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On the 1,3-dipolar cycloaddition reactions of indenone with N–N–C dipoles: density functional theory calculations

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Abstract

Density functional theory (DFT) calculations at the B3LYP/6-311G* theoretical level have been performed to study the 1,3-dipolar cycloaddition (1,3-DC) reactions between indenone (1) and different 1,3-dipoles (diazomethane and *N*-methyl *C*-methoxy carbonyl nitrilimine, compounds 2 and 3, respectively). The geometrical and energetic properties were analysed for the different reactives, transition states and cycloadducts formed (compounds 4–11). The reactions proceed in the gas-phase by an asynchronous concerted mechanism, yielding different regiochemistry dependent on the 1,3-dipole chosen, although with dipole 3 some degree of synchrony was found in the formation of cycloadduct 5. The 1,3-DC between 1 and 3 was regioselective, being the cycloadduct 11 favoured against 9. The NMR chemical shift parameters (GIAO method) were also calculated for the reactives and cycloadducts.

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1. Introduction

The 1,3-dipolar cycloaddition (1,3-DC) is a reaction governed by a concerted mechanism [1], approaching the 1,3-dipoles and dipolarophile on two parallel planes to yield a new pentagonal heterocycle ring after a rehybridization of the system. The great diversity of dipoles and dipolarophiles enable us to access cyclic systems that are very difficult to synthesise with other processes, and in some cases to improve the yield of other reactions. Moreover, 1,3-DC is also an effective procedure for the introduction of new chiral centres attached to heteroatoms [2]. Due to the concerted nature and often to the high degree of regioselectivity, only a limited number of product isomers are formed. Many theoretical approaches have been followed to explain the mechanism of these 1,3-DC reactions. Although most of the theoretical calculations yield a concerted mechanism for

the 1,3-DC, other studies suggest a stepwise biradical one [3,4]. However, worthy noting points remain to be studied concerning the asynchronous degree and the regiochemistry of these reactions.

The choice of dipoles and dipolarophiles affect the regioselectivity of the 1,3-DC reactions. Moreover, Sedqui et al. [5] describe the reaction between enones, particularly indenone, and diarylnitrilimines (DANI), they obtained as a mixture of two regioisomers with a 90:10 ratio (see Scheme 1). In the present paper, we investigated the reactions between the indenone and different 1,3-dipoles chosen as computational model systems (see Fig. 1).

On the other hand, the 1,3-DC reaction, between indenone as dipolarophile and 1,3-dipoles with the N–N–C moiety (i.e. diazomethane **2**, or *N*-methyl *C*-methoxy carbonyl nitrilimine **3**, opens a pathway to synthesise pyrazole fused rings.

Theoretical calculations have proven to be useful tools in organic chemistry [6–8] for predicting the stability of the synthesised products and reaction intermediates, and to explain the regiochemistry. Different theoretical works have

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Scheme 1. Experimental data (from [5]) of the 1,3-DC reaction between indenone and DANI.

been reported, for these 1,3-DC reactions, focusing on the electrostatic effects [9], on the role of the catalyst [10,11], or on the concerted versus stepwise mechanisms [12].

Among the theoretical methods available, the DFT calculations provided good accuracy for studying similar 1,3-DC reactions [12,13]. Moreover, the DFT methods recover some of the electron correlation energy missing at the HF level, which is necessary to investigate accurately the potential energy surface for a reaction, also allowing

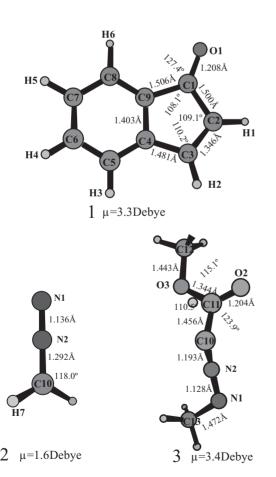


Fig. 1. Selected calculated (B3LYP/6-311 G^* /B3LYP//6-311 G^*) geometrical parameters of indenon molecule (1) and 1,3-dipoles (diazomethane, 2, and *N*-methyl *C*-methoxy carbonyl nitrilimine, 3, with the corresponding atom numbering and dipolar moment.

an approach to relatively large systems with the 6-311G* basis set. The application of these methods corroborated the experimental results, in the case of diazomethane [14], and predicted new results for the *N*-methyl *C*-methoxy carbonyl nitrilimine. The aim of the present work is to provide a theoretical basis for the understanding of 1,3-DC reactions of indenone. Several approaches were considered: frontier orbital theory (FMO), determination of the corresponding transition states (TSs), and the estimation of the reaction barriers. Finally, the gauge-invariant atomic orbital (GIAO) method [15] was used to calculate NMR chemical shift, to help the experimental cycloadduct determination, because it has shown to yield data comparable to those of the experiment [16].

2. Computational methods

The DFT calculations were carried out with the Gaussian 98 package of programs [17], using Pople's 6-311G* basis set [18,19], together with the Becke 3 parameters Lee–Yang–Parr (B3LYP) exchange correlation functional [20,21]. All the compounds studied were fully optimised without any symmetry restriction. A vibrational analysis was made to check the nature of all the stationary points. The structures 1–3, 5, 7, 9 and 11 presented no imaginary frequencies (true minima) at the corresponding theoretical level (B3LYP/6-311G*//B3LYP/6-311G*), yielding only one negative eigenvalue for the TSs 4, 6, 8 and 10 (values reported in parentheses in Figs. 2–4).

The 1 H, 13 C and 15 N NMR chemical shifts were also calculated with the Gaussian 98 program [17] by means of the GIAO method [15], using the tetramethylsilane (TMS) as 1 H and 13 C reference and dimethylformamide (DMF) as the 15 N one, at the B3LYP/6-311G* level (reference values of 13 C = 184.5307 ppm, 1 H = 32.2892 ppm and 15 N = 183.6849 ppm).

Moreover, the possibility of influence by asynchronous TSs biradical structures on the mechanism was dismissed after calculating the wavefunctions of all the TSs with unrestricted DFT theory, and using the keyword STABLE in Gaussian 98. The UB3LYP/6-311G* calculations predict the same TSs as the restricted ones, rejecting the presence of

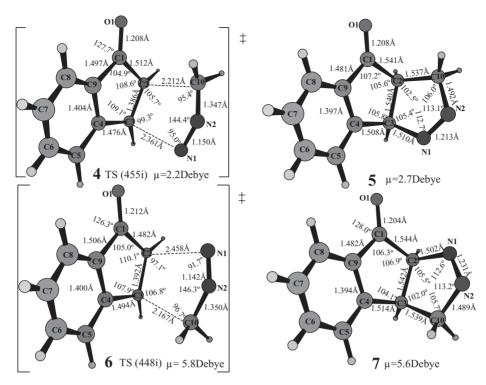


Fig. 2. Geometries (B3LYP/6-311G* level) of the TSs (4 and 6) and cycloadducts (5 and 7) for reaction 1, between indenone (1) and diazomethane (2), together with the dipole moment and in parentheses the imaginary frequency (cm⁻¹) for the TSs.

more stable biradical species, as reported previously for other 1,3-DC reactions [10].

3. Results and discussion

3.1. Geometrical parameters

Geometry optimisations, at the B3LYP/6-311G* level, were performed on structures **1–11**, and the results are presented in Figs. 1–4. Two different 1,3-DC reactions were studied between the indenone and two different 1,3-dipoles (compounds **2** and **3**, respectively; see Fig. 1). A selection of the geometrical parameters were included, for the reactives, TSs, and the cycloadducts formed, in Figs. 1–4.

Calculations gave a planar structure for the indenone (1) molecule. This moiety remained almost unchanged upon the 1,3-DC reactions. The only geometrical parameters that changed noticeably, from the indenone to the TSs and cycloadducts, were the \tilde{C}_2C_3 bond (1.346 Å characteristic of a double bond in 1), which increased to ca. 1.38 Å for the TSs, and to 1.54 Å for the cycloadducts (typical of a single C–C bond). The $\angle C_1C_2C_3$ and $\angle C_2C_3C_4$ angles remained almost similar for the TSs; however, for the products those angles shortened ca. $4^\circ.$

Concerning the 1,3-dipoles (2 and 3), the N_1 – N_2 , C_{10} – N_2 distances remained unchanged for 4 and 5 (compared to diazomethane 2); nevertheless, for 6 and 7, there was a lengthening of ca. 0.1 for N_1 – N_2 and 0.2 Å for C_{10} – N_2 , re-

spectively. Furthermore, dipole **3** showed a smaller lengthening (ca. 0.1 Å) for the C_{10} – N_2 and N_1 – N_2 bond lengths of structures **8–11**.

The new $C \cdots C$ and $C \cdots N$ bonds that formed, in the TSs, compared to the C-C and C-N distances in the cycloadducts, showed that the C-C bond formation was more advanced than the corresponding C-N distance (for the TS 4, the C-C bond was 43% longer than in its corresponding cycloadduct, whereas the C-N bond was only 56% longer, being 41 and 64%, for TS 6). These results predicted an asynchronous degree, where the C-C bond is formed faster than the C-N bond for the concerted mechanism. However, we observed that for the reaction 2 (see Figs. 3) and 4) the degree of asynchrony diminished, yielding an almost synchronic concerted mechanism for the TS 8 (here the C–C bond proved 57% longer than in its corresponding cycloadduct, whereas the C-N bond value was 59%, these being very similar). Moreover, in the TS 10, there was an opposite trend with the C-N bond formation to a larger degree than for the corresponding C–C one.

From all the above, in the reaction with diazomethane, there is a clear asynchronous degree, being the C–C bond formation being faster than the C–N one. However, with the use of the *N*-methyl *C*-methoxy carbonyl nitrilimine as 1,3-dipole, the reaction was triggered by a synchronous concerted mechanism TS **8**, or by asynchronous one (TS **10**) favouring the C–N bond formation.

Also, the C · · · C bond length was shorter than the C · · · N one, the ratio being $r_{\text{C-C}}/r_{\text{C-N}} = 0.94$, 0.88 and 0.91 for

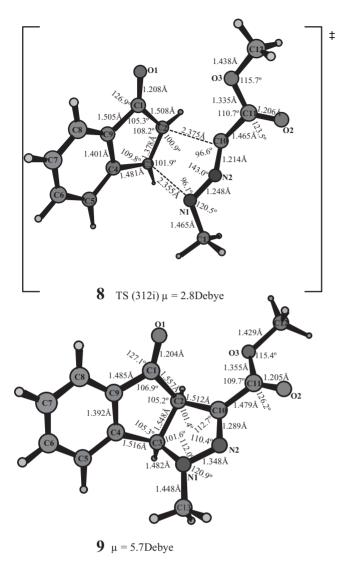


Fig. 3. Geometries (B3LYP/6-311G* level) of the TSs $\bf 8$ and cycloadducts $\bf 9$ for reaction 2 between indenone and *N*-methyl *C*-methoxy carbonyl nitrilimine, together with the dipole moment and in parentheses the imaginary frequency (cm⁻¹) for the TS.

structures **4**, **6** and **10**, respectively. However, for the TS **8** the behaviour was similar to that of the cycloadducts with common $\tilde{C}C$ bonds larger than the $\tilde{C}N$ ones $(r_{C-C}/r_{C-N}=1.01)$. These results are noticeable, given that in the five-membered cyclic product, the C–C bond is larger than the C–N one. The more advanced formation of the C–C bond can arise from a stronger interaction of the corresponding p-orbital lobes, yielding slightly earlier TS for the B3LYP functional.

The two fused five-membered rings were nearly planar but each had a slight amount of envelope conformation, in agreement with the X-ray results. Moreover, for the heterocyclic ring the atom N_1 is the flap of the envelope, the C_2 being the one in the carbon ring. Also, both rings formed a bent arrangement with a dihedral angle in the $100\text{--}125^\circ$ range for all the structures.

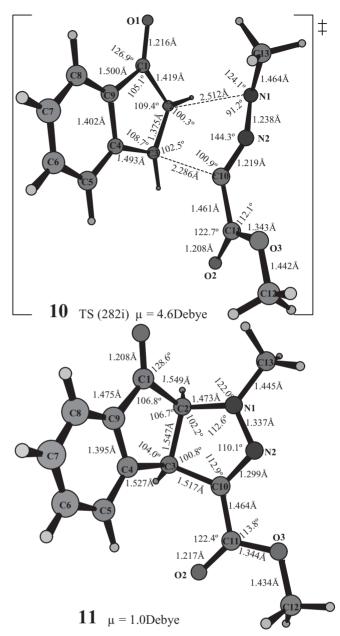


Fig. 4. Geometries (B3LYP/6-311 G^* level) of the TSs **10** and cycloadducts **11** for reaction 2 between indenone and *N*-methyl *C*-methoxy carbonyl nitrilimine, together with the dipole moment and in parentheses the imaginary frequency (cm⁻¹) for the TS.

On the other hand, Katritzky and co-workers [22] and Harlow and Simonsen [23] reported X-ray data for a diphenyl derivative of **9** obtained on sublimation, at $200\,^{\circ}$ C, of a diazocine derivative. The \tilde{N}_1N_2 and the $\tilde{C}_{10}N_2$ bond lengths being 1.37 and 1.30 Å, respectively—values very similar to the theoretical ones (1.35 and 1.29 Å, respectively).

3.2. Energetics

Two 1,3-dipoles (2 and 3) were used for the 1,3-DC reaction with indenone. FMO approach can be used to

Table 1 Frontier orbital energies (eV) for the indenone (1) and 1,3-dipoles (compounds 2 and 3), at B3LYP/6-311G* theoretical level

Compound	НОМО	LUMO	$\Delta E(I)^a$	$\Delta E(II)^{b}$
Indenone (1) Diazomethane (2)	-0.244 -0.227	-0.099 0.019 ^c	- -0.128	- -0.265
<i>N</i> -methyl <i>C</i> -methoxy carbonyl nitrilimine (3)	-0.244	-0.049	-0.145	-0.195

- ^a $\Delta E(I) = \text{HOMO}_{\text{dipole}} \text{LUMO}_{\text{indenone}}$.
- ^b $\Delta E(I) = \text{HOMO}_{\text{indenone}} \text{LUMO}_{\text{dipole}}$
- $^{\rm c}$ In diazomethane, the participating orbital is the LUMO + 1 instead of LUMO, see [24].

determine the relative reactivity of different dipoles, helping to select the best candidate for a reaction. Table 1 lists the HOMO and LUMO energies for indenone and 1,3-dipoles, together with the FMO energy gaps (eV). We conclude that the different 1,3-dipoles react with indenone under a HOMO_{dipole}-LUMO_{indenone} control, or in a normal electron-demand fashion, because the values of $\Delta E(I)$ were lower than the corresponding $\Delta E(II)$. The LUMO of diazomethane (2) presented a node on the carbon atom, therefore, this MO cannot participate in this 1,3-DC, being the LUMO + 1 the selected orbital [24].

On the other hand, the diazomethane gave the lowest values of $\Delta E(I)$, indicating that this reaction with indenone

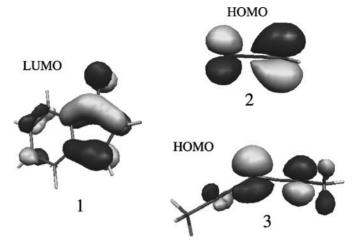


Fig. 5. LUMO of indenone 1 and HOMO of dipoles 2 and 3.

is preferred. In Fig. 5 are presented the HOMO of the 1,3-dipoles together with the LUMO of indenone.

From this figure, the LUMO of indenone presented slightly larger MO coefficient at C3 compared to the C2 atom, and the HOMO of dipoles 2 and 3 gave larger coefficients on the carbon atoms compared to nitrogen. Therefore, the favourable formation of cycloadduct 11 compared to 9, in reaction 2, can be explained by means of FMO.

Scheme 2. Energy reaction profile (kcal mol⁻¹; relative energies between products and reactives (ΔE_r) and activation energies (ΔE_a)) for the two 1,3-DC reactions studied (values in parentheses were corrected for the zero point vibrational energy (ZPVE)).

However, for reaction 1, the experimental and theoretical results favouring the formation of cycloadduct 5 compared to 7 (see Schemes 1 and 2) cannot be explained. The FMO approach to study the reactivity has many disadvantages, the main problem being that the energies are computed separately. Consequently, the steric and electronic interactions between reactants during the course of the reaction are totally neglected. To explore the changes in energies during the reaction, we evaluated the enthalpies of the reaction (between TSs and reactives) and relative energies (between products and reactives). Scheme 2 depicts those energies and the corresponding zero point vibrational energy (ZPVE) correction values in parentheses for the two reactions studied.

A qualitative reactivity can be estimated by applying Hammond's postulate [25]. Both reactions proceeded exothermically with the largest $\Delta E_{\rm r}$ energy values (ca. $-60\,{\rm kcal\,mol^{-1}}$) for reaction 2 and ca. $-30\,{\rm kcal\,mol^{-1}}$ for reaction 1. According to Hammond's postulate, the TSs should then be closer to the reactives. The activation energy values, $\Delta E_{\rm a}$, were also favoured for reaction 2. Moreover, these reactions yielded larger degrees of regioselectivity, cycloadduct 11 being favoured against 9. For the reaction 1 (between indenone and diazomethane) there was no clear regioselectivity according to the $\Delta E_{\rm a}$ and $\Delta E_{\rm r}$ values.

3.3. NMR chemical shifts

Taking into account the lack of experimental NMR data for the 1,3-DC studied, we have performed calculations with the GIAO method of the ¹H, ¹³C and ¹⁵N chemical shifts, for the reactives and products. Table 2 summarises the results (values in ppm) in order to help experimentalists with the cycloadduct characterisation. In accordance with the experimental data, for the diphenyl-1,3 dihydro-3a,8b oxo-4 indeno[2,3-d]pyrazole, obtained by a cycloaddition of indenone with DANI [5]; there is an agreement in the H₃ to H₆ hydrogens, being the experimental value falling within the 6.9–8.1 ppm range, while the calculated values changed from 7.3 to 8.3 ppm. The experimental values for H_1 and H₂ (4.77 and 6.04 ppm, respectively) [5] were closer to the theoretical values for compound 9. The value of 6.04 ppm was abnormally downshifted, and this could be attributed to the deshielding anisotropic electron current of the aromatic ring. On the other hand, the C₂ and C₃ calculated shifts matched the experimental values of 59.7 and 63.2 ppm, respectively, being in the same range as compound 9 (see Table 2).

Although there are no experimental data reported for the 15 N, it is remarkable to find a trend from these signals in Table 2, for the cycloadducts. In compounds 5 and 7, there was only one kind of signal, ca. 470 ppm corresponding to both $\rm sp^2$ nitrogens. However, for **9** and **11**, there were two different shifts, one ca. 90 ppm, corresponding to $\rm N_1$ with $\rm sp^3$ hybridisation and attached to a methyl group; and another one for the $\rm sp^3$ N₂ atom ca. 350 ppm.

Table 2 Theoretical (B3LYP/6-311 G^* //B3LYP/6-311 G^*) 15 N, 13 C and 1 H NMR chemical shifts (ppm), for compounds **1–3**, **5**, **7**, **9** and **11**

δ^a	1	2	3	5	7	9	11
$\overline{C_1}$	201.9			208.2	197.6	203.8	203.4
C_2	132.6			47.4	109.7	66.1	78.0
C_3	156.9			102.4	40.7	77.8	56.5
C_4	151.9			158.5	163.4	159.4	162.5
C_5	126.1			132.2	130.5	130.1	133.8
C_6	137.9			140.0	140.3	139.6	141.0
C_7	134.5			133.8	133.3	133.9	132.6
C_8	127.7			130.2	130.9	131.0	130.3
C ₉	135.7			140.7	140.8	142.7	140.0
C_{10}		23.3	79.3	85.2	87.1	139.0	139.3
C_{11}			156.9			165.6	170.6
C_{12}			53.9			53.2	53.4
C_{13}			43.5			40.5	39.0
N_1		190.1	86.1	472.6	473.5	95.1	89.0
N_2		-45.0	188.1	473.3	474.9	353.1	343.9
H_1	5.6			2.7	5.7	4.3	4.0
H_2	7.3			6.2	3.4	4.9	4.8
H_3	6.9			8.1	7.3	7.5	8.3
H_4	7.3			7.7	7.6	7.7	7.7
H_5	7.2			7.5	7.5	7.6	7.5
H_6	7.4			7.8	7.8	7.9	7.9

^a See Figs. 1–4 for atom numbering.

4. Conclusions

We have studied the 1,3-DC reactions between the indenone and two 1,3-dipoles (2 and 3), characterising the reactant, TSs, and different possible cycloadducts. The calculations predict a concerted mechanism for all the reactions, with the largest asynchronous degree for the reaction 1, between indenone and diazomethane. However, 1,3-DC reaction 2 with the dipole 3 yielded an almost synchronous process (compound 9).

We conclude that although the reaction mechanism has mainly an asynchronous degree, nevertheless, reaction 2, which yields the cycloadduct 11 and the TS 10, proceeds with an opposite synchronous mechanism.

Reaction 2 is favoured against 1, with lower values for the activation energy ($\Delta E_{\rm a}$) and larger ones for the relative energy ($\Delta E_{\rm r}$). Moreover, for reaction 2, the calculations predicted a selectivity, 11 being the cycloadduct favoured.

The geometries calculated at the B3LYP/6-311G* level were in agreement with previously reported experimental data [22,23], for a diphenyl derivative of structure **9**. The new bonds formed in the TSs were shorter for the $C \cdots C$ than for the $C \cdots N$ one, as opposed to the observed trend for the cycloadducts (C–C bonds larger than the C–N ones).

The calculated NMR chemical-shifts values were concordant with the experimental data available, in the sense that the C_2 or C_3 carbons attached to nitrogen (C_2 for compounds **6** and **11**, and C_3 for compounds **5** and **9**) appeared downfield.

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