

# Reaction of [60]fullerene with *trans*-epoxides: a theoretical study†

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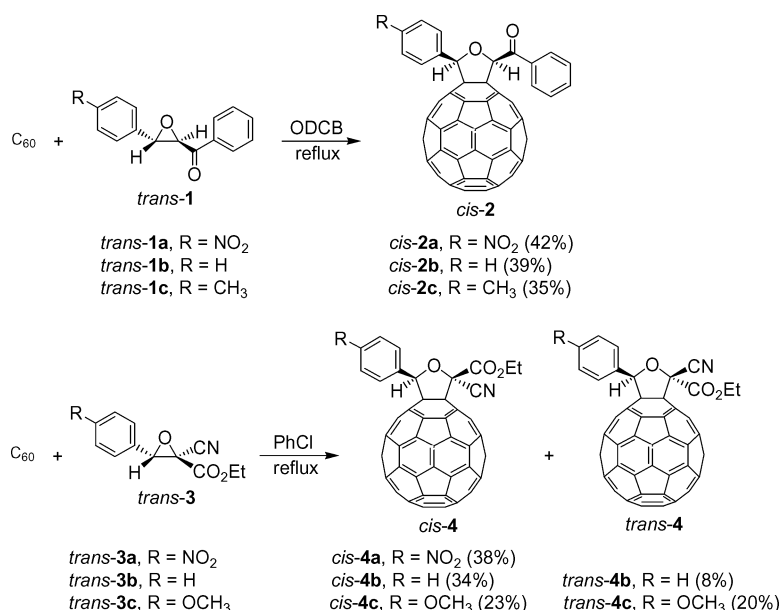
The experimental results of the reaction of C<sub>60</sub> with carbonyl ylides generated from *trans*-epoxides, which afforded *cis*-products exclusively or predominantly, can be explained well by computational investigation of the proposed reaction mechanism. Our theoretical calculations demonstrate that only *cis*-carbonyl ylides can be formed directly from *trans*-epoxides, in compliance with the Woodward–Hoffmann rule. Importantly, the ring opening of *trans*-epoxides, which is the rate-determining step, should be included in the whole reaction profiles to explain all experimental phenomena.

## Introduction

Various types of reactions have been employed to functionalize fullerenes.<sup>1</sup> Among the methodologies for the functionalization of fullerenes, the 1,3-dipolar cycloaddition reaction is one of the most commonly used protocols, and a variety of 1,3-dipoles including azomethine ylides, diazo compounds, azides, nitrile oxides, nitrile ylides, nitrile imines and pyrazolinium ylides have been investigated.<sup>1</sup> However, a lot fewer examples of the reactions of carbonyl ylides with [60]fullerene (C<sub>60</sub>) are known.<sup>2</sup>

Meanwhile, theoretical calculations on fullerene reactions have attracted much attention, and have provided powerful tools to probe the reaction mechanisms.<sup>3–5</sup> The theoretically investigated fullerene reactions mainly include [2+4],<sup>3</sup> [2+3]<sup>4</sup> and [2+1]<sup>5</sup> cycloaddition reactions. Semiempirical method AM1 was often applied in the early theoretical calculations on the reaction mechanisms of fullerenes.<sup>3a,3c–e,4a,4c,5a</sup> The PM3 method was also occasionally used to explore the reaction mechanism of fullerenes.<sup>6</sup> However, single-point B3LYP energy calculations on AM1-optimized structures have gained momentum in recent years.<sup>3f,4b,4d,4e,5b,5c</sup>

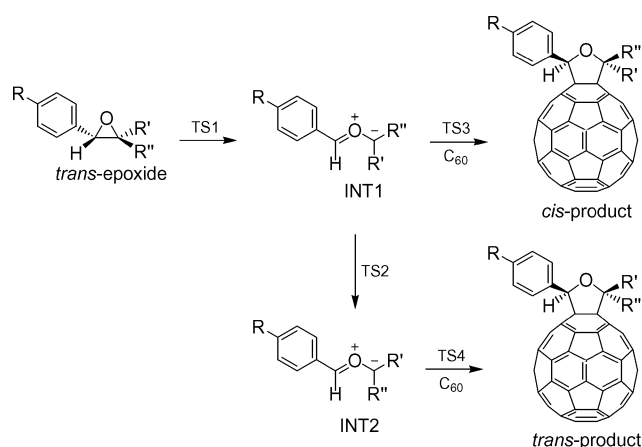
Our group has recently reported the synthesis of C<sub>60</sub>-fused tetrahydrofuran derivatives from the thermal reaction of C<sub>60</sub> with carbonyl ylides generated in situ from *trans*-epoxides.<sup>7</sup> Interestingly, we found that the reaction of C<sub>60</sub> with *trans*-2-benzoyl-3-aryloxiranes (**1a–c**) afforded only *cis*-products, while the reaction of C<sub>60</sub> with *trans*-2-cyano-2-ethoxycarbonyl-3-aryloxiranes (**3a–c**) gave *cis*-isomers exclusively or predominantly (Scheme 1). The isomeric distributions for the reaction of C<sub>60</sub> with **3a–c** were



**Scheme 1** Reaction of C<sub>60</sub> with *trans*-epoxides **1a–c** and **3a–c** giving *cis*-products exclusively or predominantly.

drastically affected by the substituent on the phenyl ring. It is unusual that both *cis*- and *trans*-products were formed when **3b** and **3c** were used, although the *cis*-products were generated preferably.

We previously proposed a reaction mechanism to explain the exclusive or predominant formation of *cis*-products from the reaction of C<sub>60</sub> with *trans*-epoxides, as shown in Scheme 2.<sup>7</sup>



**Scheme 2** Proposed reaction mechanism.

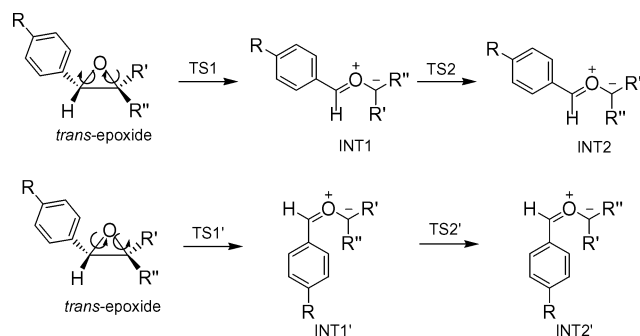
Intrigued by this novel result and in continuation of our interest in fullerene chemistry,<sup>7–9</sup> herein we report a theoretical study on the whole reaction profiles for the reaction of C<sub>60</sub> with *trans*-epoxides at the B3LYP/6–31G\*//AM1 level.

## Computational details

Because of the large size of the fullerene system, full geometry optimizations without symmetry constraints for the whole reaction profiles were carried out by the AM1 semiempirical method,<sup>10</sup> just as most of the previous theoretical calculations on the reaction mechanisms of fullerenes were.<sup>3a,3c–f,4,5a–c</sup> Single-point B3LYP<sup>11</sup> energy calculations employing the 6-31G\*<sup>12</sup> basis set were performed at the AM1-optimized structures with the help of Gaussian 03 program.<sup>13</sup> All zero-gradient structures were checked by a vibrational analysis. All transition-state structures were verified by frequency calculations, which indicated that each transition state had only one imaginary frequency. The intrinsic reaction coordinate (IRC)<sup>14</sup> analysis was followed with the AM1 method to make sure that each transition state connected the expected reactant and product. For purposes of comparison, the B3LYP/6-31G\* and B3LYP/6-31G\*//PM3 methods were also employed to investigate the ring opening of *trans*-epoxide **1a** and the whole reaction profile for the reaction of *trans*-epoxide **1a** with C<sub>60</sub>, respectively.

## Results and discussion

Two orbital-symmetry-allowed conrotatory processes are available for the thermal C–C bond cleavage of the *trans*-epoxides. The conrotatory ring openings give INT1s and INT1's *via* TS1 and TS1', respectively. Dipoles INT1s and INT1's further transform to INT2s and INT2's through C–O bond rotation (Scheme 3).



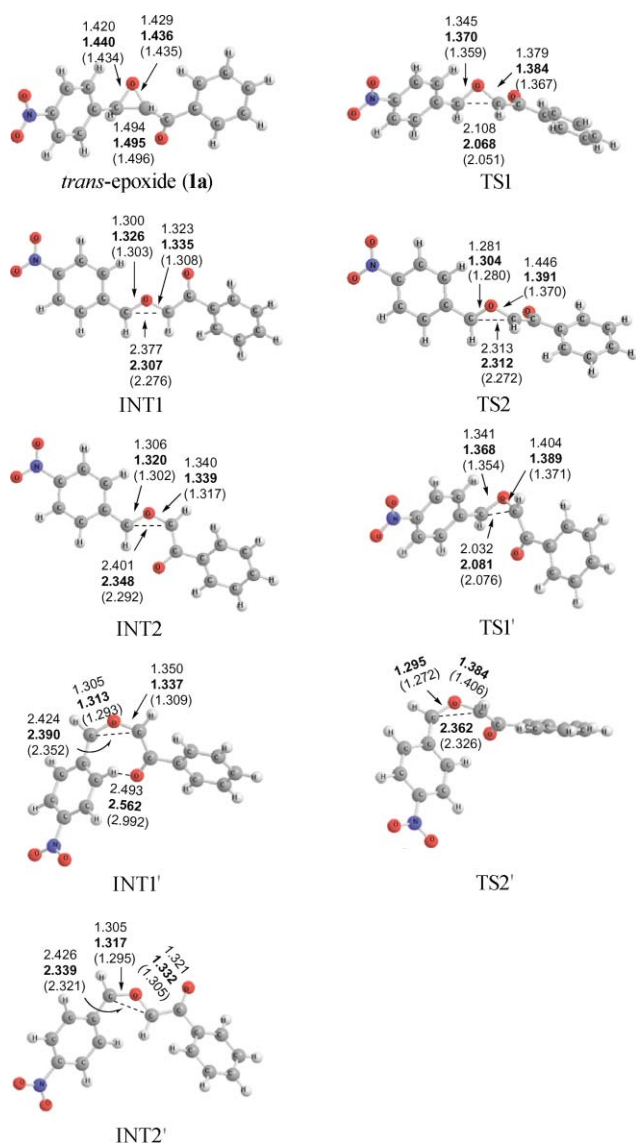
**Scheme 3** Two pathways for the thermal conrotatory C–C bond cleavage of *trans*-epoxides.

The size of the systems in Scheme 3 is small enough to allow for DFT calculations. We chose *trans*-epoxide **1a** as a model substrate and examined its conrotatory ring opening by the B3LYP/6-31G\*//AM1, B3LYP/6-31G\*//PM3 and B3LYP/6-31G\* methods. The optimized structures of the reagent, transition structures and carbonyl ylides for the ring opening of *trans*-epoxide **1a** at the AM1, PM3 and B3LYP/6-31G\* levels are shown in Fig. 1. As seen from Fig. 1, compared with the PM3-bond length, the AM1-bond length for the key breaking C–C bond of the epoxide ring in both transition structures and carbonyl ylides is generally closer to the B3LYP/6-31G\*-bond length.

Harmonic frequency analyses verified the nature of the stationary points as minima or as transition structures. The intrinsic reaction coordinate (IRC) calculations (see ESI†) showed that the obtained transition-state structures indeed connected the expected reactants and products. It is noteworthy that only TS1/TS1' leading to the thermal conrotatory C–C bond cleavage of the *trans*-epoxide **1a** could be located. The IRC analyses indicated that TS1/TS1' connected *trans*-epoxide **1a** and the *cis*-dipole (INT1/INT1') rather than the *trans*-dipole (INT2/INT2'). These results were in compliance with the Woodward–Hoffmann rule for electrocyclic ring opening in four-electron systems. Even though a few disrotatory ring openings of four-electron systems due to geometric constraints, such as in fused cyclobutenes, and electronic factors have been reported,<sup>15</sup> no TS connecting *trans*-epoxides and *trans*-dipoles (INT2/INT2') could be found in our case. However, carbonyl ylides INT2/INT2' could be formed from precursors INT1/INT1' by C–O bond rotation *via* TS2/TS2'.<sup>16</sup>

The relative energies of TS1, INT1, TS2, INT2, TS1', INT1', TS2' and INT2' for the two possible ring-opening processes of *trans*-epoxide **1a** at the B3LYP/6-31G\*//AM1, B3LYP/6-31G\*//PM3 and B3LYP/6-31G\* levels are given in Fig. 2.

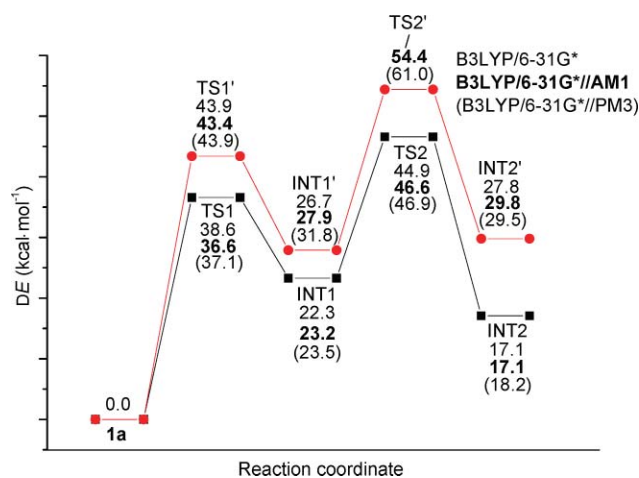
The conrotatory ring opening of *trans*-epoxide **1a** under torquoelectronic control<sup>17</sup> would require the electron-withdrawing group, *i.e.*, carbonyl moiety, to occupy the inward position in the transition structure, thus lead to the *cis*-dipole INT1'. The optimized geometry of INT1' (see Fig. 1) indicates that the C–H⋯O interaction might help to stabilize the INT1' intermediate. Nevertheless, the calculated data in Fig. 2 show that the relative energies of TS1' and INT1' are higher than those of TS1 and INT1 by all three employed methods, probably due to the less repulsive steric interaction of the aryl substituent in TS1 and INT1. On the other hand, the relative energy of the *trans*-dipole INT2 with the carbonyl and aryl moieties occupying the inward and outward positions respectively is lower than



**Fig. 1** Optimized geometries of the reagent, transition structures and carbonyl ylides for the ring opening of *trans*-epoxide **1a** (values with bold format were calculated at the AM1 level, values in parentheses were calculated at the PM3 level, and others were calculated at the B3LYP/6-31G\* level. Note that TS2' could not be located by the B3LYP/6-31G\* method).

that of the *trans*-dipole INT2', of which the carbonyl and aryl moieties are located at the reversed positions, and is also lower than that of the *cis*-dipole INT1. It should be emphasized that the calculated activation and reaction energies for each step of the ring-opening process have close values at all three levels of B3LYP/6-31G\*//AM1, B3LYP/6-31G\*//PM3 and B3LYP/6-31G\*. These results indicate that the B3LYP/6-31G\*//AM1 and B3LYP/6-31G\*//PM3 methods can reproduce well the energies calculated by the B3LYP/6-31G\* method, thus validating the B3LYP/6-31G\*//AM1 and B3LYP/6-31G\*//PM3 methods in treating carbonyl ylide formation from the epoxide.

Theoretically, cycloadditions to C<sub>60</sub> can take place at both [5,6]- and [6,6]-junctions *via* four types of addition modes: closed [6,6]-, closed [5,6]-, open [6,6]- and open [5,6]-additions, and each of these additions can proceed through either concerted or

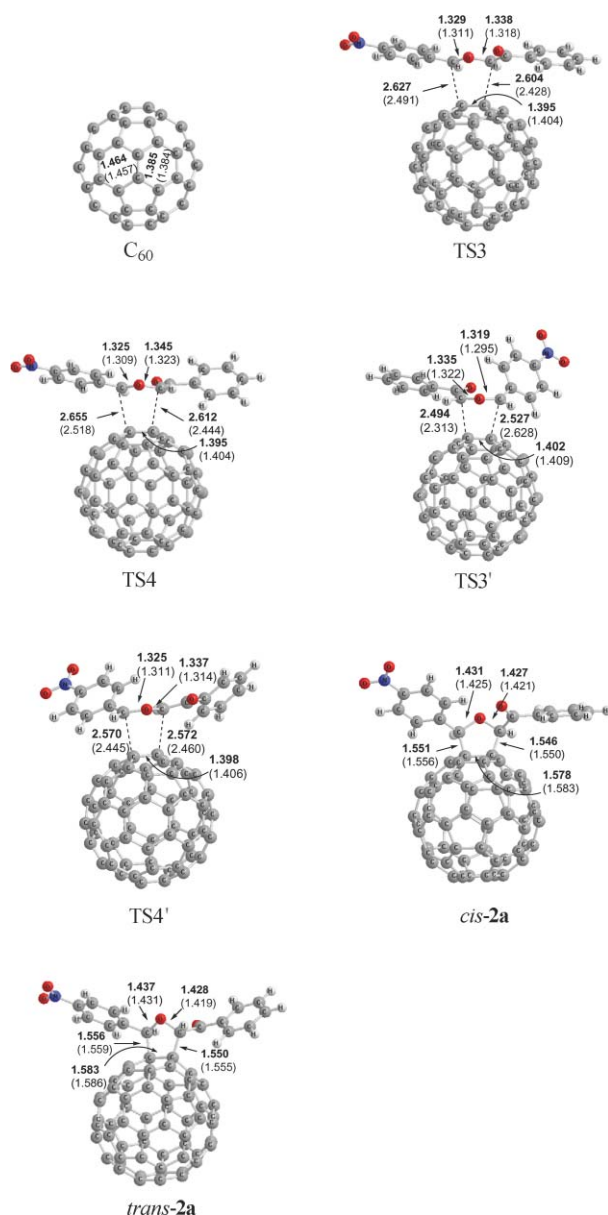


**Fig. 2** Energy profiles for the two possible ring-opening pathways of *trans*-epoxide **1a**.

stepwise paths.<sup>4c</sup> Nevertheless, previous theoretical calculations showed that additions occurred preferentially at the [6,6]-junctions of C<sub>60</sub> giving closed [6,6]-adducts for the [4+2],<sup>3a,3b</sup> [3+2]<sup>4a,4b,4c</sup> and [2+1]<sup>5a,5d-f</sup> cycloaddition reactions, fully consistent with experimental results.<sup>1</sup> Furthermore, Kavitha and Venuvanalingam have systematically investigated the 1,3-dipolar reaction of C<sub>60</sub> with diazomethane, nitrile oxide and nitrene, and concluded that closed [6,6]-additions were the most favored ones and followed a concerted mechanism.<sup>4c</sup> Experimentally, we obtained only [6,6]-adducts from the reaction of C<sub>60</sub> with *trans*-epoxides, with the *cis*-stereochemistry exclusively or predominantly.<sup>7</sup> Therefore, we only consider the concerted closed [6,6]-addition in the current work. The large size of the fullerene system prevents us from utilizing ab initio molecular quantum mechanical methods or density functional methods for full geometry optimizations of the whole reaction profile. However, the method of single-point B3LYP energy calculations at AM1-optimized geometries represents an acceptable protocol for providing reasonable estimates of reaction energies and energy barriers at low computational cost in fullerene chemistry.<sup>3f,4b,4d,4e,5b,5c</sup>

The cycloaddition of the dipoles INT1, INT2, INT1' and INT2' generated from epoxide **1a** to C<sub>60</sub> was then examined at both levels of B3LYP/6-31G\*//AM1 and B3LYP/6-31G\*//PM3 to shed light on which method is more suitable for our system. The optimized structures of C<sub>60</sub>, TS3, TS4, TS3', TS4', *cis*-**2a** and *trans*-**2a** at the AM1 and PM3 levels are exhibited in Fig. 3.

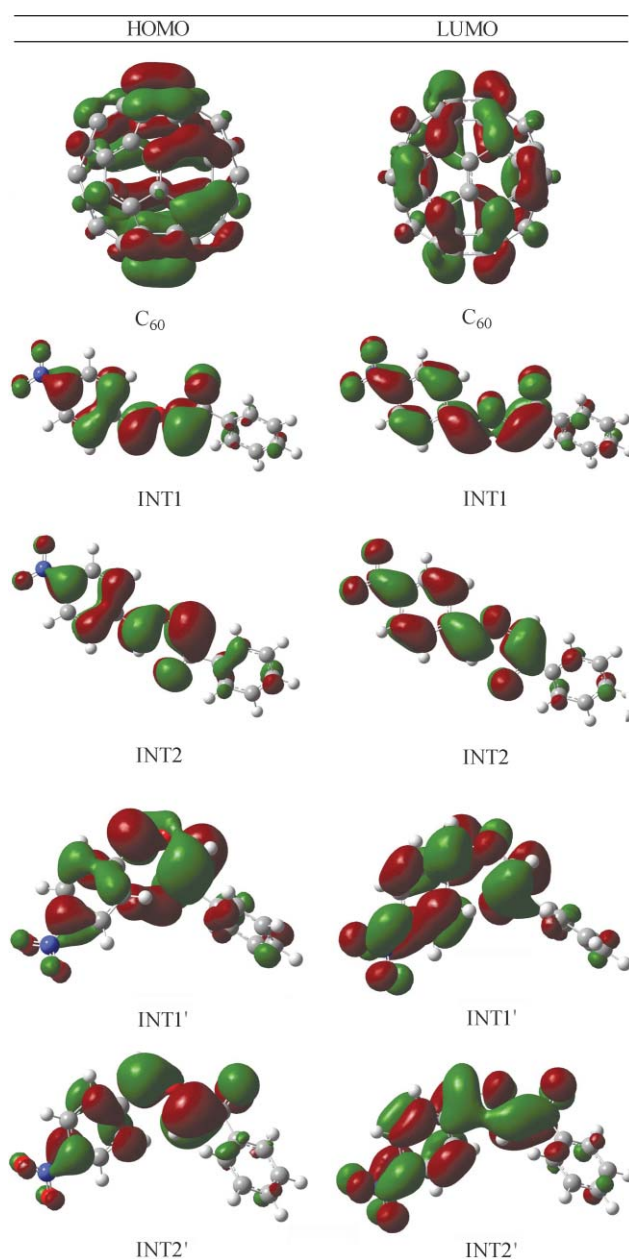
As expected, the cycloaddition step of carbonyl ylides INT1/INT1' and INT2/INT2' to C<sub>60</sub> *via* TS3/TS3' and TS4/TS4' by both AM1 and PM3 methods was found to be concerted, but asynchronous due to the unsymmetrical carbonyl ylides, as displayed in Fig. 3. This asynchronous phenomenon was similarly observed in other cycloaddition reactions of fullerenes with unsymmetrical dipoles,<sup>4b,4d,4e</sup> but was different from that involving unsymmetrical dipoles such as ozone.<sup>4a,4c,4f</sup> The cycloaddition of ozone to C<sub>60</sub> was found to be concerted and synchronous.<sup>4a</sup> In comparison, the addition of ozone to the C1–C2 and C7–C21 bonds of C<sub>70</sub> was concerted but slightly asynchronous, whereas the addition to the C5–C6 and C7–C8 bonds of C<sub>70</sub> was concerted as well as synchronous.<sup>4c,4f</sup>



**Fig. 3** Optimized geometries of  $C_{60}$ , transition structures and products for the reaction of  $C_{60}$  with carbonyl ylides generated from *trans*-epoxide **1a** (values with bold format were calculated at the AM1 level, others were calculated at the PM3 level).

The electronic origin of this concerted but slightly asynchronous cycloaddition might be visualized through the prebonding of the molecular orbitals of  $C_{60}$  and carbonyl ylides. The HOMO and LUMO molecular orbitals of  $C_{60}$  and INT1, INT2, INT1' and INT2' of *trans*-epoxide **1a** at the B3LYP/6-31G\*//AM1 level are plotted in Fig. 4, and the corresponding orbital schemes are shown in Fig. 5.

As seen in Fig. 5, the energy gaps of the LUMO( $C_{60}$ )–HOMO(dipole) for INT1, INT2, INT1' and INT2' at the B3LYP/6-31G\*//AM1 level are 2.50, 2.53, 2.58, 2.56 eV, while those of the LUMO(dipole)–HOMO( $C_{60}$ ) for INT1, INT2, INT1' and INT2' are 2.64, 2.72, 2.88 and 2.69 eV. Obviously, the interaction between the LUMO( $C_{60}$ ) and HOMO(dipole) controls the cycloaddition reaction even though the HOMO and LUMO

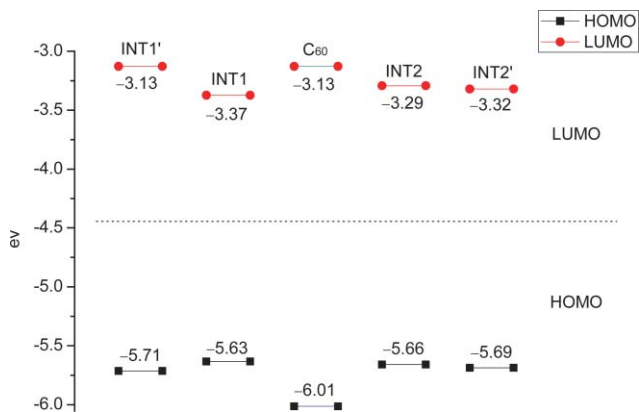


**Fig. 4** HOMO and LUMO orbitals for  $C_{60}$  and carbonyl ylides generated from **1a** at the B3LYP/6-31G\*//AM1 level.

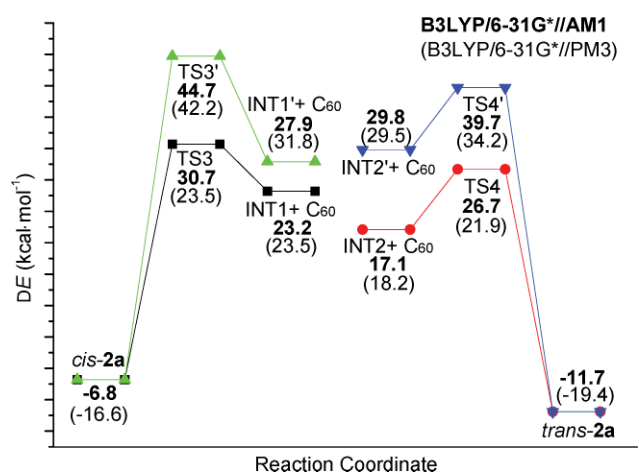
orbitals of  $C_{60}$  match the LUMO and HOMO orbital of the carbonyl ylides, respectively. Fig. 4 reveals that the two ylidic carbon atoms, which are the attacking sites, are the densest lobes with slightly different intensities in the HOMO orbitals of the carbonyl ylides, thus explaining why the cycloaddition step of the carbonyl ylides to  $C_{60}$  is a concerted but slightly asynchronous process.

The HOMO and LUMO molecular orbitals of  $C_{60}$  and INT1, INT2, INT1' and INT2' of *trans*-epoxide **1a** as well as their orbital schemes at the B3LYP/6-31G\*//PM3 level are similar to those by the B3LYP/6-31G\*//AM1 method, and are provided in the ESI†.

The energy profiles for the cycloaddition of carbonyl ylides INT1, INT2, INT1' and INT2' to  $C_{60}$  are displayed in Fig. 6.



**Fig. 5** FMO orbital scheme for  $C_{60}$  and carbonyl ylides generated from **1a** at the B3LYP/6-31G\*\*/AM1 level.



**Fig. 6** Energy profiles for the reaction of  $C_{60}$  with the carbonyl ylides from *trans*-epoxide **1a**

The above results demonstrate that the relative energies of TS1', TS2', INT1', INT2', TS3' and TS4' of epoxide **1a** are significantly higher than those of their counterparts TS1, TS2, INT1, INT2, TS3 and TS4 by both the B3LYP/6-31G\*\*/AM1 and B3LYP/6-31G\*\*/PM3 methods. Consequently, the theoretical calculations of other TS1's, TS2's, INT1's and INT2's from epoxides **1b-c** and **3a-c**, and subsequent cycloaddition to  $C_{60}$  will not be further examined.

The calculated energy barriers for the addition of carbonyl ylides INT1 and INT2 generated from *trans*-epoxide **1a** to  $C_{60}$

at the B3LYP/6-31G\*\*/AM1 level are 7.5 and 9.6 kcal mol<sup>-1</sup>, while those at the B3LYP/6-31G\*\*/PM3 level are 0.0 and 3.7 kcal mol<sup>-1</sup>. In addition, no preformed complex for  $C_{60}$  and INT1 could be found by the IRC analysis of TS3 at the PM3 level. The obtained barrier-less transition state for the 1,3-dipolar addition of INT1 to  $C_{60}$  by the B3LYP/6-31G\*\*/PM3 method indicates that the B3LYP/6-31G\*\*/PM3 method is inferior to the B3LYP/6-31G\*\*/AM1 method for our system. Taking into account the better AM1-bond length for the key broken C–C bond of the carbonyl ylides and the popularity of the B3LYP/6-31G\*\*/AM1 method in fullerene chemistry, we will explore the whole reaction profiles for the reaction of  $C_{60}$  with *trans*-epoxides **1b-c** and **3a-c**.

All of the optimized structures and energies of epoxides, TS1s, INT1s, TS2s, INT2s, TS3s, TS4s, *cis*-products and *trans*-products as well as the IRC analyses for the reaction of  $C_{60}$  with *trans*-epoxides **1b-c** and **3a-c** are shown in the ESI.† Just like *trans*-epoxide **1a**, the IRC analyses also revealed that TS1s connected the *trans*-epoxides and the *cis*-dipole INT1s rather than the *trans*-dipole INT2s, and cycloaddition of the carbonyl ylides to  $C_{60}$  is a concerted but asynchronous step.

The B3LYP/6-31G\*\*/AM1 relative energies of reactants, transition states, intermediates and products for the reaction of  $C_{60}$  with *trans*-epoxides **1a-c** and **3a-c** are shown in Table 1.

Because compounds **1a-c** and **3a-c** are different types of *trans*-epoxides, and their reactions with  $C_{60}$  gave *cis*-products only for substrates **1a-c** and *cis*-products exclusively or predominantly for substrates **3a-c**, the energy profiles for the reaction of  $C_{60}$  with **1a-c** and for the reaction of  $C_{60}$  with **3a-c** are provided in Fig. 7 and 8, respectively.

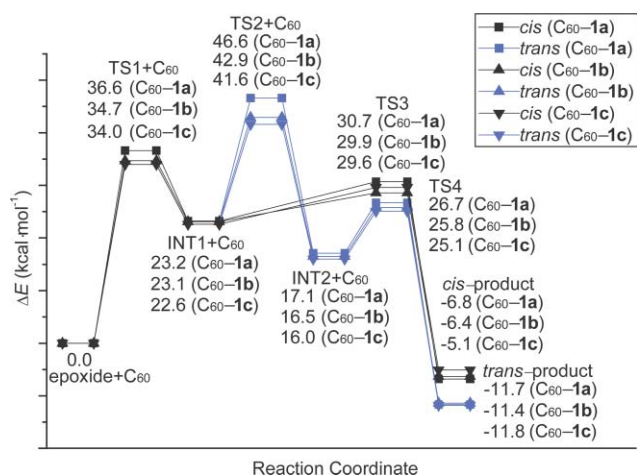
As seen from Fig. 7 and 8, the calculated relative energies of *trans*-**2a-c** and *trans*-**4a-c** are lower than those of *cis*-**2a-c** and *cis*-**4a-c**, respectively. However, *cis*-**2a-c** and *cis*-**4a** were obtained selectively, while *cis*-**4b** and *cis*-**4c** were formed preferably. Our experiment indicated that there was no conversion between the two isomeric products under the reaction conditions. Obviously, the reaction of  $C_{60}$  with both *trans*-epoxides **1a-c** and *trans*-epoxides **3a-c** should be kinetically controlled rather than thermodynamically controlled.

The energy barriers of the individual steps for the *cis*-products from the reaction of  $C_{60}$  with *trans*-epoxides **1a-c** are 34.0–36.6 and 6.8–7.5 kcal mol<sup>-1</sup>, while those for the *trans*-products are 34.0–36.6, 19.0–23.4 and 9.1–9.6 kcal mol<sup>-1</sup>. The formation of *cis*-dipoles INT1s from *trans*-epoxides is a highly endergonic process by 22.6–23.2 kcal mol<sup>-1</sup>, while the conversion of INT1s to INT2s via TS2s is an exothermic step. Carbonyl ylides INT2s are more stable

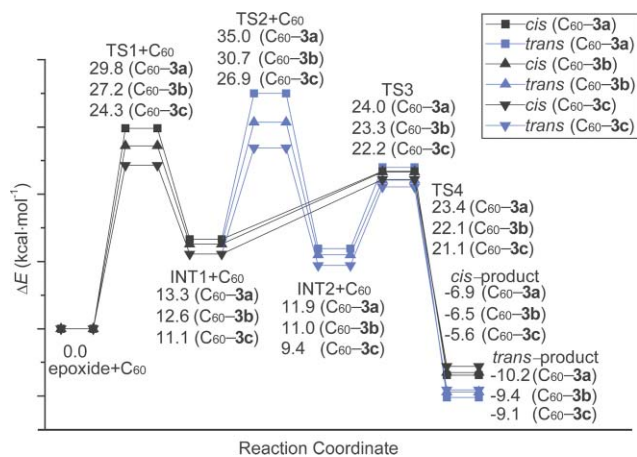
**Table 1** B3LYP/6-31G\*\*/AM1 relative energies for the 1,3-dipolar cycloaddition reaction of  $C_{60}$  with *trans*-epoxides **1a-c** and **3a-c**<sup>a</sup>

Species	$C_{60}$ - <b>1a</b>	$C_{60}$ - <b>1b</b>	$C_{60}$ - <b>1c</b>	$C_{60}$ - <b>3a</b>	$C_{60}$ - <b>3b</b>	$C_{60}$ - <b>3c</b>
reactants	0.0	0.0	0.0	0.0	0.0	0.0
TS1	36.6	34.7	34.0	29.8	27.2	24.3
INT1	23.2	23.1	22.6	13.3	12.6	11.1
TS2	46.6	42.9	41.6	35.0	30.7	26.9
INT2	17.1	16.5	16.0	11.9	11.0	9.4
TS3	30.7	29.9	29.6	24.0	23.3	22.2
TS4	26.7	25.8	25.1	23.4	22.1	21.1
<i>cis</i> -product	-6.8	-6.4	-5.1	-6.9	-6.5	-5.6
<i>trans</i> -product	-11.7	-11.4	-11.8	-10.2	-9.4	-9.1

<sup>a</sup> All energy values are given in kcal mol<sup>-1</sup>. Relative energies of various species are expressed by assuming the reactants ( $C_{60}$  and epoxide) energy as zero.



**Fig. 7** Energy profiles for the whole reaction of C<sub>60</sub> with *trans*-epoxides **1a–c** at the B3LYP/6-31G\*\*/AM1 level.



**Fig. 8** Energy profiles for the whole reaction of C<sub>60</sub> with *trans*-epoxides **3a–c** at the B3LYP/6-31G\*\*/AM1 level.

than INT1s by 6.1–6.6 kcal mol<sup>-1</sup>, thus the reversion of INT2 to INT1s would be difficult. The addition of carbonyl ylides INT1s and INT2s to C<sub>60</sub> is a facile process with a low energy barrier of less than 9.6 kcal mol<sup>-1</sup> and high exothermicity of more than 27.7 kcal mol<sup>-1</sup>. In comparison, the energy barriers of the steps for the *cis*-products from the reaction of C<sub>60</sub> with *trans*-epoxides **3a–c** are 24.3–29.8 and 10.7–11.1 kcal mol<sup>-1</sup>, and the energy barriers for the *trans*-products are 24.3–29.8, 15.8–21.7 and 11.1–11.7 kcal mol<sup>-1</sup>. The whole energy profile trend for the reaction of C<sub>60</sub> with *trans*-epoxides **3a–c** is similar to that with *trans*-epoxides **1a–c**. The above arguments for the reaction of C<sub>60</sub> with *trans*-epoxides **1a–c** can also be applied to the reaction of C<sub>60</sub> with *trans*-epoxides **3a–c**, and will not be described in detail.

It is interesting to observe that the relative single-point energies for each TS1s, TS2s, INT1s, INT2s, TS3s and TS4s at the B3LYP/6-31G\*\*/AM1 level decrease with increasing electron-donating property of the substituent on the phenyl ring of the epoxides in each series (**1a–c** and **3a–c**). This phenomenon can be ascribed to the fact that the phenyl group with an electron-donating substituent is able to stabilize the (partial) positive charge in the transition states and 1,3-dipole intermediates.

Previous theoretical calculations on the mechanisms of cycloaddition reactions of fullerenes usually focus only on the cycloaddition step of dienes, dipoles and carbenes to fullerenes.<sup>3–5</sup> The energy barriers (TS3s and TS4s relative to INT1s and INT2s) for the cycloaddition reaction of C<sub>60</sub> with 1,3-dipoles from *trans*-epoxides **1a–c** are lower than those for the cycloaddition reaction of C<sub>60</sub> with 1,3-dipoles from *trans*-epoxides **3a–c**. If only the final cycloaddition step is considered here, the former reaction would require lower reaction temperatures than the latter one, contrary to the experimental conditions. Thus, the rate-determining step could not be the cycloaddition step, but instead should be the formation of the carbonyl ylides. In addition, the energy barriers (energies of TS1 and TS2 relative to *trans*-epoxide) for the formation of 1,3-dipoles INT1s and INT2s are much higher than those for the [3+2] cycloaddition of C<sub>60</sub> with INT1s and INT2s for both *trans*-epoxides **1a–c** and *trans*-epoxides **3a–c**. Furthermore, the calculated overall energy barriers (TS1s and TS2s) for the reaction of C<sub>60</sub> with *trans*-epoxides **1a–c** are higher than those for the reaction of C<sub>60</sub> with *trans*-epoxides **3a–c**, thus requiring higher reaction temperatures for the former reaction, consistent with the experimental result (180 °C vs. 130 °C).<sup>7</sup> Hence the ring opening of the *trans*-epoxides, not just the 1,3-dipolar cycloaddition to C<sub>60</sub>, must be included in the whole reaction profiles to fully understand all experimental phenomena. The present work implies that it is better to consider and include all transformation steps from the starting reagents to the final products, not only the final cycloaddition step to fullerenes, in the reaction energy profiles wherever possible and necessary.

The same intermediates (INT1s) afford both *cis*-products and *trans*-products through two parallel pathways. Based on the overall energy profiles shown in Fig. 7 and 8, the energy difference between TS2 and TS3 should determine the observed *cis*-product/*trans*-product ratio. The large energy difference (≥12.0 kcal mol<sup>-1</sup>) between TS2 and TS3 for *trans*-epoxides **1a–c** explains well that only *cis*-products were obtained experimentally. Similarly, the energy difference between TS2 and TS3 for the reaction of C<sub>60</sub> with **3a** is 11.0 kcal mol<sup>-1</sup>, close to that for the reaction with **1c** (12.0 kcal mol<sup>-1</sup>). Nevertheless, the corresponding energy difference becomes significantly smaller when changing the substrate to **3b** and **3c**, with a value of 7.4 and 4.7 kcal mol<sup>-1</sup>, respectively. These computational data qualitatively explain why only *cis*-**4a** was obtained and the ratio of *cis*-**4b**/*trans*-**4b** and *cis*-**4c**/*trans*-**4c** decreased in the same order although the *cis*-products were generated preferably.

## Conclusions

In summary, our theoretical calculations on the proposed reaction mechanism demonstrate that only *cis*-carbonyl ylides can be formed directly from *trans*-epoxides, in compliance with the Woodward–Hoffmann rule. The calculated large energy difference between TS2 and TS3 at the B3LYP/6-31G\*\*/AM1 level can explain well why only *cis*-products were obtained experimentally for substrates **1a–c** and **3a**, while the gradually decreasing energy difference between TS2 and TS3 for **3b** and **3c** is consistent with the observed decreasing ratio of *cis*-**4b**/*trans*-**4b** and *cis*-**4c**/*trans*-**4c** in the same order. Furthermore, the ring opening of the *trans*-epoxides, which is the rate-determining step, must be included in the whole reaction profiles to fully explain all experimental phenomena.

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