

## DFT Studies of the Diels-Alder Reaction of 1,4-Diaza-1,3-butadiene with Acrolein

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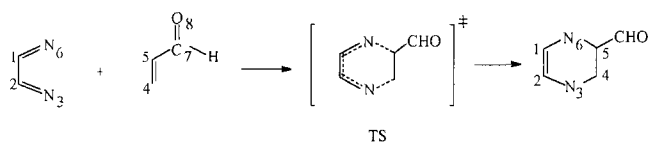
Density functional theory (DFT) is a powerful tool for predicting molecular properties.<sup>1-3</sup> This theory is an attractive methodology due to the low computational cost and better accuracy, compared with highly correlated Hartree-Fock methods.<sup>4,6</sup> On the other hand, the Diels-Alder reaction is possibly the most useful reaction for the preparation of heterocyclic compounds, which have been investigated by a variety of experimental and theoretical methods.<sup>7</sup> Dewar *et al.*<sup>8,9</sup> report the activation barrier of the Diels-Alder reaction of butadiene and acetylene, calculating the MERP (Minimal energy reaction path) to be 28 kcal/mol. Froese *et al.*<sup>10</sup> calculated the activation energy of this reaction to be 25.0 kcal/mol with B3LYP/6-31G\* basis sets.

The Diels-Alder reaction of 1,4-diaza-1,3-butadiene (1,4-DAB) is important since the reaction allows the synthesis of 2-substituted pyrazines. Specifically, N-aryl-1,4-DABs are known to give Diels-Alder products by reactions with reactive dienophiles.<sup>11</sup>

In this study, we focus our attention on the Diels-Alder reaction of 1,4-DAB with acrolein as shown in Scheme 1. The dienophile, acrolein, seems to approach the diene, 1,4-DAB. The *s-trans* conformation for acrolein was taken because the vapor consisted of a mixture of the *s-cis* and *s-trans* isomer in the ratio of approximately 1 : 3 at 35 °C.<sup>12</sup>

DFT calculations were carried out with B3LYP level<sup>13</sup> of theory with the 6-31G\* basis sets using the Gaussian 94 series of program<sup>14</sup> on a RS6K IBM workstation. Geometries for all structures were fully optimized using analytical energy gradients.<sup>15</sup> Vibration frequencies were also calculated at B3LYP level to confirm whether all the stationary points correspond to local minima or to transition state. Zero-point corrections at this level are included in relative energies. The activation energy was obtained from the *trans* isomer of 1,4-DAB. The geometries for the reactants, transition state, and product of the Diels-Alder reaction are summarized in Table 1.

The geometry of acrolein is calculated to be planar. The bond lengths and angles for acrolein are in good agreement with the experimental values obtained by Kuchitsu *et al.*<sup>16</sup> These results confirmed the following symmetries: *trans*-1,4-DAB,  $C_{2h}$ ; *cis*-1,4-DAB,  $C_2$ ; transition state,  $C_1$ ; prod-



Scheme 1

**Table 1.** Optimized geometries of *trans*-1,4-DAB, *cis*-1,4-DAB, acrolein, transition state, product at B3LYP/6-31G\* level of theory<sup>a</sup>. Total energies, E are in Hartrees (including ZPC)

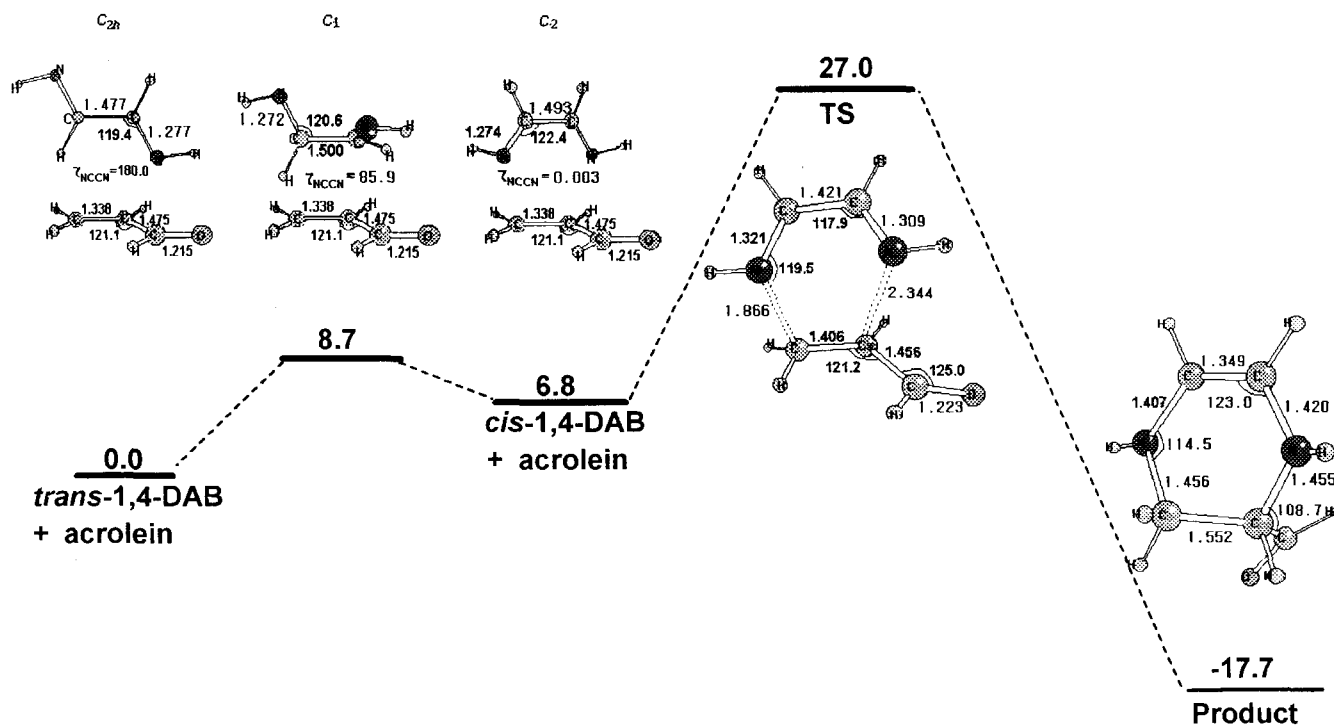
parameter	1,4-DAB		acrolein <sup>b</sup>	TS	product
	<i>trans</i>	<i>cis</i>			
R(C <sub>1</sub> -C <sub>2</sub> )	1.477	1.493		1.421	1.349
R(C <sub>2</sub> -N <sub>3</sub> )	1.277	1.274		1.321	1.407
R(C <sub>1</sub> -N <sub>6</sub> )	1.277	1.274		1.309	1.420
R(C <sub>4</sub> -C <sub>5</sub> )			1.338(1.335)	1.406	1.552
R(C <sub>5</sub> -C <sub>7</sub> )			1.475(1.478)	1.456	1.531
R(C <sub>7</sub> -O <sub>8</sub> )			1.215(1.208)	1.223	1.212
R(N <sub>3</sub> -C <sub>4</sub> )				1.866	1.456
R(C <sub>5</sub> -N <sub>6</sub> )				2.344	1.455
∠(N <sub>6</sub> C <sub>1</sub> C <sub>2</sub> )	119.4	122.4		117.9	123.0
∠(C <sub>4</sub> C <sub>5</sub> C <sub>7</sub> )			121.1(121.0)	121.2	110.5
∠(C <sub>5</sub> C <sub>7</sub> O <sub>8</sub> )			124.3(124.0)	125.0	123.8
∠(C <sub>4</sub> N <sub>3</sub> C <sub>2</sub> )				119.5	114.5
∠(N <sub>3</sub> C <sub>2</sub> C <sub>1</sub> N <sub>6</sub> )	180.0	0.003		-6.3	13.1
∠(C <sub>4</sub> C <sub>5</sub> C <sub>7</sub> O <sub>8</sub> )			180.0	167.3	-27.6
E	-188.01231	-188.00147	-191.85032	-379.81963	-379.89079

<sup>a</sup>Bond lengths in Å and bond angles in degree. <sup>b</sup>Values in parentheses are taken from Kuchitsu's experimental results.

uct;  $C_1$ . In *trans*-1,4-DAB, the C<sub>1</sub>-C<sub>2</sub> and C=N bond lengths, 1.477 Å and 1.277 Å, change to 1.493 Å and 1.274 Å in *cis*-1,4-DAB, which is a proper isomer for Diels-Alder reaction with acrolein. In *cis*-1,4-DAB, the C<sub>1</sub>-C<sub>2</sub> bond length of 1.493 Å decreases to 1.421 Å in the transition state, whereas the C=N bond lengths of 1.274 Å increase to 1.321 Å or 1.309 Å in the transition state respectively. For acrolein, the initial C<sub>4</sub>=C<sub>5</sub> double bond of 1.338 Å increases to 1.406 Å in the transition state and forms a single bond in the product with a bond length of 1.552 Å. The N<sub>3</sub>C<sub>2</sub>C<sub>1</sub>N<sub>6</sub> distortion angle of nearly 0° in *cis*-1,4-DAB changes to about -6.3° in the transition state and to 13.1° in the product. The most interesting aspect is the newly formed bonds between the diene and dienophile. The terminal bond distances in the transition state, 1.866 Å and 2.344 Å, are reduced to 1.456 Å and 1.455 Å in the product.

For the Diels-Alder reaction of 1,4-DAB with acrolein, the selected geometries and potential energies of the reactants, transition state, and product, optimized at the B3LYP/6-31G\* level, are shown in Figure 1. Both *cis*- and *trans*-1,4-DAB were examined, but the activation energy is quoted from the *trans* isomer, as mentioned earlier.

In Table 1 and Figure 1, the structures of diene and dieno-



**Figure 1.** The potential energy profile and geometries of the reactants, transition state, and product in the Diels-Alder reaction of acrolein with 1,4-diaza-1,3-butadiene. Geometries are in Å and degree at the B3LYP/6-31G\* level. Relative energies are in kcal/mol.

phile at transition state are rather close to those of the reactants, and the forming C...N distances are long. These results indicate that the transition state for the Diels-Alder reaction of 1,4-DAB with acrolein occurs quite early along the reaction coordinate. As shown in Figure 1, the C<sub>5</sub>...N<sub>6</sub> distance with the forming  $\sigma$ -bond of 2.344 Å is longer than the C<sub>4</sub>...N<sub>3</sub> distance with the other  $\sigma$ -bond of 1.866 Å at the transition state. According to the theoretical calculations, the transition state is extremely asymmetric. This asymmetry of the transition state is evidently a result of the electronic effect of the carbonyl substituent in acrolein having the electronic withdrawing property, which makes the dienophile carbon atom, C<sub>4</sub>, the further away from the substituent, more positively charged and more reactive.<sup>10</sup> This structural feature of this asymmetric transition state is consistent with that of the asymmetric transition state found for the Diels-Alder reaction between 2-methyl-1,3-butadiene and acrolein.<sup>17</sup>

On the other hand, the torsion barrier is calculated to be 8.7 kcal/mol when *trans*-1,4-DAB changes to *cis*-1,4-DAB for the Diels-Alder reaction with acrolein. This shows that the torsion barrier for *trans*-1,4-DAB is about 3.0 kcal/mol higher than that for *trans*-butadiene, calculated with G2MS geometries by Froese *et al.*<sup>10</sup>

The activation energy for the Diels-Alder reaction of *trans*-1,4-DAB with acrolein is calculated to be 27.0 kcal/mol, and the reaction is expected to be exothermic by 17.7 kcal/mol, as shown in Figure 1. The activation energy of 27.0 kcal/mol for the reaction is only 2 kcal/mol higher than the activation energy of 25.0 kcal/mol for acetylene with *trans*-butadiene<sup>10</sup> at the B3LYP/6-31G\* level. This compares with the respective corresponding experimental energies of

23.9 kcal/mol<sup>18</sup> and 24.5 kcal/mol<sup>19</sup> for ethylene with *trans*-butadiene and ethylene with cyclopentadiene.

As discussed above, the energy of the reaction is calculated to be -17.7 kcal/mol at B3LYP/6-31G\* level. The exothermicity of this reaction is much less than that for acetylene with *trans*-butadiene (-56.7 kcal/mol)<sup>10</sup> and reflects the higher energy of the product relative to the reactants compared with the product (cyclohexadiene) relative to acetylene reacting with *trans*-butadiene.

This study shows that the activation energy of the Diels-Alder reaction between acrolein and 1,4-DAB is similar to that for the reaction between acetylene and *trans*-butadiene, but the reaction of the former is asymmetric in the transition state.

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