[2n2 π + 2n2 π] Cycloadditions: An alternative to forbidden [4 π + 4 π] processes. The Case of Nitrones Dimerization.

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TOC

Abstract

A theoretical study based on the (U)M06-2X/cc-pVTZ calculations has been used to investigate the [3+3] thermal dimerization of nitrones to 1,4,2,5-dioxadiazinanes in both the gas phase and in dichloromethane solution. Calculations suggest that dimerization of nitrones takes place through a concerted mechanism involving a formal disallowed $[4\pi+4\pi]$ cycloaddition with a free energy barrier of 30.4 kcal/mol. The corresponding diradical and zwitterionic stepwise mechanisms have also been studied but the transition structures located are kinetically disfavored. An alternative mechanism through a five-membered ring intermediate formed by a classical [3+2] dipolar cycloaddition can also be discarded. The five-membered ring intermediate is unstable to cycloreversion and its isomerization to the final dioxadiazinane involves a high free energy barrier (68.6 kcal/mol). Calculations also show that the dimerization process is slower in dichloromethane than in gas phase owing to the larger polarity of nitrones and that inclusion of diffuse functions at the studied level does not modify the observed results. The apparently disfavored [3+3] dimerization of nitrones can actually be explained as a bispseudopericyclic $[2n2\pi+2n2\pi]$ process in which the favorable FO interactions between the nitrone oxygens and the $C=N \pi^*$ bypass the WH forbidness.

Introduction

The [3+2] cycloaddition reaction of 1,3-dipoles with olefinic dipolarophiles is one of the best known and most widely used method for constructing five-membered heterocycles.¹ The reaction follows the Woodward-Hoffman orbital symmetry rules. Among the most used 1,3-dipoles are nitrile oxides and nitrones leading to isoxazolines and isoxazolidines, respectively. Nitrile oxides **1** easily dimerize to give furoxans **2** through a stepwise mechanism via dinitrosoalkene diradicals as elucidated by Houk and co-workers.² Nitrones **3** also dimerizes but to form 1,4,2,5-dioxadiazinanes **4** instead of the corresponding five-membered 1,2,5-oxadiazolidine-2-oxide **5** (Scheme 1).³

Scheme 1. Dimerization of 1,3-dipoles

A similar behavior has been observed for azomethine imines **6** which also dimerize, through a formal [3+3] cycloaddition, to give 1,2,4,5-tetrazinanes **7**.⁴

Contrary to the widely recognized dimerization of nitrile oxides, the analogous process with nitrones (and azomethine imines) is a rarely reported event witnessed previously in few cases of cyclic nitrones. In a recent report, Ali and co-workers investigated the cyclodimerization of several six-membered nitrones but only conformational features of the dimers were studied.⁵ The explanation for the cyclodimerization of nitrones is still in controversy, especially because the [3+3] dimerization process belongs to the WH disallowed thermal $[4\pi + 4\pi]$ variety.

A mechanistic rationale has been proposed by those authors⁵ based on the formation of an intermediate 1,2,4-oxadiazolidine-4-oxide through a classical allowed [3+2] cycloaddition reaction followed by a ring enlargement. Nevertheless the detailed mechanism is not known and no experimental or theoretical support is given. As a consequence, no information exists to date about the electronic and steric effects on dimerization of nitrones and the nature of the transition state(s) for such processes.

In this paper, we report DFT studies (both open- and closed-shell) on the dimerization of nitrones by using a simple model and further applying to dimerization of 2,3,4,5-tetrahydropyridine-1-oxide. Contrary to the formation of furoxans from nitrile oxides, theoretical studies predict that the formation of 1,4,2,5-dioxadiazinanes from nitrones takes place through a concerted mechanism that could be also applicable to the dimerization of azomethine imines.

Computational Methods

All of the calculations were performed using the Gaussian09 program.⁶ Molecular geometries were optimized with the M06-2X functional⁷ in conjunction with both cc-pVTZ and aug-cc-pVTZ basis sets,⁸ in order to compare differences by including diffuse functions. Analytical second derivatives of the energy were calculated to classify the nature of every stationary point, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. All the located transition states were confirmed to connect to reactants and products by intrinsic reaction coordinate (IRC) calculations.⁹ For all diradical transition states and intermediates, a spin-projection scheme has been used to estimate energies of singlet diradical structures.¹⁰ However, the corresponding free energies are given without spin-correction since its effectiveness has not been completely demonstrated¹¹ (for a complete list of energy values after spin correction see Supporting information). Calculations have been carried out both in the gas phase and considering solvent effects (dichloromethane) with the PCM model.¹²

Results and Discussion

Dimerization of methanamine oxide. Three paths can be proposed for the dimerization of nitrene **8** to dioxadiazinane **9** (Scheme 2): i) a concerted mechanism **A** corresponding to a [3+3] cycloaddition reaction involving a formal [4 π +4 π] process; ii) a mechanism **B**, suggested by Ali and co-workers,⁵ consisting of the initial formation of a five-membered

intermediate **10** through a typical 1,3-dipolar cycloaddition in which one molecule of nitrone acts as a dipole and the other one plays the role of dipolarophile, followed by a second step in which intermediate **10** isomerizes to **9** through an intramolecular attack of the exocyclic oxygen atom, and iii) a diradical (open-shell) mechanism **C** through intermediate **11**. This intermediate could alternatively be zwitterionic (closed-shell) depending on the electron pairing distribution.

Scheme 2. Paths for dimerization of nitrones

When we studied the mechanism **A**, two transition states **TS1** and **TS2** were located for the concerted formation of **9**. Both transition structures correspond to endo (**TS1**) and exo (**TS2**) approaches¹³ leading to twist and chair conformations of **9**, respectively. The free energies (PCM=CH₂Cl₂/M06-2X/cc-pVTZ) associated with **TS1** and **TS2** are 33.2 and 34.4 kcal/mol, respectively. The geometries of the optimized TSs present quite similar C-O forming-bond distances (ca. 2.030-2.044 Å) (Figure 1).

In both cases the process is completely synchronous as expected from the symmetry of the system. The reaction is exothermic (-8.3 kcal/mol) and calculations predict the preferential formation of twist **T1** though the more stable **TS1**. Interconversion of twist **T1** into chair **C1** has also been calculated and it can be carried out through a typical conformational course (See supporting material).

To investigate the mechanism **B** we have calculated the corresponding transition structure **TS3** and **TS4** leading to **10** through a typical asynchronous concerted 1,3-dipolar cycloaddition. Calculations feature two approaches *endo* and *exo*, corresponding to the formation of **F1** (via **TS3**) and **F2** (via **TS4**), respectively (Figure 1). **F1** and **F2** are two invertomers of **10** differing on the relative orientation between the hydrogens attached to both nitrogen atoms (*trans* for **F1** and *cis* for **F2**). The forming C-N and C-O bonds in **TS3** are 2.302 and 1.746 Å, and in **TS4** are 2.311 and 1.678 Å, respectively. Those forming bond lengths are in agreement with asynchronous concerted processes in both cases. The calculations predict essentially the same energy barrier for *endo* (30.3 kcal/mol) and *exo* (30.2 kcal/mol) approaches. These energy barriers are lower by ca. 3 kcal/mol than those found for the concerted [3+3] dimerization (Scheme 2, mechanism **A**).

Figure 1. Dimerization processes of methanamine oxide **6** to 1,4,2,5-dioxadiazinanes **9** through concerted processes computed at M06-2X/cc-pVTZ level of theory in gas phase (normal font) and considering solvent effects (PCM=CH₂Cl₂, italic font).

The allowed [3+2] cycloaddition is kinetically more favourable than the [3+2] dimerization but it is thermodynamically disfavoured since the 1,2,4-oxadiazolidine-5-oxide **10** is fleeting intermediates unstable to cycloreversion. The intramolecular ring enlargement of 1,2,4-oxadiazolidine-5-oxide **10** to the experimentally observed 1,4,2,5-dioxadiazinane **9** involves a very high barrier. Unfortunately, no transition state for the formation of **9** from **10** could be found starting from either **F1** or **F2**. However, a scan of the potential energy surface for such a transformation revealed that a minimum value of the corresponding transition states should be higher than 50 kcal/mol thus rendering the process unfavorable.¹⁴

Accordingly, the rate-limiting step for the dimerization of nitrones through the formation of **10** is the isomerization of such intermediate to **9**, a process clearly higher in energy than the concerted process (Scheme 2, mechanism **A**). This point has been corroborated by locating the corresponding transition structure for the dimerization of cyclic nitrones as described below.

We have also investigated the formation of **9** through a stepwise mechanism (Scheme 2, mechanism **C**). Whereas no transition state for the formation of the corresponding zwitterionic intermediate **11** could be found, the corresponding diradical transition structures and intermediates were located. The first step is the formation of diradical intermediate **D1** via transition state **TS5** with a barrier of 39.0 kcal/mol (Figure 2).¹⁵ The forming C-O bond in **TS5** is 1.566 Å. In **D1** the two nitrogen atoms adopt an anticlinal orientation with a dihedral angle N-O-C-N of 168.3°. The second step is a rotation around the new formed C-O bond to afford **D2**, in which the dihedral angle N-O-C-N is 53.7°. The barrier height for this rotational step (through **TS6**) is only 1.4 kcal/mol. In

the third step an intramolecular radical coupling of **D2** generates chair **C1** via formation of the second C-O bond. The transition state **TS7** is shown in Figure 2 and the free energy for this step is 4.6 kcal/mol.

Figure 2. Dimerization process of methanamine oxide **6** to 1,4,2,5-dioxadiazinane **9** through diradical processes computed at UM06-2X/cc-pVTZ level of theory in gas phase (normal font) and considering solvent effects (PCM=CH₂Cl₂, italic font).

The length of the C-O forming bond in **TS7** is 2.499 Å. The dimerization through this diradical mechanism is exothermic (-15.5 kcal/mol) with a rate-determining step having a barrier of 39.0 kcal/mol. Mechanism **C** is 5.8 kcal/mol higher than the concerted mechanism **A**. Consequently, at this point, calculations suggest that dimerization of nitrones could take place through a concerted mechanism rather than by a diradical stepwise one.

The formation of the five-membered ring **10** has also been studied through a diradical mechanism (Figure 2). UM06-2X calculations revealed that **F1** can also be obtained from diradical **D3** by forming the N-C bond.¹⁶ It is expected that **D3** can be easily formed from previously located **D1** via rotation because **D3** is 1.5 kcal/mol lower in energy than **D1**; indeed, **TS8** is 2.1 kcal/mol higher than **D1**. The barrier for the transformation of **D3** into **F1** is practically non-existing (0.4 kcal/mol). The located **TS9** is also a diradical species with one electron mainly on the terminal oxygen and the other one delocalized between the terminal carbon atom and adjacent nitrogen. The forming N-C bond length is 2.551 Å and the two nitrogen atoms are in a synclinal conformation with a dihedral angle N-O-C-N of -23.9°. Again, even though it is possible to consider the formation of **F1**, the rate-limiting step is the isomerization of **F1** to **C1**, rendering the whole process markedly unfavorable.

In order to compare the process with the previously reported one for nitrile oxides by Houk and co-workers,² we also investigated the diradical coupling of nitrones through carbon atoms en route to the hitherto not observed 1,2,5-oxadiazoline-2-oxides **13**. We modeled the formation of **13** through diradical **12** (Scheme 3).

Scheme 3. Diradical coupling of nitrones through carbon atoms

The intermediate diradical **D4** (**12**), formed through **TS10** with a lower barrier than that of **TS5** (by 18.6 kcal/mol, Figure 2), showed to be stable (1.6 kcal/mol above **N1**) in agreement with Houk's results on nitrile oxides. The forming C-C bond in **TS10** is 2.027 Å. Intermediate **D4** adopts an orientation with a dihedral angle N-C-C-N of -61.6° in which the nitrogen atoms adopt a gauche relative disposition.

The formation of the final 1,2,5-oxadiazoline-2-oxide **F3** (**13**) should account through transition state **TS11** which showed a N-O forming bond of 1.954 Å. Compound **F3** showed to be less stable than the corresponding intermediate **D4** by 13 kcal/mol. The different behavior observed for nitrones with respect to nitrile oxides might be due to the instability of the corresponding five-membered dimer **F3** whose formation is thermodynamically disfavored with respect to **C1**.

In summary, we have considered for the methanamine oxide model both direct and two-step dimerization processes being calculated in closed- and open-shell environments. The inclusion of diffuse functions does not modify the results obtained at a triple Z level

(see supporting). In general, the activation energies in DCM increase between 3-4 kcal/mol for concerted mechanisms and 5-6 kcal/mol for diradical processes. The preliminary data indicate that the process is favored through the concerted (closed-shell) pathway represented in Figure 1 (Scheme 2, mechanism A).

Dimerization of 2,3,4,5-tetrahydropyridine-1-oxide. We have also investigated the dimerization process for the more realistic cyclic nitron **14** (Scheme 4), reported by Ali and co-workers.⁵

Scheme 4. Dimerization of 2,3,4,5-tetrahydropyridine-1-oxide **14**.

For the methanamine oxide model, the free energy profile suggests a direct mechanism involving a concerted transition state for the rate-limiting step. In spite of this preference, we also performed open-shell calculations in order to verify the reproducibility of our results for nitron **14**. The inclusion of diffuse functions was not considered because of the high computational cost associated to Dunning basis sets and because of the minimal differences observed in the previously studied model (methanamine oxide). The PCM model using dichloromethane as a solvent was employed in all the calculations.

In their work Ali and co-workers investigated the conformational preferences of **15**. The configuration of the dimer was confirmed to be all-trans, having trans-trans ring fusion. Two conformers were detected by NMR at temperatures below -40°C; whereas the major

one **a** (98%) has a tetraequatorial conformation around the central dioxadiazinane ring, the minor one **b** (2%) has a *trans-cis* fusion (Scheme 5).

Scheme 5. Conformational equilibrium of dioxadiazinane **15**.

Figure 3 shows the calculated energetics for the dimerization of **14** through the direct concerted pathway (mechanism **A**). Two different approaches of the nitrones lead to two transition structures, **TS12** and **TS13**, with very similar barriers of 30.8 and 30.4 kcal/mol, respectively.

From the more stable **TS13** conformer **T2** is formed. This conformer corresponds to a product having an axial bridge-head carbon (*trans-cis* fusion) which is not observed experimentally. In fact, **T2** is thermodynamically unfavored (0.8 kcal/mol) and unstable to cycloreversion.

On the other hand **TS12**, only 0.4 kcal/mol higher in energy than **TS13**, leads to the **C2** having a *trans-trans* fusion. The compound **C2** is 7.7 kcal/mol more stable than **T2** and thus it is possible to conclude that the formation of **C2** is thermodynamically favored. Moreover, through a typical conformational itinerary (see supporting material) **C2** is transformed into the more stable (-11.6 kcal/mol) **C3** having an all-trans disposition with all non-H bonds in an equatorial orientation. In **TS12** both forming bonds are identical (1.990 Å) and the two nitrone systems form a completely symmetric transition structure.

Figure 3. Dimerization process of nitrene **14** (N2) to **15** (C3) through concerted processes, computed at M06-2X/cc-pVTZ level of theory in gas phase (normal font) and considering solvent effects (PCM=CH₂Cl₂, *italic font*).

The alternative mechanism through a five-membered ring intermediate proposed by Ali and co-workers^[5] has also been investigated for nitron **14** (Figure 3). Two different approaches of the nitron acting as a dipolarophile on the nitron acting as a dipole lead to **TS14** and **TS15** with activation free energies of 32.7 and 31.5 kcal/mol, respectively. The relative energy of intermediate **F4** is found to be higher in 22.6 kcal/mol than that of the reactants. This reaction is therefore thermodynamically unfavored. The following discussion will only deal with the more stable **F5**, obtained from the lower transition state **TS15** which, by the way, is 0.7 kcal/mol higher in energy than **TS12** corresponding to the concerted process. Isomerization of **F5** into the dimer **C2** takes place after conformational equilibrium to afford **F7** through **TS16** to give **F6** and then **TS17**. The rate-limiting step of this mechanism is, indeed, transformation of **F7** into **C2** through **TS18**. The barrier height for this last step is 68.6 kcal/mol, demonstrating that this pathway is clearly kinetically unfavored.

The diradical stepwise mechanism (Figure 4) shows somewhat different results to those observed for the methanamine N-oxide model. Although **TS19**, equivalent to **TS5** in the model, was located in gas phase, when solvent effects were included it was not possible to locate such a transition state.¹⁷ Moreover, a single point calculation considering solvent effects using the geometry obtained in gas phase provided a free energy barrier of 38.4 kcal/mol. However, a close inspection of the single point model revealed that it was a zwitterion with $S^2 = 0$ and not a diradical. A search of a full optimized zwitterionic transition state and intermediates did not provide any positive result as in the case of the methanamine oxide.

Figure 4. Dimerization process of **14** (N2) to **15** (C2) computed at UM06-2X/cc-pVTZ level of theory in gas phase (normal font) and considering solvent effects (PCM=CH₂Cl₂, *italic font*).

The located **TS19** in gas phase has one electron on the terminal oxygen atom and the other one delocalized between the nitrogen and carbon atoms of the other piperidino ring, in a similar way to that observed for the methanamine *N*-oxide model. The forming

C-O bond length is 1.603 Å with the two nitrogen atoms in a synclinal conformation with a dihedral angle N-O-C-N of 112.8°. After formation of diradical intermediate **D5**, conversion to the required **D6** (according to the IRC analysis of the next **TS21**) should take place through a rotational transition state (**TS20**) which has not been possible to locate at any level. Intermediate **D6** has essentially the same energy that **D5**. The final step to form **C2** takes place through **TS21** and it requires 3.0 kcal/mol. In spite of the above results¹⁸ the rate limiting step seems to be the last bond closing in intermediate **D6** corresponding to transition state **TS21**, with an activation energy of 41.4 kcal/mol. Such a barrier is 10.6 kcal/mol greater than the one for the concerted mechanism discussed above (**TS12**), thus confirming the direct concerted pathway as the preferred one. The formation of **F7** from the diradical intermediate **D5** has not been considered since the mechanism through an intermediate five-membered ring should be definitively discarded according to the results illustrated in Figure 3.

Concluding Remarks

The preference of the dimerization of nitrones for the [3+3] concerted process stands in a marked contrast with the dimerization of nitrile oxides reported by Houk and co-workers[2] which was clearly demonstrated to follow a diradical stepwise mechanism. Indeed, we have performed preliminary calculations with azomethine ylides, having the same electronic disposition of nitrones and the dimerization process also follows a diradical stepwise mechanism. On the other hand, the same preliminary calculations with azomethine imines showed an identical behavior to nitrones following a concerted pathway for the dimerization to 1,2,4,5-tetrazinanes. The predilection of nitrones (and azomethine imines)

for the concerted [3+3] dimerizations is somewhat perplexing since the dimerizations are formally thermally disallowed $[4\pi+4\pi]$ processes according to the Woodward-Hoffmann rules. The WH rules for cycloadditions are however based on symmetry arguments and do not necessarily apply to the cycloadditions of unsymmetrical addends. In the well-known case of [2+2] ionic cycloadditions the forbidden nature of the pericyclic $[2\pi+2\pi]$ process is avoided by adopting a two-step mechanism involving the formations of zwitterionic intermediates which then collapse to the cyclobutane.¹⁹ In the case of the nitron [3+3] dimerization, the concerted nature of the process is instead maintained but its forbidden nature is relaxed by the asymmetry of the addends. The frontier orbitals of nitrones (and azomethine imines) are mainly located at nitron carbon (LUMO) and nitron oxygen (HOMO)²⁰ and the favourable double coupling of the electrophilic C and nucleophilic O ends of nitron accounts for the formation of the dioxadiazinane dimers.

Figure 5 compares the HOMO-LUMO interactions in the [2+2] ionic cycloadditions (a), [3+3] nitron dimerizations (b and b') (equivalent to azomethine imines dimerizations) and the related case of azomethine ylides (c). In the latter symmetrical case the FOs are of different symmetry and do not overlap while in the former cases a sizeable overlap is evident as well as the favorable dipolar interactions exemplified by the antiparallel arrows. In the nitron dimerizations noteworthy is also the secondary overlap interaction between the orbitals at N which explains the striking preference for the endo TS.

Figure 5. The sizable HOMO-LUMO overlaps in the [2+2] ionic cycloadditions (a) and nitron [3+3] concerted dimerizations (b and b') (The two nitrones involved in the dimerization are represented in plain and bold text). With azomethine ylides (c) HOMO-LUMO overlap is relieved in the concerted dimerizations since the overlaps between the 1,3-dipole ends differ in sign and cancels each other.

Figure 6 stresses the similarity of the single 4 electron shift in the [2+2] ionic cycloadditions and the complementary disjoint (in different regions of space) double 4 electron shift in the nitron [3+3] concerted dimerizations. Such a double shift is not possible in the symmetrical azomethine ylides concerted dimerizations because of lack of HOMO-LUMO overlap but it would be possible for azomethine imines.

Figure 6. The 4 electron shift promoted by HOMO-LUMO interaction in the [2+2] ionic cycloadditions and the independent disjoint double 4 electron shift in the nitron [3+3] concerted dimerizations $[2n2\pi + 2n2\pi]$.

In summary, with respect to the zwitterionic stepwise route, the concerted [3+3] nitrene dimerizations combines the more favorable double $2n2\pi$ interactions and dipolar interactions. The nitrene concerted dimerizations involve two disjoint 4 electron shift and are not pericyclic processes, i.e. they have a cyclic perimeter but no cyclic delocalization.

Owing to the lack of the cyclic delocalization these concerted dimerizations belong to the pseudopericyclic variety. As originally defined by Lemal in the case of a sigmatropic automerization “a pseudopericyclic reaction is a concerted transformation whose primary changes in bonding compass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles”²¹. Birney has extensively studied pseudopericyclic chelotropic decarboxylations²² and cycloadditions²³ and evidenced that these pseudopericyclic processes have usually two of these interchanges.

In our [3+3] dimerizations there are four of these interchanges (at the two oxygens and the two nitrogen sites) as depicted in the $[2n2\pi+2n2\pi]$ processes of Figure 6. We name then the [3+3] dimerization as bispseudopericyclic processes to stress its parentage and differences.²⁴ Bispseudopericyclic processes should be typical for the dimerization of 1,3-dipoles as represented by $a=b + -c-$ (or $X=Y-Z$) but their ease depends upon the relative electrophilicity and nucleophilicity of the dipole ends a and $c-$, as well as on the competition of other possible competing events (in the case of nitrile oxide the Houk diradical dimerization is the lowest path, with nitrenes diradicals are still easily formed but the path is a dead end).

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Supporting Information

Details on conformational itineraries; absolute (hartrees) and relative (kcal/mol) electronic and free energies at (U)M06-2X/cc-pVTZ, (U)M06-2X/aug-cc-pVTZ and PCM(DCM)/(U)M06-2X/cc-pVTZ levels of theory, including spin corrected energy values in the case of diradical species, stationery points and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>

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- (13) The *endo* approach is defined as that in which the nitrogen atom of the first nitron molecule is oriented inside the π -system of the second nitron molecule. The *exo* approach corresponds to that in which the nitrogen atom is oriented outside the π -system.
- (14) The exploration of the PES was made through scan analyses and locating pseudotransition structures with frozen variables. In all cases energy values are above 50 kcal/mol. These transition structures could, however, be located and fully characterized in the more realistic case of 2,3,4,5-tetrahydropyridin-1-oxide (see below).
- (15) A total of six different approaches of the two nitrones (3 alternate conformations multiplied by 2 nitron faces) were explored leading to transition structures higher in energy. The lowest energy found corresponded to **TS5**.
- (16) The possibility of obtaining a five-membered ring through the attack of a nitron nitrogen atom to the nitron carbon atom of a second molecule by forming a diradical

intermediate is negligible since any TS calculated under that consideration led to energy barriers higher than 50 kcal/mol.

- (17) The stability of the biradical wavefunction was checked (keyword STABLE). Unfortunately, the same unsuccessful results were obtained after further optimization considering the solvent and utilizing the previously verified most stable wavefunction. By considering solvent effects in the single point calculation the population analysis showed that the most stable wavefunction corresponds to a closed shell electronic structure.
- (18) The search for stationery points here is extremely difficult because of the extreme flatness of the PES (note that **TS19**, **D5** and **D6** are in the range of 0.1 kcal/mol). We suppose that the method we used (even though it uses a triple Z Dunning basis set) is not accurate enough to assess with exactness so close energy values. Despite this uncertainty the overall mechanism cannot be questioned.
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