An investigation of molecular mechanism and the role of Te-bridged-atom in the formation of polysubstituted pyridines *via* Hetero-Diels–Alder reaction of isotellurazole with acetylenic dienophile: a molecular electron density study

ABDELILAH BENALLOU*

Team of Chemoinformatics Research and Spectroscopy and Quantum Chemistry, Physical and Chemistry Lab, Faculty of Science, University Chouaib Doukkali, B. P. 20, 2300 El Jadida, Morocco
E-mail: abdo_benallou@yahoo.fr

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Abstract. An electron localization function (ELF) analysis and a detailed computational study of the hetero-Diels–Alder (HDA) reaction between isotellurazole and acetylenic dienophile have been performed. Then, B3LYP/Lanl2dz + 6-31+g(d) basis set level has been used to characterize the molecular mechanism and reactivity. The conceptual and computational DFT show that the most favorable regioisomeric product is the ortho/endo adduct, for which the energetic cost is 39.4 kcal/mol. Furthermore, ELF topological analysis envisages that the electron density of the pseudo-radical centers of the most electrophilic and nucleophilic atoms of the molecules come mainly from the charge transfer which takes place along the reaction pathway. The high asynchronicity of the bond formation means that two-stage one-step is the most appropriate mechanism for this reaction. However, the weak electronic contribution of the heavy chalcogen-bridged Tellurium atom in the C1–Te–N2 sequence has increased the activation barrier of the reaction. Otherwise, it has assisted the easy removal of the atom in the intermediary cycloadduct in the end of the reaction leading to the polysubstituted pyridine. So, despite the fact that Te atom is electronically rich, it plays a marginal role for improving reactivity of this [4+2] cycloaddition process.

Keywords. ELF topological analysis; NBO; HDA; IRC; conceptual DFT; TST.

1. Introduction

The use of Tellurium (Te) atom in synthetic organic chemistry is rare compared to other atoms such as oxygen- or nitrogen-bridged five- or six-membered heteroaromatics.^{1–5} However, Shimada *et al.*, have successfully used the Te atom in the synthesis of polysubstituted pyridines *via* Hetero-Diels–Alder reaction of isotellurazole with acetylenic dienophile at room temperature.⁶ It is worthy to note that the pyridine cycloadduct is an important natural product in biological, pharmaceutical and agrochemical products. The Hetero-Diels–Alder (HDA) reactions, including a heteroatom such as O, N, S,... etc. have significant importance due to their potential for the construction of six-membered heterocycles.^{7–11} This is facilitated by the presence of

electron withdrawing group (EWG) in the dienophile, by lowering the activation energy.¹² In this decade, calculations of the quantum mechanical observables along the reaction pathway have led to the understanding the bond forming and breaking processes.^{13,14} For this purpose, the electron localization function (ELF)¹⁵ method and bonding evolution theory (BET)¹⁶ have emerged to analyze the reaction mechanism.^{17–22} In the course of our studies, we evaluated the role of Te-bridged atom in the HDA reaction and highlight the cycloadduct regiochemistry in the HDA reaction of isotellurazole **1** with acetylenic dienophile **2**. Theoretical study has established the formation of intermediary cycloadducts and the subsequent excision of tellurium from the cycloadducts to form polysubstituted pyridines (Scheme 1).⁶

*For correspondence

Scheme 1. Regioselectivity mode of Hetero-Diels-Alder reaction of isotellurazole with acetylenic dienophile to yield poly-substituted pyridines.

In order to understand the role of Te-bridge in the progress of the HDA reaction and an insight into the nature of transition state and mechanism, the bond formation along the reaction pathway was studied. Effectively, the combination of DFT and ELF theory was used to characterize the reaction pathway through optimized geometries for the corresponding stationary points along the Intrinsic Reaction Coordinate (IRC) path²³ on the potential energy surface. To this end, the nucleophilic and electrophilic Fukui functions-based frontier molecular orbital (FMO) theory²⁴ and Houk rule-based Conceptual DFT (CDFT) were used. Whereas in Houk rule, ‘small-small’ and ‘large-large’ type interactions are more favored than interactions ‘large-small’ and ‘small-large’. However, this Houk approach is based essentially on the coefficients of orbital molecular HOMO/LUMO.

2. Computational

The optimizations of stationary points were performed using the Berny analytical gradient method,²⁵ and the IRC paths²⁶ were traced in order to check the energy profiles connecting the transition state (TS) to the two associated minima using the second order Gonzalez–Schlegel integration method.²⁷ The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method²⁸ and by ELF topological analysis.¹² The ELF study was carried out with the Multiwfn program²⁹ using the corresponding mono determinant wave functions of the selected structures. All computations were realized using the B3LYP exchange–correlation functional,³⁰ together with the standard Lanl2dz basis set level.³¹ This large basis set was successfully used for representing all atomic number mainly for the Te atom, and it has been considered as one of the most reliable basis set with B3LYP

hybrid for the heavy atom, however for N, O, C and H atoms we have employed the 6-31+g(d) basis set. The calculations were performed with the Gaussian 09 suite of programs,³² whereas, the charge transfer (CT) was calculated using the natural population analysis (NPA).³³ The global electrophilicity index ω ,³⁴ is given by the following expression, $\omega = \mu^2/2\eta$, in terms of the electronic chemical potential μ and the chemical hardness η . Both quantities was approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO, e_H and e_L , as $\mu = (e_H + e_L)/2$ and $\eta = (e_L - e_H)$, respectively.³⁵ Then the local electrophilicity for a site or an atom (k)³⁶ is given by the equation: $\omega_k = \omega f_k^+$. The nucleophilicity index N ,³⁷ based on the HOMO energies obtained within the Kohn–Sham scheme,³⁸ and defined as $N = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE})$. Similarly, the local nucleophilicity index N_k ³⁹ is defined as the product of global nucleophilic index N and the nucleophilic of the Fukui index $N_k = N f_k^-$. The nucleophilicity is referred to tetracyanoethylene (TCE), because it presents the lowest HOMO energy in a large series of molecules, where f_k^- and f_k^+ are the Fukui functions for nucleophilic and electrophilic attacks, respectively.⁴⁰

3. Results and Discussion

In order to establish the nature of the mechanism of the reaction, and to evaluate the changes of electron density along IRC of the HDA reactions between isotellurazole (1) and acetylenic dienophile (2), an analysis of the regioselectivity to choose the most favorable ortho/meta product based on DFT reactivity descriptors was performed; followed by an examination of the stationary points involved in the two regioisomeric patterns associated with the endo approach. Equally, a mechanistic study between isotellurazole 1 and acetylenic dienophile

Table 1. HOMO and LUMO energies, chemical potential μ , chemical hardness η , global electrophilicity ω and global nucleophilicity N .

Parameter	Isotellurazole	Acetylenic dienophile
HOMO (au)	−0.22056	−0.27545
LUMO (au)	−0.05933	−0.05921
μ (au)	−0.140	−0.167
η (au)	0.161	0.216
ω (eV)	1.65	1.75
N (eV)	2.87	1.11

2 and also a characterization of the C–C and N–C bond-formation step in the HDA reaction has been carried out. Simultaneously, an ELF bonding analysis along the new bond-formation/breaking pathway to this reaction was completed; likewise, an exploration of the role of heavy chalcogen bridged tellurium atom in the advancement of this reaction was achieved.

3.1 Regioselectivity study and analysis of the local and global descriptors based on CDFT reactivity

In this part, the characteristics of both isotellurazole (**1**) and acetylenic dienophile (**2**) entities are entirely determined, and then the distribution of the global and local electrophilicity and nucleophilicity indices of each molecule was performed; at this point the chemical potential μ and chemical hardness η have been used to characterize and describe the reactivity of these compounds. Thus, the CDFT reactivity indices of diene and dienophile substrates are given in Table 1.

Here, attention is paid to study the reactivity of the reactants, so we have noted that the chemical potential of isotellurazole is mostly higher compared with the acetylenic dienophile in which $\mu(-0.140) > \mu(-0.167)$, which clearly indicates that the global charge transfer is automatically taking place from diene (isotellurazole **1**) to dienophile (acetylenic **2**). While, the global electrophilic and nucleophilic index shows that

the acetylenic dienophile is more highly electrophilic than that of isotellurazole substrate, where $\omega(1.75) > \omega(1.65)$, so the isotellurazole moiety behaves as nucleophile in this reaction such as $N(2.84) > N(1.07)$. Subsequently, on the one hand, the charge transfer will take place from diene (**1**) to dienophile (**2**). On the other hand, the polarity of this reaction is moderate.

Further, to envisage the selectivity of this HDA reaction, we have utilized the local nucleophilicity N_k and electrophilicity ω_k indices,⁴¹ in which the first new σ bond will take place by the most favorable interaction between two more nucleophilic and electrophilic sites and by the Houk rule,⁴¹ The results are shown in Figure 1.

The selectivity of this reaction is fundamental to determine the most favorable product. So, in Figure 1, we have noted that the most appreciable interactions are between N2 and C3 atoms, which belong to the isotellurazole **1** and the acetylenic dienophile **2**, respectively. The local nucleophilic index of N2 is 4.83 eV that represents the major nucleophilic value of isotellurazole; furthermore, the local electrophilic index of C3 is 17.68 eV, being classified as the maximum value in the acetylenic dienophile moiety. Therefore, the most favorable interactions would take place between N2 and C3 centers. Subsequently, the ortho/endo adduct is the most stable product. Similarly, Houk rule reveals that the highest values of the coefficients of molecular orbital HOMO/LUMO is appreciated between N2 and C3 atoms and is followed by C1 and C4 interactions. Subsequently, it provides the ortho/endo adduct as majority product.

3.2 Analysis of the stationary points involved in the two regioisomeric patterns associated with the endo approach of isotellurazole **1** with acetylenic dienophile **2**

In order to evaluate the most stable regioisomeric channel in this HDA reaction, the most relevant features of

Figure 1. Schematic regioselectivity by using the local nucleophilicity N_k (**1**, in blue) and electrophilicity ω_k (**2**, in red) indices (eV) and Houk rule (in parentheses).

Figure 2. Bond distances (Å), and Wiberg index (given in parentheses) of ortho and meta transition state structures.

Figure 3. Energy profile in the gas phase for the HDA reaction between isotellurazole **1** and acetylenic dienophile **2**.

the *endo* regioisomer of TS_{ortho} and TS_{meta} are given in Figures 2 and 3. However, in this study we have utilized the most suitable B3LYP/Lan12dz basis set level to the heavy atom and the first- and second-row atoms are represented by the 6-31+g(d) basis set, for rapidity and reliability of the results. An analysis of the potential energy surface (PES) is performed in the gas phase at 298 K, the results show that this cycloaddition reaction takes place *via* an asynchronous transition state of both regioisomeric channels, in which Wiberg index allows us to note that the bond distances are completely different. The new bonds of N2-C3 and C1-C3 involved of the ortho and meta regioisomeric patterns have the smallest distances, in which the bond distances are 1.66 Å (0.71) and 1.83 Å (0.61) (Figure 2). Subsequently, this HDA reaction is highly asynchronous. As a consequence, N2-C3 and C1-C3 bonds will be formed

first along IRC of both ortho and meta adducts, respectively. On the other hand, the thermodynamic results show that the mechanism of meta regioisomeric process is highly energetic, such as that we have established that the activation energies are 39.4 kcal/mol and 42.1 kcal/mol for ortho and meta, respectively; likewise, the calculation of the free energies of activation ΔG provides a similar outcome, the barrier activation of ortho adduct is somewhat smaller compared with meta regioisomeric process. We have found that, 44.2 kcal/mol for ortho and 46.5 kcal/mol for meta structure. Consequently, the most favorable adduct of this reaction is ortho regioisomer, and therefore the activation barriers of both channel is very high. This is in good agreement with the feeble charge transfer; NBO analysis reveals that the charge transfer is about 0.11 e and 0.07 e of ortho and meta regioisomer, respectively. Unfortunately, comparable thermodynamic results related to the O, N or S bridged atoms of azadiene moiety are unavailable in the literature. It is interesting to note that these intermediary cycloadducts are not having sufficient stability to compare with the reagent (3.4 kcal/mol for Te-ortho intermediate and 2.1 kcal/mol for Te-meta intermediate). Subsequently, these products would probably lose the Te atom easily in thermal conditions to give polysubstituted pyridines as final product.

3.3 ELF bonding analysis of the bond-formation/breaking step in the IRC path in the HDA reaction of isotellurazole **1** with acetylenic dienophile **2**

In this section, we focus to understand the molecular mechanism, and also to comprehend the asynchronous bond-formation in this HDA reaction; likewise, an estimation of the Te-bridged contribution to the reactivity is fundamental. Our aim is to characterize the distribution of electronic density along the progress of the reaction. For this purpose, an ELF analysis along IRC of the most favorable *endo/ortho* channel was performed. The electronic populations of the most relevant ELF valence basins of selected structures along IRC are listed in Table 2, while the attractor positions for the most relevant points associated with the formation of the C1-C4 and N2-C3 single bonds, are shown in Figure 4.

For a greater understanding of bond formation in this reaction, the electronic population obtained from ELF analysis for some attractor showed that C3-C4 triple bonds of dienophile (**2**) presents three disynaptic basins V(C3,C4), V'(C3,C4) and V(C3,C4), whose electronic population is 2.48e, 2.39e and 0.23e, respectively. Whereas, in phase I this C3-C4 triple bonds would change sequentially to double bonds (2 π → π).

Table 2. Valence basin populations of the most relevant points calculated from the ELF of HDA reaction of isotellurazole with acetylenic dienophile, associated with the C1–C4 and N2–C3 bond-formation step. Bond order (Wiberg index) and charge transfer in *e* (NBO).

Phase	R	I	II	III	IV	V	VI	VII (TS)	VIII	IX	X	PR
d(C1–C4)	5.30	3.00	2.88	2.80	2.74	2.68	2.65	2.63	2.45	2.22	2.05	1.56
d(N2–C3)	6.65	2.24	2.16	1.91	1.80	1.74	1.70	1.66	1.60	1.57	1.55	1.47
BO(C1,C4)	0.001	0.034	0.051	0.104	0.147	0.198	0.227	0.257	0.355	0.549	0.633	0.992
BO(N2,C3)	0.020	0.131	0.184	0.373	0.496	0.617	0.668	0.712	0.803	0.886	0.911	1.013
CT	0.007	0.040	0.099	0.128	0.133	0.121	0.113	0.107	0.059	0.027	0.060	0.129
V(C1)										0.33	0.46	
V'(C1)												0.72
V(N2)						0.30						
V'(N2)	3.33	3.14	3.17	3.10	3.12	2.87	2.81	2.78	2.73	2.73	2.74	2.81
V(C3)					0.14	0.26						
V(C4)							0.60	0.68	0.75	0.87	0.89	
V(C1,Ca)	3.24	3.06	2.96	2.84	2.75	2.68	2.63	2.60	2.45	2.25	2.19	2.05
V'(C1,Ca)	3.24	3.06										
V(Ca,Cb)	2.51	2.59	2.73	2.92	3.04	3.13	3.20	3.23	3.37	3.53	3.59	1.89
V'(Ca,Cb)					3.04	3.13	3.19	3.23	3.37	3.53	3.59	1.83
V(Cb,N2)	2.57	2.47	2.33	2.11	1.96	1.84	1.80	1.76	1.67	1.59	1.58	1.55
V'(Cb,N2)	2.57											
V(N2,Te)	1.19	1.27	1.32	1.48	1.52	1.53	1.53	1.52	1.48	1.42	1.38	1.08
V(C1,Te)	1.82	1.83	1.85	1.88	1.89	1.91	1.92	1.92	1.97	1.74	1.66	
V(C1,Cc)	2.16	2.24	2.25	2.26	2.28	2.29	2.30	2.30	2.29	2.24	2.20	2.18
V(C4,Cd)	2.63	2.84	2.89	3.13	3.27	3.43	2.89	2.87	2.82	2.68	2.62	2.55
V(C1,C4)												2.03
V(N2,C3)							0.71	0.81	1.01	1.21	1.25	1.58
V(C3,C4)	2.48	2.47	2.46	2.37	2.26	2.17	2.12	2.08	2.00	1.95	1.94	1.80
V'(C3,C4)	2.39	2.42	2.40	2.28	2.21	2.13	2.10	2.08	2.00	1.94	1.93	1.73
V''(C3,C4)	0.23											
V(Te)	2.33	2.33	2.34	2.35	2.37	2.38	2.39	2.40	2.42	2.44	2.45	2.54
V'(Te)	2.39	2.41	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.44	2.44	2.52
V'''(Te)												0.33

Equally, in phase I and II, C1–Ca and Cb–N2 double bonds of azadiene (**1**) which has two pairs of disynaptic basins V(C1,Ca);V'(C1,Ca) and V(Cb,N2);V'(Cb,N2), having electron density of 3.24e and 2.57e, would transform finally to the single bond ($\pi \rightarrow \sigma$). For this instance, at the beginning of the reaction, the monosynaptic basins of V(C3,C4), V'(C3,C4), V(C1,Ca) and V(Cb,N2) would sequentially lose more electron density until the end of the reaction. In this sense, in phase IV, Ca–Cb single bond of azadiene (**1**) with electronic population 2.51e becomes double bond ($\sigma \rightarrow \pi$), which presents two disynaptic basins of V(Ca,Cb) and V'(Ca,Cb) integrating 3.04e of each one; however these latter basins benefit to an important electron density along IRC. The most relevant change is located in phases IV and V, as revealed in our analysis that the appearance of two monosynaptic basins V(C3) and V(N2) associated with the C3 and N2 atoms, which integrate to 0.14e and 0.30e, respectively. So, in this case, the two pseudo-radicals, monosynaptic basins are necessary for the formation of the new bond C3–N2 and completed,

whereas the other terminal monosynaptic basin at the C1 and C4 atoms are not yet formed. Exactly, in phase VI, a new bond of C3–N2 is created with an electronic population of 0.71e, similarly at this phase, a new monosynaptic basin under C4 atom has appeared and integrates to 0.60e. In phase IX, another relevant change takes place at the azadiene moiety (**1**) such as a new monosynaptic basin of V(C1) appeared finally, and integrates to 0.33e. Therefore, the formation of the attractor responsible for the formation of the C1–C4 bond is now completed, in this way, the two monosynaptic basins related to the C1 and C4 atoms merge into one disynaptic basin of V(C1,C4) associated with the C1–C4 σ bond at the end of the reaction, whose electronic population is 2.03e.

Interestingly, this mechanistic process takes place through two-stage one-step; the first stage between phase I and phase VI, while the second stage between phase VII and the product. Simultaneously, the charge transfer (CT) has known two important stages, the first at the formation of C3–N2 bond and the second, at

Figure 4. ELF attractors of some selected points of the IRC associated with the formation of the new C–C and N–C single bond in the HDA reaction of isotellurazole **1** with acetylenic dienophile **2**.

the formation of the C1–C4 bond, although maximum CT along IRC occurs in phase IV corresponding with the formation of the first bond, 0.133e. Otherwise, the

electron density of the disynaptic basin V(C1,Te) and V(N2,Te) associated with the C1–Te and N2–Te bonds proceed step by step to decrease more, until the split

Figure 5. The bonding changes at selected points involved in the HDA reaction of isotellurazole **1** with acetylenic dienophile **2**.

Figure 6. Electronic population, (ine), of some relevant attractors along IRC.

of these basins at the end of the reaction, $V(C1)$ and $V(Te)$. This major change has facilitated the excision of the Te atom from the intermediary cycloadduct to yield pyridine molecule in accordance with the experimentally observed results.⁶ Moreover, the formation of the new C-C and N-C σ bond appeared highly asynchronous, in which Wiberg index calculation reveals that the formation of N2-C3 σ bond is always in advance to that of C1-C4 σ bond, as shown in Table 2; whereas, note that Wiberg index (N2-C3) > Wiberg index (C1-C4). A conclusion has been attained from this study, that the HDA reaction proceeds through two-stages one-step *via* pseudo-radical formation at the most relevant center between azadiene moiety of **1** and the acetylenic part of the dienophile **2**, so the first stage is located between the reagent and phase VI, in which N2-C3 σ single bond will

be formed first, while in the second stage between the phase VII and the product, where C1-C4 σ single bond is formed completely at the end of the reaction. So, this mechanism is a not concerted process. A summarized picture illustrating the bonding changes along selected points involved in this HDA reaction is presented in Figure 5, while a representation of the change of electron density along some relevant attractors is given in Figure 6.

Some conclusions can be drawn from this study. The large electronic population under lone pairs of Te atom, as well as the moderate electronic population of the N2-Te and C1-Te bonds, and the split of the C1-Te bond in the end of the reaction reveal that N2-Te and C1-Te bonds are totally polarized and that the total electron density is concentrated either in N2 or Te as well as in C1

Table 3. Atomic contribution to electronic population (in e) of N2-Te and C1-Te bonds.

Phases	N2-Te Bond				C1-Te Bond			
	N2		Te		C1		Te	
	Population	%	Population	%	Population	%	Population	%
R	1.15	100	0.00	0	1.82	100	0.00	0
I	1.33	103	0.00	0	1.84	101	0.00	0
II	1.40	106	0.00	0	1.86	100	0.00	0
III	1.47	100	0.00	0	1.87	100	0.00	0
IV	1.52	100	0.00	0	1.89	100	0.00	0
V	1.53	100	0.00	0	1.91	100	0.00	0
VI	1.51	98.7	0.00	0	1.92	100	0.00	0
VII	1.51	100	0.00	0	1.94	101	0.00	0
VIII	1.48	100	0.00	0	1.97	100	0.00	0
IX	1.44	105	0.00	0	2.04	117	0.00	0
X	1.43	103	0.00	0	1.74	105	0.00	0

Figure 7. C–C bond formation model in the Hetero-Diels–Alder reaction of isotellurazole **1** with acetylenic dienophile **2**.

or Te. To this end, we calculate the atomic contribution to the electronic population of the N2-Te and C1-Te bonds, and the results are given in Table 3.

Due to the low hetero-aromaticity of Te atom, the total electronic population of both C1-Te and N2-Te bonds have been absorbed by the C1 and N2 atoms (Table 3), these latter atoms represent the most nucleophilic centers of azadiene (**1**) reagent. An inequitable reorganization of electron density makes these bonds extremely polarized, and thus the electronic population of the tellurium atom is concentrated under lone pairs, and it makes this atom electronically very rich. So, on the one hand, the feeble electronegativity character of

the heavy chalcogen-bridged atom has helped for the whole concentration of electron density at the N2 and C1 atoms, and subsequently polarizes C1-Te and N2-Te bonds. These factors explain the facile breaking of these bonds and the subsequent removal of the tellurium atom at the end of the reaction. On the other hand, the pseudo inactive character of Te atom (neither electron donor nor attractor) has negatively influenced the development of this reaction (high activation energy). Simultaneously, Te atom plays a small role in the high regio-selectivity observed in this Hetero-Diels-Alder reaction, due to the trivial charge transfer of the C1-Te-N2 bridged sequence.

Figure 8. Energy profile, in (kcal/mol), along two-stage one-step mechanism associated with the formation of the C1–C4 and N2–C3 single bonds of the HDA reaction of isotellurazole **1** with acetylenic dienophile **2**.

Consequently, the formation of the pseudo-radical at N2 and C3 atoms is due mainly to the asymmetric distribution of electron-density in the isotellurazole and acetylenic dienophile moieties. Therefore, the asymmetric formation of these pseudo-radical centers of two reagents is responsible for the asynchronous bond formation and the regioselectivity observed in this HDA reaction. Accordingly, this HDA reaction takes place along two-stage one-step mechanism (Figure 7). Whereas, in Figure 8, we have presented the relative position of the selected points along IRC with respect to the energy profile along two-stage one-step mechanism of the HDA reaction between isotellurazole **1** and acetylenic dienophile **2**.

4. Conclusions

The molecular mechanism of the Hetero-Diels-Alder (HDA) reaction of isotellurazole with acetylenic dienophile has been studied at the B3LYP/lanl2dz + 6-31+G(d) level of theory. A conceptual DFT and a thermodynamic study reveal that the ortho/endo mode is the most stable and favorable adduct in this reaction. Importantly, this reaction takes place along two-stage one-step mechanism. In the first stage of the reaction, the N2–C3 bond is formed between the pseudo-radical centers positioned at the most electrophilic carbon (C3) of acetylenic dienophile **2**, and the most nucleophilic center based on electron density provided by the lone pairs of the N2 nitrogen of isotellurazole **1**. In the second stage of the reaction, the C1–C4 bond is formed

between the pseudo-radical center positioned at the C1 carbon of isotellurazole and the C4 carbon of acetylenic dienophile. Furthermore, the low hetero-aromaticity of the Te atom makes C1–Te and N2–Te bonds extremely polarized, and thus, the weak electronegativity character of this heavy chalcogen-bridged atom has helped in the transfer of electron density to the N2 and C1 atoms, assisting the easy removal of tellurium atom from the intermediary adduct in thermal conditions. Simultaneously, the pseudo-neutral character of the Te atom has increased the activation energy and this cycloaddition [4+2] pathway is highly energetic. Thus, the electron density characterization along IRC reaction path is useful to explain the molecular mechanism and the experimentally observed results.

Supplementary Information (SI)

Coordinates, energies and frequencies for all the stationary points as well as the IRC of the most favorable regio-isomeric channel involved in HDA reaction are available in Supplementary Information which is available at www.ias.ac.in/chemsci.

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