substitution of both terminal methylene groups in **1a** reverses the order of relative stability of the valence isomers. Finally, the calculations show that heteroatom substitution lowers the energy barriers to cyclization of **2a** and **3a** in the S_0 and T_1 electron excited states.

Introduction

The thermal and photochemically induced ring closure of 1,3,5-hexatriene to 1,3-cyclohexadiene (**1a**) ↔ (**2a**) are key steps in the biosynthesis of the vitamin D series (the provitamin D ↔ previtamin D interconversion)[1,2] as well as the basic reactions defining the mechanisms of thermochromic and photochromic behavior of fulgides and fulgimides,[3] [10]-annulenes,[4] and diarylethylenes.[5] The analogous transformations of compounds in which the terminal methylene group is substituted by the isoelectronic oxygen or nitrogen atoms form the basis of the photo- and thermochromic behavior of such classes of compounds as spiropyrans,[6] chromenes,[7] spirooxazines,[8] dihydroquinolines,[9] and others.



1 2

a) X=Y=CH2 ; b) X=NH,Y=CH2; c) X=O, Y=CH2; d) X=Y=O

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The principle reason for the unremitting theoretical attention given to these processes is related to the fact that, along with the cyclizations of 1,3-butadiene into cyclobutene, the thermal and photocyclizations of 1,3,5-hexatriene into 1,3-cyclohexadiene are classic examples of electrocyclic reactions conforming to the Woodward–Hoffmann orbital symmetry conservation rules.[10] These rules correctly predict the stereochemical course of thermal and photoreactions but afford no details or explanations of a number of important mechanistic peculiarities, which include the following. (1) The minimal energy reaction paths found by the MO calculations do not retain the symmetry properties as would be expected on the basis of orbital symmetry conservation.[11,12] (2) The photoreactions may occur as a diabatic process[12,13] in which case an adherence to the Woodward–Hoffmann rules might simply be coincidental. (3) There is a question of transferability of the predictions of the steric course of the ring-closing reactions of polyenes to their heteroanalogs, in particular, an existence of dis- and conrotatory reaction channels. Even though the final products arising at the ends of these different reaction channels are structurally identical (X = O), the reaction pathways are computationally distinguishable,[14] thus representing a special example of chemical hysteresis.[15] (4) Quantitative estimates of the energy preference of the symmetry-allowed reaction paths are compared to the forbidden ones. (5) The planar cZc-conformation of 1,3,5-hexatriene (**1a**) was once considered the starting species which undergoes the ring cyclization. However, the cZc-conformation is in fact highly strained and does not correspond to a minimum on the PES. The real structure is substantially skewed from planarity.[12,16] This means that, in rigorous terms, no symmetry at all is retained by the rearranging molecule while passing on along the reaction pathway. It is well-known[10] that the Woodward–Hoffmann rules are based on the principal of maximum overlap. Therefore, a connection to its demands should be traced in the analysis of factors controlling a steric course of the thermal reaction.

The present work addresses the aforementioned questions and serves to generalize the conclusions on the mechanisms of type **1** ↔ **2** reactions obtained in the semiempirical MINDO/3 level of approximation. It is expedient to consider this reaction in light of data for the simpler and better studied cyclization reaction of 1,3-dienes.

The thermal and photocyclizations of 1,3-butadiene[13a–e,17] into cyclobutene are the most intensely investigated electrocyclic reactions. In the search for reaction paths it is usually assumed[13a–d] that the rearranging valence isomers retain C_s- or C_2-symmetry for respective disrotatory and conrotatory trajectories along the whole route from the reactant to the product. However, with such a symmetry constraint no transition-state structure corresponding to the thermally forbidden disrotatory reaction path was located. The energy maximum along the C_s-trajectory was found to be a second-order saddle point, and the corresponding unstable structure was characterized by two negative force constants.[13d] Hence, it cannot be regarded as the genuine transition-state structure.[18]

The quantum-mechanical calculations at the different levels of approximation revealed the diabatic mechanism of the photocyclization reaction of 1,3-butadiene into cyclobutene which included the $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_0$ transitions, according to our recent "half-electron" MINDO/3 calculations[13e] having been carried out (in contrast to all previous calculations) with no symmetry constraints imposed on the reaction trajectories; 1,3-butadiene after the $S_0 \rightarrow S_1$ excitation surmounts the energy barrier of 8.4 kJ/mol following along the semirotatory[11a–d] asymmetric reaction path toward the reaction funnel on the S_1 energy surface and through the $S_1 \rightarrow S_0$ transition to cyclobutene. The low-temperature UV and NMR experiments at 15K did not reveal the existence of a low energy barrier on the S_1 surface,[19] but confirmed the role of the internal conversion $S_1 \rightarrow S_0$ stage.

Calculation Methods

The semiempirical MINDO/3 calculations[20] were carried out on a ES-1060 or ES-1061 computer. The reactant, product, and intermediate structures were calculated employing the Davidon–Fletcher–Powell method[21] for full geometry optimization. For a search of the reaction paths of both the photo- and thermocyclizations of 1,3,5-hexatriene, the reaction coordinate regime[22] was used, the distance between the carbon (or carbon and heteroatom) centers of the terminal groups being chosen as the reaction coordinate. The steps equal to 0.2 and 0.1 Å were used

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Table I. MINDO/3 Calculated Heats of Formation (ΔH_f), Heats of Reaction ($\Delta(\Delta H_f)$), and Activation Enthalpies ($\Delta H^\ddagger = \Delta H_f(\mathrm{TS}) - \Delta H_f(\mathrm{Reactant})$) for the Dis- and Conrotatory Reaction Paths between 1,3,5-Hexatriene (**1a**) and 1,3-Cyclohexadiene (**2a**) and Their Isoelectronic Analogs **1b–d** and **2b–d**, Respectively (kJ/mol)

		ΔH_f			$\Delta H^\ddagger$		
					ring closing		
reaction	electronic state	1	2	$\Delta(\Delta H)_f$	dis	con	ring opening
1a ↔ **2a**	S_0	202.7	77.4	125.3	139.9	201.3	265.2
				133.5[a]	103.0[a]		
				60.7[b]	123.8[c]		
	T_1	380.7	264.4	116.3		88.0	204.3
1b ↔ **2b**	S_0	175.3	102.4	72.9	95.2	106.4	168.1
	T_1	366.4	244.6	121.8		32.2	156.0
1c ↔ **2c**	S_0	−27.5	−79.4	51.9	101.5	137.1	153.4
				8.4–15.5[d]	56–79.5[d]		55.2–75.3[d]
	T_1	143.6	76.8	66.8		42.4	109.2
						23.4[e]	
1d ↔ **2d**	S_0	−232.2	−16.7	−215.5	272.8		57.3

[a] MINDO/2.[26] [b] Reference 27. [c] Reference 28. [d] Exp. substituted 2*H*-pyrans.[29] [e] MINDO/3.[30] [f] Exp. substituted 2*H*-pyrans.[31]

at the initial stage of the reaction paths and those of 0.05 Å in the vicinity of the transition-state structures. The structure found as an energy maximum on this reaction path was then refined by employing either the norm gradient optimization method[23] or the Bartell–Viner procedure as described in ref 24. The assignment of the stationary points to the transition-state structures has been checked by the analysis of the Hessian matrix[23] and the form of the corresponding elementary displacements vectors. The excited states of the molecules were calculated in the "half-electron" approximation.[25]

It is necessary to point out that semiempirical techniques in general underestimate electron lone pair–lone pair repulsion, but on the other hand MINDO/3 probably overestimates the stability of the product and that is why MINDO/3 is quite applicable for our task.

Results and Discussion

The Thermocyclization of 1,3,5-Hexatriene (1a) into 1,3-Cyclohexadiene (2a). According to the MINDO/3 calculations the cyclohexadiene is more stable than the isomeric triene, which is in accord with experimental data (see also Table I). The first quantum-chemical analysis of this reaction was carried out[26] with the semiempirical MINDO/2 and the norm gradient minimization methods.[23] The structure corresponding to the transition state of the reaction **1a** ↔ **2a** on the ground-state PES was found to possess C_s-symmetry (Table I).

It has previously been assumed[12] that 1,3-cyclohexadiene formation derives from the planar cZc-conformation of 1,3,5-hexatriene which is structurally prepared for immediate cyclization.[1a] However, according to our most recent calculations, the minimum on the PES of the ground state corresponds to the structure twisted about the single C2–C3 bond by an angle $\varphi = 40°$. This value is close to that ($\varphi = 48°$) obtained in the ab initio 6-31G calculations.[32] The transition-state structure was located by following small changes in the C1–C6 bond length as the reaction coordinate. The transition state was found to correspond to a conrotatory cyclization, as can be seen by the shape of the elementary displacement vectors portrayed in Figure 1b.

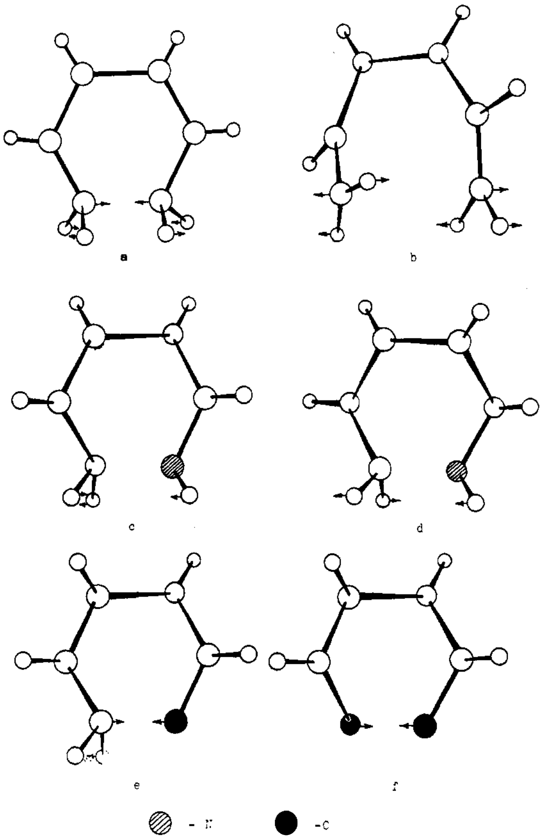

Figure 1. Transition-state structures of the thermal ring-closing reactions: (a) dis-**1a** ↔ **2a**; (b) con-**1a** ↔ **2a**; (c) dis-**1b** ↔ **2b**; (d) con-**1b** ↔ **2b**; (e) dis-**1c** ↔ **2c**; (f) dis-**1d** ↔ **2d**.

It should be noted that the conrotatory reaction proceeds as a semirotatory process.[11c–f] i.e., at the initial stage

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Table II. Dihedral Angles Used To Identify the Dis- and Conrotatory Reaction Paths in the Electrocyclization of 1,3,5-Hexatriene (1a) to 1,3-Cyclohexadiene (2a) and Isoelectronic Analogs 1b–d to 2b–d

		dihedral angle (deg)	
reaction	electronic state	H7–Y1–X6–C5	H8–C5–X6–Y1
1a ↔ **2a**			
disrotatory	S_0	23.9	−130.4
conrotatory	S_0	73.7	113.7
conrotatory	T_1	40.5	152.8
minimum	S_1	65.1	132.3
1b ↔ **2b**			
disrotatory	S_0	38.4	−157.9
conrotatory	S_0	58.2	165.2
conrotatory	T_1	52.4	156.7
minimum	S_1	40.4	158.0
1c ↔ **2c**			
disrotatory	S_0	20.3	−142.0
conrotatory	T_1	22.9	142.7
1d ↔ **2d**			
disrotatory	S_0	24.1	−133.1

a rotation of a single terminal group occurs, whereas the other terminal group starts to rotate in the vicinity of the transition state. The conrotatory transition-state structure has no symmetry elements.

The stationary point on the ground-state PES corresponding to the transition state structure allowed by the Woodward–Hoffmann rules (the disrotatory cyclization) was located using the norm gradient minimization method and scanning the PES in a vicinity of the conrotatory transition-state structure. The corresponding energies characteristics of the reaction are given in Table I. The disrotatory transition-state structure was found to possess C_s-symmetry (Figure 1a).

The Thermocyclization of 2,4-Pentadienal Imine (1b) into 1,2-Dihydropyridine (2b). The planar cZc-conformation of 2,4-pentadienal imine has been chosen as the starting point for the geometry optimization. However, as was in the case of 1,3,5-hexatriene, this conformation does not correspond to a minimum on the ground-state PES and relaxes to the twisted structure with a torsional angle of 75° about the C2–C3 bond. The cyclic isomeric form **2b**, as in the case of the parent hydrocarbons, is lower in energy (by 72.9 kJ/mol). The substitution of one of the terminal methylene groups in **1a** by an imino group lowers the magnitude of the heat of formation of the ring-closing reaction by 52.4 kJ/mol. By employing the Bartell–Viner procedure for the search of the transition-state structures for dis- and conrotatory cyclization reaction paths, two stationary points (TS1, TS2) on the ground-state PES, connecting the reactant (**1b**) and the product (**2b**), which possess only one negative force constant have been revealed. Figure 1c,d presents the stereoprojections and the elementary displacements vectors. The position of the H7 and H8 atoms relative to the C5–X6–C1 plane was used to assign the transition-state structures TS1 and TS2 to either dis- or conrotatory types.

Values of the torsion angles H7–C1–X6–C5 and H8–C5–X6–C1 for the obtained transition-state structures are given in Table II. These data show that for the disrotatory transition state of the thermal reaction **1a** ↔ **2a** and the TS1 structure with X = NH, the H7 and H8 atoms are both turned to the same side relative to the C5–X6–C1 plane. In contrast to the disrotatory TS of the reactions **1a** ↔ **2a** and **1b** ↔ **2b**, the conrotatory TS of these reactions has the H7 and H8 atoms lying above and below the C5–X6–C1 plane. Therefore, the TS1 and TS2 structures ought to be assigned to the dis- and conrotatory ring-closing reaction paths, respectively. As expected, the "symmetry allowed" disrotatory TS1 structure is lower in energy compared to its "symmetry forbidden" conrotatory TS2 counterpart, but the energy difference (11 kJ/mol) is smaller than that for the parent hydrocarbon electrocyclic reaction (see Table I).

The Thermocyclization 2,4-Pentadienal (1c) into 2*H*-Pyran (2c). The previous MINDO/3 investigation[33] of this reaction was carried out using the nascent C–O bond as the reaction coordinate. The calculated energy barrier of the ground-state ring-opening **1c** ↔ **2c** reaction was found to be equal to 137.1 kJ/mol, 2*H*-pyran being 51 kJ/mol more stable than the cZc-conformation of 2,4-pentadienal. This reaction was also studied[34] by the MNDO method.[35] Two torsion angles about the formal single bonds were chosen as the reaction coordinates. Vibrational analyses were not carried out, and therefore it was not possible to identify the stationary points for these transformations. The energy barrier of the thermal ring-opening reaction **2c** → **1c** was calculated to be 48.1 kJ/mol.[34a] The barrier to the ring-closing process was not at all revealed. The same approach has recently been applied[34b] in the AM1[36] investigation of the valence isomerization reaction of indolinespiropyran, which contains the 2*H*-pyran moiety. The calculated energy barrier of thermocyclization of the merocyanine form into the spyrochromene isomer was estimated to be 112.9 kJ/mol, which is 42 kJ/mol higher than the experimental value.[37] The substantial difference between the calculated and experimental values has been attributed to solvation effects that were not taken into account.

We, therefore, reinvestigated the **1c** ↔ **2c** thermal reaction using the same technique employed for the thermal reaction **1b** ↔ **2b**. Two transition-state structures have also been located on the ground-state PES. But only one of these, obtained by the geometry optimization of the conformation of **1c** resembling the disrotatory transition-state structure of the thermal ring-closing reaction **1a** ↔ **2a**, connects the reactant and product valleys (Figure 1e). The second saddle point of the first rank (one negative force constant) corresponds to the transition-state structure of the intramolecular H-transfer reaction.

From the geometry parameters given in Table II it follows that the first aforementioned transition-state structure corresponds to the disrotatory cyclization mode, the calculated energy barrier for this reaction being 35.6 kJ/mol lower than that reported in the earlier study.[33a] All attempts to locate the "symmetry forbidden" conrotatory transition-state structure of the thermal reactions by scanning the PES of **1c** and **2c** in the vicinity of various starting geometries when moving to the saddle point along the reaction coordinate (the C–O distance in **1c**, C–O bond in **2c**) from either reactant or product failed.

The Thermocyclization of But-2-ene-1,4-dione (1d) into 1,2-Dioxacyclohexadiene (2d). The energy characteristics of the thermal reaction **1d** ↔ **2d** are given in Table I. As follows from the data in Table II the value of $\Delta\Delta H$ is negative. This indicates the progressive trend toward destabilizing the ring-closed isomeric forms, relative to their triene isomers, upon substituting terminal meth-

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[37] Bercovici, T.; Heiligman-Rim, R.; Fischer, E. *Mol. Photochem.* **1969**, *1*, 23.

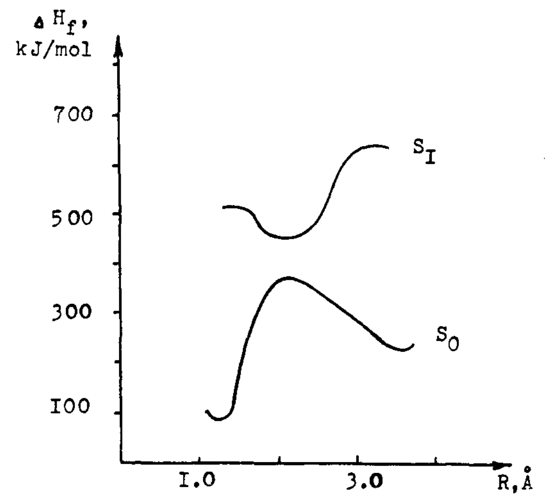

Figure 2. Energy profile of the reaction **1a** ↔ **2a** in the first excited electronic state.

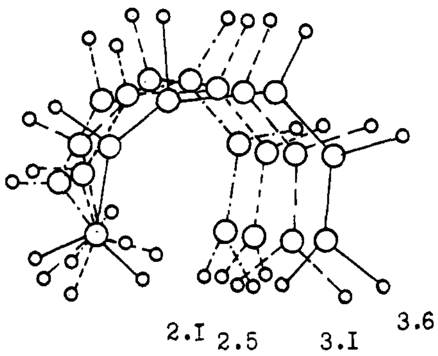

Figure 3. Snap-shot pattern of the nuclear displacements during the reaction **1a** ↔ **2a** in the excited S_1 state.

ylene groups by the isoelectronic heteroatoms. The diheterosubstitution leads to an inversion of the order of stability of these forms.

A careful search for the transition state structures of the **1d** ↔ **2d** reaction revealed only the disrotatory cyclization mode (Table II and Figure 1f). As seen from Table I, the alteration of the relative stability leads to sizeable increases in the energy barrier to the thermal reaction **1d** ↔ **2d**.

The Photocyclization of 1,3,5-Hexatriene. The First Excited Singlet State. The energy profiles for the **1a** ↔ **2a** reaction in both the S_0 and S_1 electron states along the reaction coordinate, i.e., the length of the forming carbon–carbon bond, are shown in Figure 2. The terminal methylene groups in the S_1-state electrocyclization were found to rotate in a conrotatory fashion, the rotation occurring asynchronously (semirotatory[11a–c]). At the first stage of the **1a** → **2a** reaction (2.5 Å < R < 3.5 Å) only one methylene group rotates. The activation energy barrier of 20 kJ/mol is surmounted at R = 3.1 Å. The next stage of the reaction (2.1 Å < R < 2.5 Å) is characterized by the overtaken rotation of the second methylene fragment (Figure 3).

When moving along the S_1-asynchronous conrotatory gradient path, the system relaxes into a well closely approaching the hill on the symmetry-forbidden conrotatory S_0 ground-state reaction path, thus forming a "funnel" through which the diabatic $S_1 \rightarrow S_0$ transition may occur. When passing along the conrotatory reaction path on the S_0 PES the system finds itself in a local minimum corresponding to the topomer of 1,3-cyclohexadiene, whose appearance is predicted by the Woodward–Hoffmann rules. In fact, C_2-symmetry is not conserved along the conrotatory reaction path on the S_1 PES, and the very stereochemical outcome is not due to the orbital conservation requirements, as found to be the case in the 1,3-diene–cyclobutene photochemical interconversion.[13e] The geometry of the intermediate corresponding to the minimum on the S_1 PES is shown in Figure 4. According to a recently suggested definition[38] the structure may be described as a biradicaloid species since it has two nearly degenerate singly-occupied molecular orbitals localized on distantly situated centers.

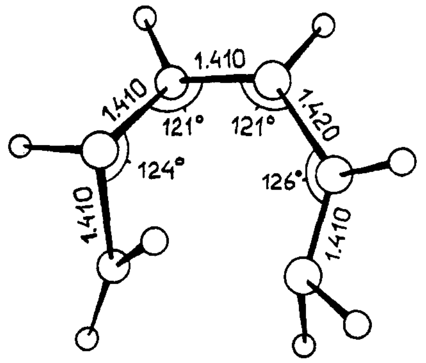

Figure 4. Structure of the intermediate appearing at the S_1 PES of the photoreaction **1a** ↔ **2a**.

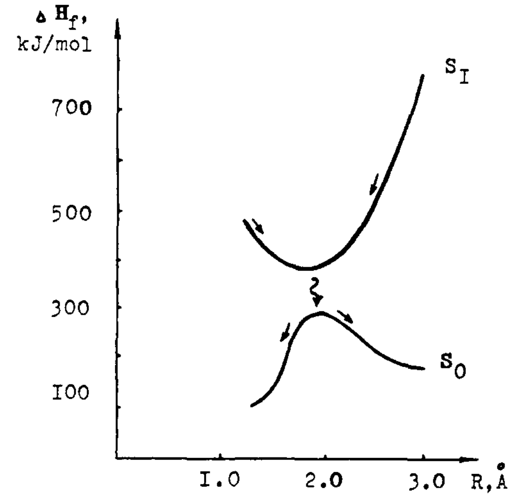

Figure 5. Energy profile of the photoreaction **1b** ↔ **2b**.

No activation barrier has been revealed by the calculations for the reverse ring-opening reaction on the S_1 excited state. This computational prediction is opposite to that obtained from ab initio CI calculations for the 1,3-diene to cyclobutene equilibrium reaction which indicates a presence of the energy barrier for the ring-opening reaction.[39] Our conclusion about the diabatic character of the mechanism of the photoreaction **1a** ↔ **2a** was confirmed by the more recent ab initio 4s2p$^+$ MRD CI calculations.[13f]

The Reactions 1b ↔ 2b and 1c ↔ 2c. According to the MINDO/3 calculations 2,4-pentadienal imine in its stable twisted cZc-conformation converts, after excitation to the S_1 electronic state, through the barrierless conrotatory reaction channel into an intermediate which is a minimum (at the C⋯N distance of 1.8 Å) on the S_1 excited PES (Figure 5). The geometry characteristics of the relevant structure are given in Table IV (supplementary material). It is seen from the shape of the energy profile for the conrotatory thermal reaction that in the vicinity of the same region along the reaction coordinate (1.8 Å)

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the energy hill corresponding to the transition-state structure exists, which provides an ideal pathway for the funneling of S_1 into the S_0 manifold.

The value of the energy difference between the PES's of the S_1 and S_0 states at $R = 1.9$ Å is equal to 44.7 kJ/mol; i.e., the process of the internal conversion $S_1 \rightarrow S_0$ serves as the dominating energy deactivation process.[40]

The mechanism of photochemical ring-opening reaction of 2*H*-pyran in the S_1 excited state is similar; i.e., after excitation the system barrierlessly relaxes to the conrotatory type intermediate (see Table II). After the radiationless transition onto the ground-state PES through the internal conversion it can relax into either 2*H*-pyran or 2,4-pentadienal. A low-energy conrotatory photocyclization channel for 2,4-pentadienal has not yet been found and therefore requires further study. The use of either the length of the forming C–O bond or the value of the corresponding dihedral angle as a reaction coordinate leads to a disrotatory type reaction path with a high activation barrier (>90 kJ/mol).

The First Excited Triplet (T_1) State. The activation barrier of the ring-closing reaction in the first excited T_1 state is calculated to be rather high and equal to 88 kJ/mol. In order to determine whether the photoreaction occurs via the T_1 state, not only does the value of the activation barrier have to be estimated but also the mode by which the T_1 state is populated must also be determined. If the T_1 PES is populated through energy-transfer triplet sensitizers, the calculated activation barriers are as informative as they are in the case of the ground-state reaction. But if the T_1 population occurs through intersystem crossing, then the height of the activation barrier depends on what section of the T_1-state PES this transition happens since the reaction from the "hot" triplet state is possible. Current computer simulation technology cannot address this question.

The transition-state structure for their interconversion has been reached at 2.4 Å (for photoreaction **1a** ↔ **2a** in the T_1-state $R = 2.1$ Å). The calculated activation barrier of the photocyclization equals 32.2 kJ/mol; i.e., the iminosubstitution facilitates the photocyclization in the T_1 state, as was also in the case of the thermoreaction (see Table I).

The energy barriers of the thermal reaction **1b** ↔ **2b** for the T_1 state are listed in Table I. An important point is that all localized transition-state structures on the T_1 state PES belong to the conrotatory type (Table II).

Summary and Concluding Remarks

From earlier computational findings,[12,14] the main peculiarities of the reaction paths and the equilibria of the processes **1** ↔ **2** produced by the heteroatom substitution at the terminal methylene groups of 1,3,5-hexatriene and our interpretation of these peculiarities may be summarized as follows:

1. The photocyclization of 1,3,5-hexatriene includes the diabatic stage—the transition from the PES of the S_1 state on the ground-state PES occurs as a result of internal conversion. The intermediate on the S_1-state PES may be a biradicaloid, although its assignment cannot be unequiovocally made within the "tight–loose" classification.[11a–c]

2. The transition-state structure obtained from the 1,3,5-hexatriene ↔ 1,3-cyclohexadiene disrotatory forbidden ground-state reaction was found to be asymmetric.

3. For the ground- and excited-state reactions **1** ↔ **2** of π-heteroanalogs of 1,3,5-hexatriene (X = O, NH) two reaction paths attributed to the dis- and conrotatory modes were distinguished, the former being lower in energy than for the ground-state reaction. The orientation of the C2–H and C5–H bonds relative to the C1–X6-C5 plane (see Table II) serves as the structural criterion allowing one to assign a reaction channel to either dis- or conrotatory type.

4. Heteroatom substitution at one of the terminal methylene groups of 1,3,5-hexatriene leads to narrowing of the energy gap between the cyclic and open isomeric forms of (**1**, X = O, NH), the cyclic form being more stable. The diheteroatom substitution (the reaction **1d** ↔ **2d**) gives rise to reversal in the relative stability order (the open now being more stable).

Supplementary Material Available: MINDO/3 calculated geometries of compounds **1a–d** and **2a–d**, disrotatory transition-state structures for thermal cyclizations **1a–d** ↔ **2a–d**, conrotatory transition-state structures for thermal cyclization **1a,b** ↔ **2a,b**, and conrotatory transition-state structures for photocyclization **1a–c** ↔ **2a–c** in the T_1-state (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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