

# Transannular Ring Closure of 10-Membered Cyclic Diynes: Model Calculations

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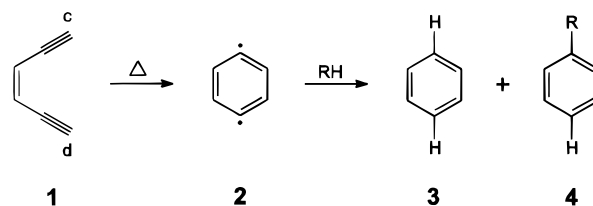
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**Abstract:** The transannular ring closure reaction of the 10-membered cyclic diynes cyclodeca-1,6-diyne (**9a**), 1,6-diazacyclodeca-3,8-diyne (**9b**), and 1,6-dioxacyclodeca-3,8-diyne (**9c**) to the corresponding bicyclo[4.4.0]deca-1,6-diene-2,7-diyl systems (**11a–c**) has been investigated using quantum mechanical methods. To optimize the geometries of the ground states, **9a–c**, the transition states, **10a–c**, and the intermediates, **11a–c**, we employed the CASSCF(8,8)/6-31G\* procedure. The inclusion of dynamic correlation (CASPT2[0] and CASPT2-[g1]) approximations was necessary to reproduce the thermodynamic parameters obtained experimentally for **9a** → **11a**. Our calculations reveal that the activation energy for the ring closures **9** → **11** depends on the distance between the triple bonds. The alternative of the ring closure of **9a** to bicyclo[5.3.0]deca-1,6-diene-2,6-diyl (**13a**) is predicted to occur at a higher activation energy (ca. 7 kcal/mol) than that for ring closure to **11a**. A comparison with the Bergman cyclization reveals late transition states for **9a–c** → **11a–c**, in which the conjugation of the developing 4π system plays no role.

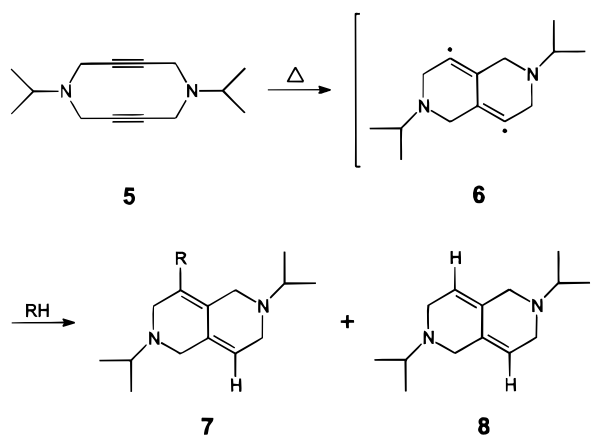
The thermal cyclization of (*Z*)-hex-3-ene-1,5-diyne (**1**) to 1,4-dehydrobenzene (**2**) and via hydrogen abstraction to benzene (**3**) was studied in the 1970s by R. G. Bergman et al.<sup>1,2</sup> At the end of the 1980s, it was recognized that, in a number of natural products,<sup>3</sup> such as calicheamicin, esperamicin, and dyneamicin, a ring closure of an enediyne generates a 1,4-dehydrobenzene fragment, which is capable of abstracting hydrogen atoms from DNA. This realization, coupled with the antitumor activities of the above natural products, spurred a number of investigations, including the synthesis of simple cyclic models,<sup>4</sup> thermochemical investigations,<sup>5</sup> sophisticated calculations,<sup>6,7</sup> and the synthesis of calicheamicin.<sup>8</sup> Studies on simple monocyclic enediynes revealed that the distance between the terminal carbon atoms of the triple bonds strongly affects the activation energy for ring closure. It was found that monocyclic enediynes in which this distance (*c–d* in Scheme 1) is less than 3.2 Å cyclize rapidly at 25 °C.<sup>4</sup>

The enediyne studies motivated us to investigate those nonconjugated cyclic diynes of medium ring size in which the

## Scheme 1



## Scheme 2



distance between the two triple bonds was found to be 3 Å or less.<sup>9</sup> The first investigations we carried out involved the thermolysis of 1,6-diisopropyl-1,6-diazacyclodeca-3,8-diyne (**5**),<sup>10</sup> as shown in Scheme 2. Carrying out the thermolysis of **5** in the presence of hydrocarbons, such as 1,4-cyclohexadiene, 9,10-dihydroanthracene, and cyclooctane, yielded the products

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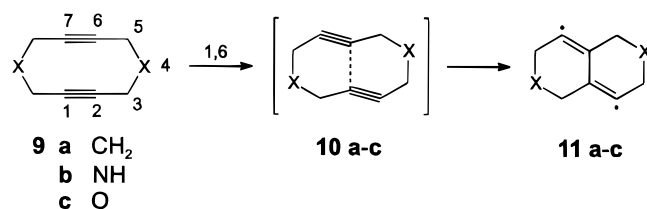
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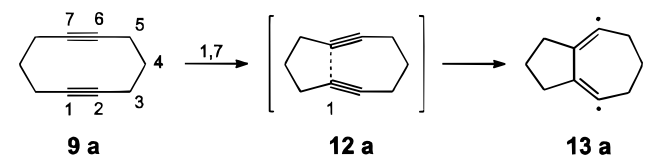
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## Scheme 3



## Scheme 4



7 and 8. These findings led us to study this reaction in more detail. The questions which were of interest to us were the following: (1) Is the reaction limited to the 1,6-diazacyclodeca-3,8-diyne system? (2) Why is only the bicyclo[4.4.0]deca-1,6-diene-2,7-diyl system formed? (3) What is the electronic nature of the putative butadiendiyl biradical intermediate?

To answer these questions, we carried out several additional experimental and computational studies. Among them was the investigation of the gas-phase thermolysis of 1,6-cyclodeca-diyne<sup>11</sup> and a kinetic study of the reaction of **5** with 9,10-tetrauterioanthracene in different solvents.<sup>12</sup>

In this paper, we report quantum chemical studies concerned with the ring closures of cyclodeca-1,6-diyne (**9a**), 1,6-diazacyclodeca-3,8-diyne (**9b**), and 1,6-dioxacyclodeca-3,8-diyne (**9c**) to the corresponding biradical intermediates (**11a-c**) and the transition states (**10a-c**) for these reactions (see Scheme 3). For **9a**, we describe our explorations of the reaction path for a 1,7-ring closure to bicyclo[5.3.0]deca-1,6-diene-2,6-diyl (**13a**) via transition state **12a** (Scheme 4) and compare the energetics of this reaction with that of the 1,6-ring closure of **9a** to **11a**. The gas-phase thermolysis of **9a** to **11a** yielded an activation energy of 28.9 kcal/mol. For the back reaction of **11a** to **9a**, the activation energy was determined to be 4.3 kcal/mol.<sup>11</sup>

## Methods

Molecular orbital (MO) methods were used to calculate the structures of the reactants (**9a-c**), the biradical intermediates (**11a-c** and **13a**), and the transition states connecting them. For the diradical species **11a-c** and **13a**, we assumed a half-chair conformation of the five-, six-, and seven-membered rings. We further assumed that *C<sub>i</sub>* symmetry is maintained during the reaction of **9a-c** to **11a-c**, while in the cyclization of **9a** to **13a** we assumed that *C<sub>s</sub>* symmetry is preserved.

Reactants **9a-c** and intermediates **11a-c** and **13a** have different types of electronic structures. While **9a-c** are closed-shell molecules, the intermediates are biradicals. Thus, for calculating the reaction paths, a multiconfigurational approach must be used. We chose to perform complete active space self-consistent field (CASSCF)<sup>13</sup> calculations. To include the effect of dynamic electron correlation,<sup>14</sup> we used a multireference second-order perturbation treatment (CASPT2)<sup>15,16</sup> based on the CASSCF wave functions.

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**Model I.**<sup>17-19</sup> The geometrical parameters of **9a-c**, **11a-c**, and **13a** as well as the transition states **10a-c** and **12a** were optimized using CASSCF(8,8)/6-31G\* calculations. The active space for **9a-c** contained all of the in- and out-of-plane  $\pi$  and  $\pi^*$  orbitals. For the rest of the stationary points, the in-plane  $\pi$  and  $\pi^*$  orbitals were replaced by the newly formed  $\sigma$  and  $\sigma^*$  orbitals and the combinations of the nonbonding  $\sigma$  orbitals belonging to the irreducible representations  $A_g$  and  $A_u$ . Frequency calculations were then carried out at each of the structures located to verify the nature of the stationary point. It turned out that **9a-c**, **11a-c**, and **13a** have no imaginary frequency, whereas each of **10a-c** and **12a** have exactly one.

**Model II.** The geometrical parameters of **9a-c** were optimized by the CASSCF(8,8)/6-31G\* procedure. The geometrical parameters of the transition states **10a-c** and **12a**, as well as the local minima **11a-c** and **13a**, were found by carrying out single-point CASPT2/6-31G\* calculations at different C(1)-C(6), C(1)-C(7) for **12a**, **13a** distances, with all other geometrical parameters optimized at the CASSCF level. The C(1)-C(6) distance was changed in increments of 0.025 Å, and for transition states **10a-c**, the C(1)-C(6) distance of maximum energy was located. For intermediates **11a-c**, the C(1)-C(6) distance of minimum energy was found. To locate **12a**, the C(1)-C(7) distance was changed in increments of 0.025 Å. For the intermediate **13a** the C(1)-C(7) distance of minimum energy was found. All electrons, except those in the 1s core orbitals of heavy atoms, were correlated in the CASPT2 calculations.

**Model IIa.** The calculations for **9a** → **11a** and **9a** → **13a** were performed with CASPT2[0]<sup>15</sup> approximation.

**Model IIb.** Instead of the CASPT2[0], we used the CASPT2[g1]<sup>16</sup> procedure.

## Results

Since we have been able to study the ring closure of **9a** to **11a** in the gas phase,<sup>11</sup> we investigated the reaction paths from **9a** to **11a** and **13a** in more detail than those from **9b** and **9c** to, respectively, **11b** and **11c**. Therefore, we will first discuss the results found for **9a**.

**Geometries.** In Table 1 we compare the geometrical parameters derived for **9a** with the different models and the results of an X-ray investigation.<sup>20</sup> The agreement between experiment and calculation is very good. Interestingly, the bond lengths obtained at the RHF/3-21G level are somewhat closer to experiment than the ones derived from the CASSCF(8,8)

(17) CASSCF(8,8) and all CASPT2 calculations were carried out with the following programs: (a) Andersson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS*, Version 3; University of Lund, Sweden, 1994. (b) Andersson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS*, Version 4; University of Lund, Sweden 1997.

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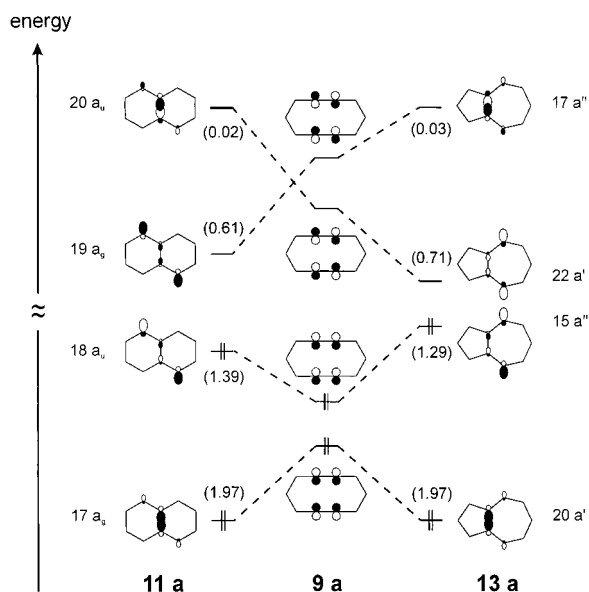
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**Table 1.** Comparison between Measured (X-ray) and Calculated Bond Lengths (Å) and Bond Angles (deg) of **9a**

method	C(1)–C(7)	C(1)–C(6)	C(1)–C(2)	C(2)–C(3)	C(1)–C(10)	C(10)–C(1)–C(2)	C(1)–C(2)–C(3)
X-ray	2.991(2)	3.217	1.188(2)	1.466(3)	1.473(2)	171.2(2)	172.2(2)
HF/3-21G	2.979	3.206	1.188	1.468	1.468	172.8	172.9
CASSCF(8,8)/3-21G	2.998	3.232	1.209	1.474	1.474	172.4	172.4
CASSCF(8,8)/6-31G*	3.066	3.296	1.210	1.476	1.476	171.0	171.1

**Table 2.** Bond Lengths (Å) and Bond Angles (deg) Calculated for the Transition State **10a** and the Intermediate **11a**

method	C(1)–C(6)	C(1)–C(2)	C(2)–C(3)	C(1)–C(10)	C(10)–C(1)–C(2)	C(1)–C(2)–C(3)
<b>10a</b>						
CASSCF(8,8)/6-31G*	1.779	1.287	1.488	1.506	135.2	134.6
CASPT2/6-31G*	1.925	1.260	1.483	1.500	141.8	139.2
<b>11a</b>						
CASSCF(8,8)/6-31G*	1.564	1.320	1.493	1.514	127.4	130.5
CASPT2/6-31G*	1.525	1.325	1.493	1.516	126.2	130.1

**Figure 1.** Correlation between the in-plane  $\pi$  and  $\pi^*$  MOs of **9a** with the corresponding MOs of **11a** (left) and **13a** (right). For each orbital of **11a** and **13a**, the occupation numbers  $n(\varphi)$  are given in parentheses.

calculations. We ascribe this to our limitation of the active space (8/8). Due to this restriction, the weights of the  $\pi^*$  levels were overestimated. Consequently, this resulted in a lengthening of the triple bonds. In Table 2 we list the calculated geometrical parameters derived for the transition state **10a** and the local minimum **11a**. It is seen that the geometries vary significantly between the CASSCF(8,8) and CASPT2 methods for locating **10a** and **11a**. However, with both methods, the C(1)–C(6) bond length calculated for transition state **10a** is clearly closer to diradical **11a** than to reactant **9a**. Thus, we are obviously dealing with a “late” transition state for this reaction. This is also in line with Hammond’s postulate.<sup>21</sup>

**Electronic Structure.** During the reaction of **9a** to **11a**, the two  $\pi$  and two  $\pi^*$  linear combinations in the molecular plane— $17a_g(\pi_+)$ ,  $18a_u(\pi_-)$ ,  $19a_g(\pi^*_+)$ , and  $20a_u(\pi^*_-)$ —are transformed into the C(1)–C(6)  $\sigma$  ( $17a_g$ ) and the corresponding  $\sigma^*$  orbital ( $20a_u$ ) plus the two nonbonding orbitals,  $18a_u$  and  $19a_g$ . The latter pair is close in energy, with  $18a_u$  calculated to be slightly lower in energy (see left side of Figure 1). If we consider only the two highest occupied MOs shown in Figure 1, we can write a two-configuration wave function for **11a** as follows:

$$\Psi = \alpha | \dots 17a_g^2 18a_u^2 \rangle - \beta | \dots 17a_g^2 19a_g^2 \rangle$$

(21) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. See also: Farcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76.

**Table 3.** Calculated Occupation Numbers of Orbitals  $18a_u$  and  $19a_g$ <sup>a</sup>

C(1)–C(6) (Å)		$n(18a_u)$	$n(19a_g)$
3.296	<b>(9a)</b>	1.933	0.059
2.700		1.925	0.060
2.300		1.905	0.093
2.100		1.876	0.126
1.925	<b>(10a)</b>	1.796	0.208
1.900		1.776	0.228
1.700		1.554	0.450
1.525	<b>(11a)</b>	1.394	0.610

<sup>a</sup> The values are taken from CASSCF(8,8)/6-31G\* calculations

**Table 4.** Energies (kcal/mol) of **10a** and **11a**, Relative to **9a**, Obtained by Different Types of Calculations (See Text)

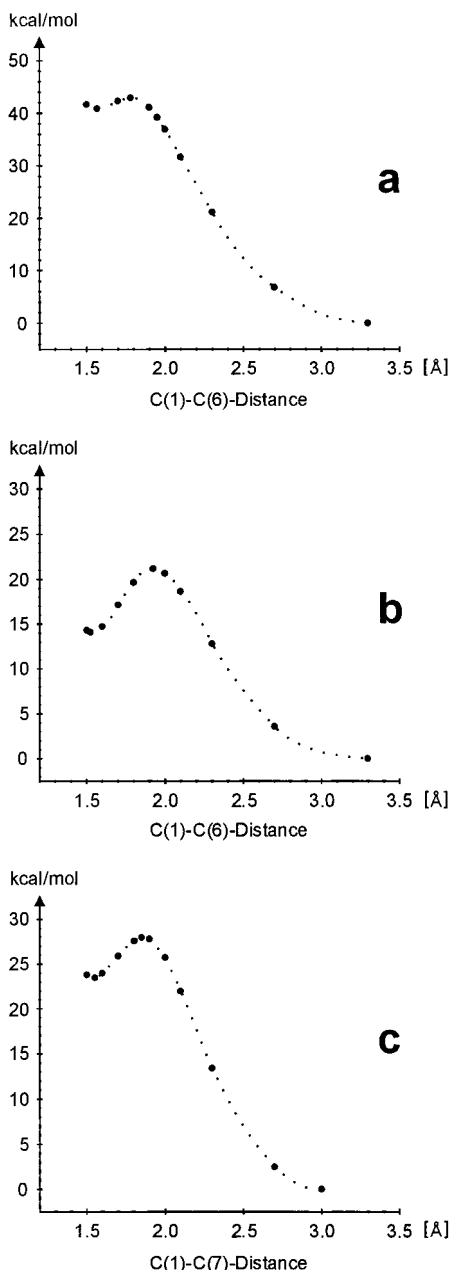
	<b>10a</b>	<b>11a</b>
CASSCF(8,8)/6-31G* (model I)	43.0	40.9
CASPT2[0]/6-31G* (model IIa)	21.1	14.1
CASPT2[g1]/6-31G* (model IIb)	21.4	15.1
CASPT2[0]/6-31G**	21.0	13.8
CASPT2[g1]/6-31G**	21.3	14.8

If **11a** were a perfect biradical both frontier orbitals,  $18a_u$  and  $19a_g$ , would be equally populated. Thus, the occupation numbers  $n(\varphi)$  of these two orbitals should be a good measure of the biradical character along the reaction coordinate.

In Table 3 we have listed the occupation numbers of  $18a_u$  and  $19a_g$ . The results in Table 3 reveal that the biradical character increases on going from **9a** to **11a**, but **10a** and **11a** are still far away from being “perfect”. The occupation number of  $18a_u$  remains larger than that of  $19a_g$  in **11a**. This outcome is also in line with our finding that the triplet state ( $^3A_u$ ) is above the singlet state ( $^1A_g$ ) (see below, Table 7). This means that, like the case in butane-1,4-diyl,<sup>22</sup> through-bond coupling becomes important in **11a**.

**Thermodynamic Data.** The energies of **11a** and **10a**, relative to that of **9a**, are given in Table 4 for each of the different models. At the CASSCF(8,8)/6-31G\* level (model I), the activation energy was predicted to be 43 kcal/mol (Figure 2a). A comparison with the experimental value ( $\Delta H^\ddagger = 28.9$  kcal/mol)<sup>11</sup> reveals that this result is far off. We ascribe this failure to the neglect of dynamic correlation, which must be included to describe the electronic structure of biradicals property.<sup>14</sup> At the CASPT2[0]/6-31G\* (CASPT2[g1]/6-31G\*) level (model II), we calculate an activation energy of 21.1 (21.4) kcal/mol for the ring closure process of **9a** to **11a** and an energy difference of 14.1 (15.1) kcal/mol between **9a** and **11a**. When we used

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**Figure 2.** Reaction profile of the cyclization of **9a** to **10a** with C(1)–C(6) as reaction coordinate using model I (a) and model IIa (b). Reaction profile for the cyclization of **9** to **13a** with C(1)–C(7) as reaction coordinate using model IIa (c).

the 6-31G\*\* basis set instead of the 6-31G\* one, the change in energies amounts to only 0.1–0.3 kcal/mol. Each of the CASPT2 values is smaller than the corresponding experimental values but much closer to the latter than the CASSCF.

The calculations on **9a**, **10a**, and **11a** reveal that the inclusion of the dynamic correlation energy is necessary in order to obtain realistic values for the activation energy.<sup>14</sup> Since CASPT2 uses second-order perturbation theory, it overestimates the dynamic correlation energy. Nevertheless, the CASPT2 energies are in much better agreement with experiment than the CASSCF energies

#### Comparison between a 1,6- and 1,7-Ring Closure of **9a**.

As mentioned in the introduction, there are two possible modes of the ring closure between the triple bonds of **9a–c** since the formation of a  $\sigma$  bond can occur between C(1) and C(6) or C(1)

**Table 5.** Bond Lengths (Å) and Bond Angles (deg) Calculated for the Transition State **12a** and the Intermediate **13a** Using Model IIa

	<b>12a</b>	<b>13a</b>
C(1)–C(7)	1.850	1.550
C(1)–C(2)	1.268	1.320
C(2)–C(3)	1.488	1.494
C(1)–C(10)	1.505	1.520
C(10)–C(1)–C(2)	139.6	127.7
C(1)–C(2)–C(3)	141.8	135.4

**Table 6.** Energies (kcal/mol) of the Transition States (TS) **10a–10c**, **12a**, and **15<sup>#</sup>** and the Local Minima (LM) **11a–c**, **13a**, and **15**, Relative to **9a–c** and **14**, Obtained by Models I and II

	Model I		Model IIa		Model IIb	
	TS	LM	TS	LM	TS	LM
<b>9a</b> → <b>10a</b> → <b>11a</b>	43.0	40.9	21.1	14.1	21.4	15.1
<b>9b</b> → <b>10b</b> → <b>11b</b>	40.4	39.1	17.8	10.7	18.0	10.9
<b>9c</b> → <b>10c</b> → <b>11c</b>	38.1	36.4	16.9	9.9	17.1	10.5
<b>9a</b> → <b>12a</b> → <b>13a</b>	49.2	48.1	27.6	23.2	28.0	24.0
<b>14</b> → <b>15<sup>#</sup></b> → <b>15</b>	49.4	46.8	29.5	22.7	29.7	24.0

and C(7) of 1,6-cyclodecadiyne. The 1,6-ring closure has been treated in detail in the preceding section.

Using models IIa and IIb, we have calculated the energetics for the reaction of **9a** to **13a** via **12a**. It was found in both models that the energy of transition state **12a** is 7 kcal/mol above that of **10a**, and the local minimum in **13a** is 9 kcal/mol higher in energy than that in **11a** (see Figure 2c). The energies of the transition states mirror the energies of the products. This is anticipated for late transition states as in our cases.

The higher energy for the 1,7-ring closure can be traced back to a stronger destabilization of the HOMO, which cannot be fully compensated by a stronger stabilization of the HOMO-1 (see Figure 1, right side). As a consequence, a smaller HOMO–LUMO gap is predicted for the 1,7-ring closure as compared to the 1,6-ring closure. This can be seen from the occupation numbers given in Figure 1. It is seen that the occupation number of the HOMO of **11a** is larger and that of the LUMO is smaller than the corresponding values calculated for **13a**. In Table 5 we have listed the geometrical parameters calculated for **12a** and **13a** using model IIb.

#### Comparison between the Reaction Coordinates of **9a–c**.

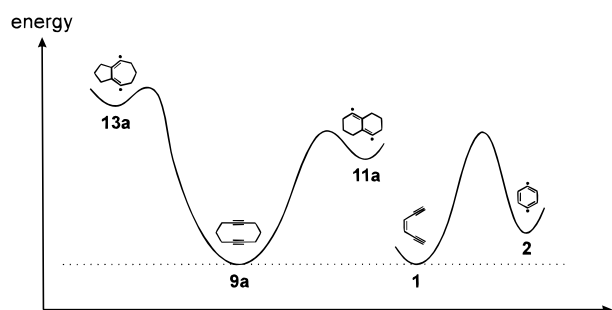
Using models IIb and IIc, we have calculated the reaction coordinate for the ring closure of **9a–c** to **11a–c**. In Table 6 we have summarized the calculated activation energies. For the reaction of **9a–c** to **11a–c**, respectively, we find for both models the highest activation energy for **9a** and the lowest for **9c**. For the back reaction, **11a–c** to **9a–c**, the activation energy is about the same. We ascribe this to a smaller C(1)–C(6) (C(1)–C(7)) distance, which was found to be 3.22 Å (2.99 Å) for **9a**, 3.16 Å (2.93 Å) for **9b**, and 3.14 Å (2.91 Å) for **9c**. We do not find any contribution of the lone pairs at the nitrogen atoms (**9b**) or oxygen atoms (**9c**) to the activation energy. Our qualitative finding that **5** reacts faster than **9a** is in line with these predictions. To determine the effect of resonance stabilization in the transition state from **1** → **2**, we also calculated the reaction path **14** → **15**, which was already performed at the CASSCF/6-31G\* level.<sup>23</sup> We used models I and II assuming that  $C_2$  symmetry is preserved during the reaction from **14** to **15** (cf. Table 6).

In Table 7 we list the energy differences between the lowest singlet ( $^1A_g$ ) and triplet ( $^3A_u$ ) states of the local minima **11a–c**

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**Table 7.** Energy Difference,  $\Delta$  (kcal/mol), between the Singlet ( $^1A_g$ ) and Triplet ( $^3A_u$ ) States of **11a–11c** and **13a** Using Model IIb

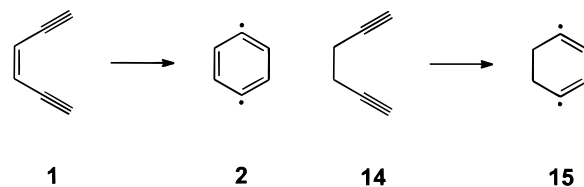
	$\Delta$
<b>11a</b>	9.7
<b>11b</b>	13.5
<b>11c</b>	12.8
<b>13a</b>	4.8

**Figure 3.** Comparison of the reaction profiles for **1** to **2** and **9a** to **11a** and **13a**, respectively.

and **13a** using model IIb. For the 1,6-ring closure, the energy of the singlet state was predicted to be well below the triplet state. This is partly due to a relatively large HOMO–LUMO gap in **11a** (see Figure 1, left-hand side). For **13a**, the HOMO–LUMO gap is smaller due to a destabilization of **15a''** and a stabilization of **22a'** (see Figure 1, right-hand side). As a result, a small singlet–triplet gap for **13a** was found.

### Discussion and Conclusion

In Figure 3 we have compared parts of the potential energy surface of the Bergman cyclization (**1**  $\rightarrow$  **2**) and the 1,6-cyclization of 1,6-cyclodecadiyne (**9a**  $\rightarrow$  **11a**). As reaction coordinate, we chose in both systems the distance between the centers 1 and 6. This comparison reveals, for the geometry of the corresponding transition states C(1)–C(6), distances of 2.11 Å for the Bergman cyclization and 1.93 Å for the cyclization of **9a** to **11a**; i.e., the latter transition state is “later” than that of the Bergman cyclization. The comparison furthermore shows very similar values for the measured (calculated) activation energies. In the case of **1**  $\rightarrow$  **2**, the value is 28.2 kcal/mol<sup>5</sup> (CASPT2/DZP, 23.1 kcal/mol<sup>6</sup>) and for **9a**  $\rightarrow$  **11a**, 28.9 kcal/mol<sup>11</sup> (CASPT2/6-31G\*, 21.4 kcal/mol). This similarity of the energies is accidental, because the differences in the structures and reactions of **1** and **9a** are too big to conclude directly anything from this resemblance. Since both transition states are different in their C(1)–C(6) distances, the question arises as to the contribution of the resonance energy, especially in the case of the Bergman cyclization. To elucidate the difference between the two reactions, we consider the ring closure of 1,5-hexadiyne (**14**) to 1,3-cyclohexadiene-1,4-diyl (**15**) (Scheme 5). This is the model reaction for **1**  $\rightarrow$  **2** without the aromatic stabilization, and it has been studied theoretically<sup>23</sup> at the CASSCF/6-31G\* level and experimentally in the gas phase.<sup>24</sup> The calculated

**Scheme 5**

activation energy from **14** to **15** obtained by CASPT2 calculations amounts to 29.5 kcal, whereas the activation energy for the back reaction (**15**  $\rightarrow$  **14**) amounts to 6.8 kcal/mol (cf. Table 6). The comparison of the activation energies for **1**  $\rightarrow$  **2** and **14**  $\rightarrow$  **15** leads to a stabilization of the transition state of **1**  $\rightarrow$  **2** of about 6 kcal/mol by delocalization. The “aromatic” stabilization of the Bergman cyclization is rather small. This is understandable if one considers the relatively long C(1)–C(6) distance in the transition state. The effect of conjugation in the reaction of **1**  $\rightarrow$  **2** comes into consideration only after the transition state has passed. It finally shows up in the stabilization of **2** (19.8 kcal/mol)<sup>5</sup> as compared to **11a** (4.3 kcal/mol).<sup>11</sup> The activation energy of the Bergman cyclization can be lowered by incorporating **1** into a medium-sized ring system. This ensures the necessary bending of the  $\sigma$ -bonds at the sp centers in the ground state. By the same token, one can incorporate the diyne system of **9a** into a conjugated system. This leads to 1,6-didehydro-[10]annulene, which shows a half-life time of 25 min at  $-51$  °C.<sup>25</sup> As anticipated, it undergoes a rapid first-order cyclization to 1,5-dehydronaphthalene.

From our computations, we conclude that our model calculations using a multiconfigurational approach are able to reproduce the experimentally determined activation energies in the case of the system **9a–10a–11a** reasonably well. This justifies the extension to the systems **9b** and **9c**. The result that the activation energy correlates with the transannular distance of the triple bonds is of interest insofar as it guides us in our search for substances with lower activation energies. Also of interest, with respect to our experimental efforts to determine the spin state of the intermediates (**11a–c**), is the finding that the reaction proceeds on the singlet surface throughout and there is a considerable energy difference between the singlet and triplet states. This has been confirmed very recently by trapping experiments.<sup>12</sup> A third point which we would like to make considers the 1,6- vs 1,7-ring closure. In our experiments with transannular ring closure, we mostly find the bicyclo[4.4.0]deca-1,6-diene system.<sup>10,11,26</sup> The results of our calculations rationalize this in a satisfactory way.

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