Theoretical Investigation of the Conrotatory Ring Opening of Cyclobutene and 1,2-Dihydro-1,2-diazacyclobutadienes with Ab Initio and Density Functional Gaussian-Type-Orbital Approach

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ABSTRACT

The theoretical study of the thermally allowed conrotatory opening of cyclobutene (1) and cis- (2) and trans-1,2-dihydro-1,2-diazacyclobutadiene (3) were performed with ab initio and density functional calculations. The reactants and the transition states were fully optimized by using the 6-31 + G** basis set with RHF, MP2, SVWN, and BLYP methods. The calculated activation barriers for the ring opening of 1 with both MP2 and SVWN incorporating ZPVE correction give extraordinary agreement with the experimental value. The predicted activation energies for 2 and 3 are lower than in the case of the cyclobutene ring opening. Of the two 1,2-dihydro-1,2-diazacyclobutadiene isomers, the trans isomer has a lower activation barrier. The structural and energy differences and the trend among these compounds are interpreted in terms of orbital overlap and steric interactions in the course of the conrotatory ring opening. © 1995 John Wiley & Sons, Inc.

Introduction

Cyclobutene and its heterocyclic derivatives play an important role not only from a theo-

retical standpoint in giving a better understanding of the mechanisms of pericyclic reactions [1] but also have considerable practical importance for the synthesis of valuable organic compounds [2]. Heterocyclobutene can serve as a source of organic compounds that contain the heterobutadiene moiety.It is interesting to see whether the breaking of the heteroatom–heteroatom bond follows the Woodward–Hoffmann rules for electrocyclic reac-

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tions and the effect of the *cis–trans* isomerism on the activation energy of heterocyclobutene opening.

The most valuable characteristic of computational chemistry is its accuracy and efficiency in predicting the molecular geometry, vibrational frequency, isomer stability, and reaction outcome. These predictions are becoming invaluable in planning organic synthesis, molecular biology, catalyses, and material science. For many organic compounds that include only second-row elements when bond formation–breaking and weak complexation is not involved, Hartree–Fock calculations produce reasonable geometries, energies, and vibrations [3]. Electron correlation and multireference representation is not implemented in Hartree–Fock calculations needed when modeling bond formation–breaking or weakly bonded complexes. Inclusion of correlation typically increases the computational requirements dramatically and seems to be practical only for small molecules [4]. Although in many computational chemistry studies second-order Møller–Plesset perturbation theory as well as quadratic CI calculations have been used routinely [3], there are only a few density functional theory (DFT) [5] studies for transition states. That is surprising because there is increasing evidence that DFT offers a promising alternative to the Hartree–Fock approach [6] and gives much better accuracy than do RHF or even MP2 calculations for normal systems [7] and when loose complexes are formed [8].

The study of the butadiene ring opening has been carried out at different theory levels [9]. A recent study was carried out by Bachrach and Liu [10] up to the MP2/6-31G*//HF/6-31G* level. Their prediction of the activation energy was 4.5 kcal above the experimental value of 32.9 [11], although Houk has previously reported better results at the MP2/6-31G* level [9]. Although there is no experimental data for 1,2-dihydro-1,2-diazacyclobutene to compare with the theoretical results, there is experimental evidence that the ring opening of dicarboxylate diazete goes very smoothly [12]. Previously predicted activation barriers for *trans*- and *cis*-1,2-dihydro-1,2-diazete are 22.95 and 24.58 at MP2/6-31G*//HF/6-31G*, respectively [13]. Here, we are presenting our study of these rings opening with both ab initio and density functional theory approaches.
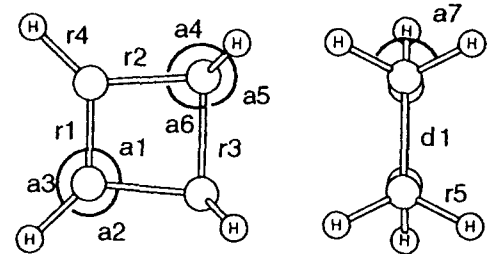
Computational Methods

Gaussian 92/DFT [14] was employed to fully optimize the geometries without any symmetry constraints at the restricted Hartree–Fock (RHF) level [3] with the standard basis set, 6-311 + G(d, p). At the correlated level, the structures were optimized by applying second-order Møller–Plesset (MP2) theory, keeping the core electrons frozen (FC) [15]. The geometries of the studied structures were also optimized by the LSDA [16] and BLYP [17] DFT methods with the same basis set.

Results and Discussion

All calculations on these systems were performed with relatively large basis sets (6-311 + G**) because the previous results on the cyclobutene ring opening, even with 6-31G* at the MCSCF [18] and MP4(SDTQ) [9] levels, are more than 1 kcal/mol from the experimental value. It is also indicative that the activation barrier obtained with MP2/6-31G**//MP2/6-31G* are almost the same as the ones with the MP4(SDTQ)/6-31G*//MP2/6-31G* (36.8 vs. 36.6 kcal/mol) theoretical model [9]. Therefore, it was of interest to determine whether the larger basis set with ab initio and density functional theory methods will be able to predict the correct activation energy for the conrotatory cyclobutene ring opening. Furthermore, the same theoretical model should be able to predict the activation energies for the diazacyclobutene isomers.
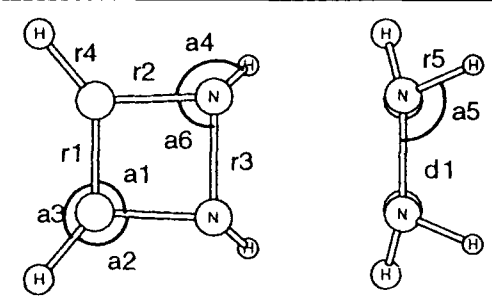
GEOMETRIES

The geometries of the reactants in our theoretical study of ring opening are presented in Tables I–III. The geometries optimized with different ab initio and DFT methods as expected have different geometries. Although the predicted geometries of the four-membered rings with four different theoretical models are very similar, there are some very interesting structural characteristics. If we assume that MP2/6-311 + G** gives the most reliable geometry parameters of the reactants, then RHF/6-311 + G** and SVWN/6-311 + G** constantly underestimate the bond distances, while BLYP/6-311 + G** overestimates them by less than

TABLE I _____
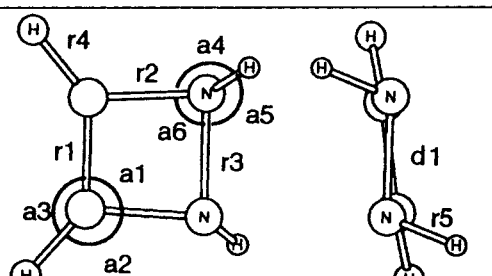**Geometrical parameters of cyclobutadiene (1).**

Theor. Model	r1	r2	r3	r4	r5	a1	a2	a3	a4	a5	a6	d1
RHF / 6-311 + G**	1.323	1.516	1.563	1.076	1.086	94.5	132.3	133.3	115.7	114.9	85.5	0.0
MP2 / 6-311 + G**	1.352	1.519	1.571	1.086	1.094	94.0	132.4	133.5	115.7	114.5	85.9	0.0
SVWN / 6-311 + G**	1.340	1.500	1.551	1.093	1.103	94.0	132.4	133.6	115.9	114.8	86.0	0.0
BLYP / 6-311 + G**	1.350	1.530	1.587	1.091	1.100	94.4	132.0	133.5	115.9	114.8	85.6	0.0

1% on average (Table IV). It should be noted, though, that all employed theoretical models generated structures of the reactants have very similar structural characteristics and no significant changes from previously obtained results [9]. The difference from the MP2/6-311 + G**-generated structure and the one generated by the other theoretical models are below 1% in bond distance and below 0.1% in bond angles (Table IV). Though the agreement for 2 and 3 are excellent, the differences are higher than for 1, which is expected for molecules that contain heteroatoms. On average, the difference is in the range of 1.6% for the bond distances and below 1% for the bond angles.

The geometries of the transition state for conrotatory ring opening are presented in Tables V–VII. The sums of the bond distances and the bond angles, as well as their deviation from the MP2/6-311 + G** values for the transition-state structures, are presented in Table VIII. Because the number of bonds and angles for these three systems (cyclobutene and two of diazetes) are different, their comparison can be performed only qualitatively. On the basis of results obtained with different theoretical models for the reference structure of the reactants, it is expected that the best agreement in the prediction of the structural parameters will be obtained for all-carbon transition

TABLE II _____
Geometrical parameters of _cis_-1,2-dihydro-1,2-diazete (2).

Theor. Model	r1	r2	r3	r4	r5	a1	a2	a3	a4	a5	a6	d1
RHF / 6-311 + G**	1.324	1.428	1.452	1.070	1.003	92.6	127.8	138.8	114.9	112.0	87.4	0.0
MP2 / 6-311 + G**	1.361	1.436	1.474	1.081	1.021	92.3	126.9	138.8	115.0	111.6	87.7	0.0
SVWN / 6-311 + G**	1.356	1.415	1.438	1.087	1.027	91.7	127.0	139.0	118.5	114.2	88.4	0.0
BLYP / 6-311 + G**	1.360	1.450	1.503	1.085	1.029	92.8	126.5	138.6	115.6	111.6	87.2	0.0

TABLE III

Geometrical parameters of *trans*-1,2-dihydro-1,2-diazete (2).

Theor. Model	r1	r2	r3	r4	r5	a1	a2	a3	a4	a5	a6	d1
RHF / 6-311 + G**	1.323	1.428	1.449	1.070	1.003	92.4	128.3	139.4	114.8	109.5	87.3	6.0
MP2 / 6-311 + G**	1.357	1.437	1.480	1.080	1.022	92.2	127.8	140.0	114.5	108.4	87.3	8.0
SVWN / 6-311 + G**	1.351	1.418	1.444	1.086	1.029	91.7	128.0	140.0	117.0	110.7	87.9	6.8
BLYP / 6-311 + G**	1.356	1.451	1.509	1.084	1.030	92.8	127.4	139.8	114.9	108.5	86.8	7.5

structure 4. Indeed, the agreement is extraordinary between the noncorrelated RHF method and the other correlational methods. The maximal bond distance deviation, as expected, is between MP2 and RHF, and that is only 0.84%. Surprisingly enough, better agreement in the bond distance is obtained with SVWN than with the usually more accurate BLYP DFT method. The bond difference is only 0.02% from the one predicted with the MP2 me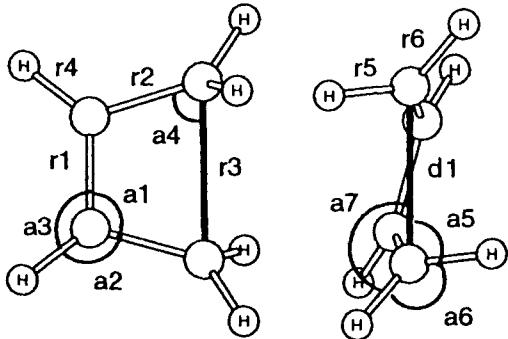thod (Table VIII). The bond angles are, on aver-age, 0.1% different for all four methods. That represents an extraordinary agreement in the geometry prediction of the transition state 4 by both Gaussian and DFT methods. The agreement is not so great anymore in the case of the dihedral angles. The difference for the CCCC dihedral angle (ring pucker) is over 2% (Table V).

The accuracy of geometry prediction for the transition structure 5 and 6, where bonds are broken–formed, should be lower. Furthermore, be-

TABLE IV

Calculated sum of bond distances and angles for four-membered rings 1, 2, and 3.
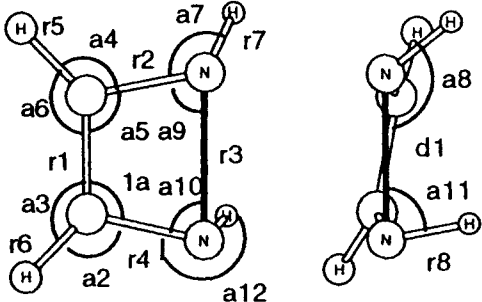
	Sa	%a	Sr	%r
Cyclobutene (1)				
RHF / 6-311 + G**	6.564	−0.88	676.2	0.03
MP2 / 6-311 + G**	6.622	0.00	676.0	0.00
SVWN / 6-311 + G**	6.587	−0.83	676.7	0.10
BLYP / 6-311 + G**	6.658	0.54	676.2	0.03
cis-1,2-Dihydro-1,2-diazete (2)				
RHF / 6-311 + G**	6.277	−1.51	673.5	0.18
MP2 / 6-311 + G**	6.373	0.00	672.3	0.00
SVWN / 6-311 + G**	6.323	−0.78	678.8	0.97
BLYP / 6-311 + G**	6.427	0.85	672.3	0.00
trans-1,2-Dihydro-1,2-diazete (3)				
RHF / 6-311 + G**	6.273	−1.62	671.7	0.22
MP2 / 6-311 + G**	6.376	0.00	670.2	0.00
SVWN / 6-311 + G**	6.328	−0.75	675.3	0.76
BLYP / 6-311 + G**	6.430	0.85	670.2	0.00

TABLE V

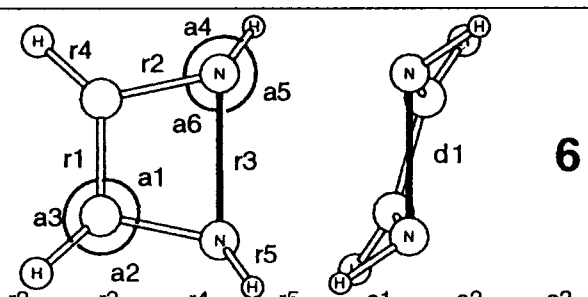Calculated geometry characteristics of transition state 4 cyclobutene ring opening.

Theor. Model	r1	r2	r3	r4	r5	r6	a1	a2	a3	a4	a5	a6	a7	d1
RHF / 6-311 + G**	1.367	1.416	2.127	1.077	1.072	1.084	104.2	126.2	129.4	73.6	85.8	113.9	133.0	−21.8
MP2 / 6-311 + G**	1.385	1.431	2.131	1.087	1.084	1.094	103.7	126.2	129.9	74.0	83.8	114.6	133.2	−22.2
SVWN / 6-311 + G**	1.372	1.413	2.126	1.095	1.091	1.102	104.3	126.0	129.5	73.8	82.9	114.2	133.8	−20.7
BLYP / 6-311 + G**	1.380	1.441	2.154	1.093	1.088	1.100	104.5	126.0	129.3	73.7	86.2	113.8	132.3	−19.7

TABLE VI

Calculated geometry characteristics of transition state 5 for cis-1,2-dihydro-1,2-diazete ring opening.

Theor. Model	1	2	3	4	5	6	7	8	9	10	11	12
MP2 / 6-311 + G**												
Distance r (Å)	1.368	1.395	1.935	1.400	1.085	1.083	1.039	1.022				
Angle a (°)	102.2	122.0	133.5	124.2	100.0	135.8	112.3	125.8	78.7	77.0	79.8	108.2
Dihedral angle d1 (°) (N — C — C — N) = − 14.0												
RHF / 6-311 + G**												
Distance r (Å)	1.357	1.352	1.909	1.374	1.076	1.072	1.015	0.998				
Angle a (°)	101.1	122.6	133.3	125.3	100.8	133.8	114.7	130.3	78.6	77.0	82.0	110.7
Dihedral angle d1 (°) (N — C — C — N) = − 15.4												
BLYP / 6-311 + G**												
Distance r (Å)	1.369	1.397	1.956	1.414	1.091	1.088	1.045	1.028				
Angle a (°)	102.0	121.6	133.0	124.3	101.0	134.5	113.8	127.4	78.5	76.8	83.0	109.5
Dihedral angle d1 (°) (N — C — C — N) = − 11.8												
SVWN / 6-311 + G**												
Distance r / Å	1.365	1.362	1.925	1.376	1.095	1.091	1.044	1.028				
Angle a (°)	101.9	121.7	132.5	124.6	100.7	134.6	114.9	131.2	78.7	77.0	80.6	110.3
Dihedral angle d1 (°) (N — C — C — N) = − 12.4												

TABLE VII

Calculated geometry characteristics of transition state 6 for *trans*-1,2-dihydro-1,2-diazete ring opening.

Theor. Model	r1	r2	r3	r4	r5	a1	a2	a3	a4	a5	a6	d1
RHF / 6-311 + G**	1.365	1.354	1.889	1.073	1.016	99.8	125.7	133.8	113.8	124.4	77.8	−21.0
MP2 / 6-311 + G**	1.380	1.388	1.896	1.084	1.038	99.4	125.5	134.7	111.8	122.0	78.3	−20.5
BLYP / 6-311 + G**	1.379	1.397	1.925	1.089	1.045	100.0	125.0	134.0	112.7	121.7	77.9	−19.0
SVWN / 6-311 + G**	1.375	1.362	1.900	1.092	1.045	99.9	125.5	133.5	113.4	125.0	78.0	−19.6

CONROTATORY RING OPENING OF CYCLOBUTENE

cause of the steric interactions in the conrotatory opening of **2**, the discrepancy in the geometry prediction is expected to be higher in **5**. That was confirmed by the calculations. The maximal disagreement in bond prediction for **5** is over 2% (Table VIII). The closest structure to the MP2/6-311 + G** was obtained with the nonlocalized BLYP/6-311 + G** density functional method. This agreement is even more pronounced in the case of transition structure **6** for the conrotatory ring opening of *trans*-1,2-dihydro-1,2-diazete (**3**). A similar pattern of geometry predictions was observed for the dihedral angles. The dihedral angle in the *cis* isomer **2** is much higher (3.6°) than for the *trans* isomer (2.0°) (Tables VI and VII).

ENERGIES

The total energies of the species involved in the ring openings are presented in Table IX. Before discussing the activation energies for ring opening, it is interesting to examine the difference in stabil-

TABLE VIII

Calculated sum of bond distances and angles for transition states 4, 5, and 6 for the four-membered ring opening.

	Sr	%r	Sa	%a
T **4** for cyclobutene ring opening				
RHF / 6-311 + G**	8.143	−0.84	766.1	0.09
MP2 / 6-311 + G**	8.212	0.00	765.4	0.00
SVWN / 6-311 + G**	8.199	−0.02	764.5	−0.01
BLYP / 6-311 + G**	8.256	0.54	765.8	0.01
T **5** for cis-1,2-dihydro-1,2-diazete ring opening				
RHF / 6-311 + G**	10.327	1.71	1299.5	−0.82
MP2 / 6-311 + G**	10.153	0.00	1310.2	0.00
SVWN / 6-311 + G**	10.388	2.31	1305.4	−0.37
BLYP / 6-311 + G**	10.286	1.31	1308.7	−0.11
T **6** for trans-1,2-dihydro-1,2-diazete ring opening				
RHF / 6-311 + G**	6.697	−1.31	675.3	0.54
MP2 / 6-311 + G**	6.786	0.00	671.7	0.00
SVWN / 6-311 + G**	6.835	0.72	671.3	0.06
BLYP / 6-311 + G**	6.774	0.18	675.3	0.54

TABLE IX

Total energies (au) of reactants and transition-state structures.

	E_I	E_{II}	E_{III}	E_{IV}	E_V	E_{VI}
1	− 154.93784	− 155.51098	− 154.93648	− 155.51225	− 155.12334	− 155.92999
2	− 186.88567	− 187.52001	− 186.88269	− 187.52264	− 187.04888	− 188.00246
3	− 186.89425	− 187.52821	− 186.89121	− 187.53092	− 187.05586	− 188.00947
4	− 154.86666	− 155.45649	− 154.86527	− 155.45778	− 155.06866	− 155.88367
5	− 186.82566	− 187.48228	− 186.82195	− 187.48550	− 187.00415	− 187.97170
6	− 186.83266	− 187.49201	− 186.83015	− 187.49445	− 187.01171	− 187.97997

E_I — RHF / 6-311 + G** // RHF / 6-311 + G**; E_{II} — MP2 / 6-311 + G** // RHF / 6-311 + G**; E_{III} — RHF / 6-311 + G** // MP2 / 6-311 + G**; E_{IV} — MP2 / 6-311 + G** // MP2 / 6-311 + G**; E_V — SVWN / 6-311 + G** // SVWN / 6-311 + G**; E_{VI} — BLYP / 6-311 + G** // SVWN / 6-311 + G**.

ity of the two isomers of diazabutadiene **2** and **3** and the influence of steric factors on the relative energies of the transition structures **5** and **6**. As can be expected on the basis of chemical intuition, the *trans* isomer **3** should be more stable compared to the *cis* isomer **2**. The difference is within the 1 kcal/mol range (4.38–5.38). The correlation methods predict a lower energy difference (Table X). By examining the structure of the transition states **5** and **6**, it can be said that the steric interactions have to be considerable in the conrotatory ring opening of **2**. Thus, it is expected that transition state **6** would be more stable than is transition state **5** in relation to reactants **2** and **3**. The energy evaluation by noncorrelated methods (ΔE_I and ΔE_{III}) predict the opposite. The correlational methods do show an increase of steric interactions in transition structure **5**, so the prediction of the energies is as expected. Here, since transition states are involved, the energy difference between the methods is above 1 kcal/mol even when comparing only the correlation methods.

The predicted activation energies for conrotatory ring opening are presented in Table XI. The predicted activation barrier for the cyclobutene ring opening are in the range from 27.41 to 44.69

kcal/mol depending on the method. Even with a large basis set like 6-311 + G**, RHF predicts an activation barrier that is more than 10.0 kcal/mol higher than the experimental value (Ea_I). The zero-point vibrational energy correction does not significantly improve on it. The RHF/6-311 + G** energy evaluation on MP2/6-311 + G**-optimized structures gives an almost identical value with the energy evaluation on the RHF/6-311 + G** geometries. That is not surprising since we demonstrated above that the geometries of both reactants and the transition structures are not method-sensitive. The energy evaluation at the MP2/6-311 + G**//RHF/6-311 + G** level with a zero-point vibrational energy correction is in excellent agreement with the experimental activation energy that is within the range of the experimental error (Ea_V, Table XI). That demonstrates the necessity of using the extended basis set for the correct energy evaluation even in the case when only carbon and hydrogen are present in the structures. The activation energy obtained from smaller basis sets like MP2/6-31G*//RHF/6-31G* was 6.5 kcal/mol away from experimental results [10, 13]. The activation energy from MP2/6-311 + G** with ZPVE (Ea_{VII}) is even closer to the experimental value (the differ-

TABLE X

Relative stability of the *trans* isomer in respect to the *cis* isomer of 1,2-dihydro-1,2-diazete in the ground and in the transition state (kcal / mol).

Species	ΔE_I	ΔE_{II}	ΔE_{III}	ΔE_{IV}	ΔE_V	ΔE_{VI}
2 / 3	− 5.38	− 5.14	− 5.35	− 5.20	− 4.38	− 4.40
5 / 6	− 4.39	− 6.10	− 5.15	− 5.82	− 4.75	− 5.19

ΔE_I — RHF / 6-311 + G** // RHF / 6-311 + G**; ΔE_{II} — MP2 / 6-311 + G** // RHF / 6-311 + G**; ΔE_{III} — RHF / 6-311 + G** // MP2 / 6-311 + G**; ΔE_{IV} — MP2 / 6-311 + G** // MP2 / 6-311 + G**; ΔE_V — SVWN / 6-311 + G** // SVWN / 6-311 + G**; ΔE_{VI} — BLYP / 6-311 + G** // SVWN / 6-311 + G**.

TABLE XI

Activation energies (kcal / mol) of ring opening for cyclobutene (4), cis-1,2-dihydro-1,2-diazete (5), and trans-1,2-dihydro-1,2-diazete (6).

TS	Ea_I	Ea_{II}	Ea_{III}	Ea_{IV}	Ea_V	Ea_{VI}	Ea_{VII}	Ea_{VIII}	Ea_{IX}	Ea_X	Ea_{XI}	Exp. [11]
4	44.66	42.83	44.69	34.20	32.38	34.18	32.52	34.31	32.64	29.70	27.41	32.9 ± 0.5
5	37.66	36.00	38.11	23.68	22.02	23.31	21.85	28.07	26.93	19.30	17.88	
6	38.65	36.28	38.31	22.71	20.34	22.88	20.81	27.67	25.55	18.51	16.50	

Ea_I — RHF / 6-311 + G** // RHF / 6-311 + G**; Ea_{II} — RHF / 6-311 + G** // RHF / 6-311 + G** + ZPVE^a; Ea_{III} — RHF / 6-311 + G** / / MP2 / 6-311 + G**; Ea_{IV} — MP2 / 6-311 + G** // RHF / 6-311 + G**; Ea_V — MP2 / 6-311 + G** // RHF / 6-311 + G** + ZPVE^a; Ea_{VI} — MP2 / 6-311 + G** // MP2 / 6-311 + G**; Ea_{VII} — MP2 / 6-311 + G** // MP2 / 6-311 + G** + ZPVE^a; Ea_{VIII} — SVWN / 6-311 + G** // SVWN / 6-311 + G**; Ea_{IX} — SVWN / 6-311 + G** // SVWN / 6-311 + G** + ZPVE^a; Ea_X — BLYP / 6-311 + G** // BLYP / 6-311 + G**; Ea_{XI} — BLYP / 6-311 + G** // BLYP / 6-311 + G** + ZPVE^a.
a = Zero-point vibrational energy.

ence is only 0.48 kcal/mol). However, the best agreement is obtained with the SVWN DFT method with the same basis set. The difference is only 0.28 kcal/mol (Ea_{IX}, Table XI). To our surprise, BLYP/6-311 + G** does not give such accurate prediction of the activation barrier. The obtained activation energy is 4.5 kcal/mol lower than the experimental value. Comparison of the geometries of transition state 4 generated with these two DFT methods shows that one generated with SVWN is much closer to the MP2 geometry (Table V). Thus, the activation barrier prediction follows the accuracy of the obtained transition-state geometry.

The pattern of the activation barriers for the conrotatory opening of diazacyclobutenes 2 and 3 is similar to the one for cyclobutene. The agreement in the activation energies between MP2 and SVWN is not as good. The SVWN energies are around 3 kcal/mol higher. The activation energy for the conrotatory ring opening of 3 is around 20 kcal/mol. As expected, all correlated methods predict that the activation energy for the conrotatory ring opening of the trans isomer is lower than for the cis isomer while RHF predicts the opposite. This finding is in agreement with experimental results that 1,2-dihydro-1,2-diazetes are very reactive compounds [12].

Conclusion

The ring opening of 1, 2, and 3 goes through a concerted conrotatory mechanism. The two nitrogen atoms do not induce changes in the mechanism which is well established for the all-carbon compound. The correct prediction of activation energy of cyclobutene is obtained with both MP2

and SVWN at the 6-311 + G** basis-set level. The geometries of transition states and reactants are very similar regardless of the method used, while for the activation energies, correlation methods must be used. The trans isomer 3 is predicted to have a lower activation energy due to increased steric interactions in the course of the conrotatory ring opening of the cis isomer 2. The activation barriers are in the range to make this compound relatively stable in respect to the ring opening. That can be explained by the fact that these compounds might have slight aromatic character.

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