**Electronic supplementary information**

**Generation of a substituted 1,2,4-thiadiazole ring via the [3+2] cycloaddition reaction of benzonitrile sulfide toward trichloroacetonitrile. A DFT study of the regioselectivity and of the molecular mechanism**

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**S2**

*ELF topological analysis of 32CA reaction between BNS1 and TCAN2.*

The electron density, *ρ*(*r*), of a molecular system can represent all information hidden in the wave-function of such system. Thus, a successive detection of the electron density changes along a chemical reaction in which a continuous redistribution of *ρ*(*r*) proceeds with the reaction can provide valuable information about bonds forming/breaking patterns. In this way, from the molecular mechanistic point of view, our questions can greatly be addressed [1]. One of the most popular function, introduce by Becke and Edgecombe [2], is electron localization function, ELF, by which essential information about the electron density shared between neighboring atoms can be extracted [1].

 A great deal of work has confirmed that the ELF topological analysis of the bonding changes along a reaction path is a powerful tool to establish the molecular mechanism of a reaction [3-5]. After an analysis of the electron density, ELF provides basins which are the domains in which the probability of finding an electron pair is maximal. The basins are classified as core and valence basins. The latter are characterized by the synaptic order; *i.e.* the number of atomic valence shells in which they participate [6]. Thus, there are monosynaptic, disynaptic, trisynaptic basins and so on. Monosynaptic basins, labelled as V(A), correspond to lone pairs or non-bonding regions, while disynaptic basins, labelled as V(A,B), connect the core of two nuclei A and B and, thus, correspond to a bonding region between A and B. This description recovers the Lewis bonding model, providing a very suggestive graphical representation of the molecular system.

The ELF topological analysis of significant organic reactions involving the formation of new C–C single bonds has shown that it begins in the short C–C distance range of 1.9–2.0 Å by merging two monosynaptic basins, V(Cx) and V(Cy), into a new disynaptic basin V(Cx,Cy) associated with the formation of the new Cx–Cy single bond [39]. The Cx and Cy carbons characterized by the presence of the monosynaptic basins, V(Cx) and V(Cy), are called *pseudoradical* centers [7].

In order to understand the molecular mechanism of the 32CAreaction between **BNS1** and **TCAN2**, an ELF topological analysis of theMPWB1K/6-311G(d) wave functions of some relevant points, **P1** through **P5**, was performed along the IRC profile associated with the more favorable **TS1**.The IRC profile of **TS1** including the attractor positions associated with points **P1**-**P5** is given in Fig. S1. As shown in Fig. S2, the most relevant basins in separate **BNS1** and **TCAN2** are those corresponding to the interacting systems; *i.e.* the C1–N2, N2–S3, and C4–N5 bonds. In **BNS1**, while the C1–N2 bonding region is characterized with the presence of V(C1,N2) and Vʹ(C1,N2) disynaptic basins integrating 2.83 and 2.64e, respectively, the N2–S3 bonding region is characterized with the presence of V(N2,S3) disynaptic basin integrating 2.67e. Moreover, lone pairs of S3 are described with the presence of two V(S3) and Vʹ(S3) monosynaptic basins integrating 2.75 and 2.89e, respectively. Consequently, based on the ELF valence basins population, while N2–S3 bond presents a singlet character, the sum of V(C1,N2) and Vʹ(C1,N2) disynaptic basins population, 5.47e, is close to 6e indicating a triple character for C1–N2 bond. On the other hand, the sum of V(S3) and Vʹ(S3) monosynaptic basins populations is 5.64e which is very close to 6e demonstrating that S3 sulfur atom bears a negative charge. The ELF valence shapes for **BNS1** are in agreement with the corresponding Lewis structure presented in Scheme 3. Additionally, the C4–N5 bonding region in **TCAN2** is identified with the existence of V(C4,N5), Vʹ(C4,N5), and Vʹʹ(C4,N5) disynaptic basins integrating 1.54, 1.53, and 1.54e, respectively. The sum of mentioned disynaptic basins population is 4.61e indicating a noticeable difference of 6e which is expected for C4–N5 triple bond. It is worth noting that the presence of a highly electron withdrawing CCl3 substitution on the **TCAN2** leads to the polarization of C4–N5 σ bonding electrons toward C4 resulting a significant decrease in C4–N5 bonding population. The lone pair of N5 nitrogen atom is also characterized with the presence of a V(N5) monosynaptic basin integrating 3.09e. This value which is different from the expected value of 2e indicates that the more electronegative N5 nitrogen atom exhibits a higher propensity than C4 carbon atom to attract electron density of C4–N5 bonding region to itself.

As two reagents approach each other along the reaction channel, At **P1**, *d*(C1–N5) = 2.382Å and *d*(S3–C4) = 2.573Å, a new V(N2) monosynaptic basin with an initial population of 0.33e emerges over N2 nitrogen atom. The electronic density of this basin comes mainly from the V(C1,N2) and Vʹ(C1,N2) disynaptic basins, which are depopulated to 2.39 and 2.59e, respectively. At **P2** where *d*(C1–N5) = 2.212Å and *d*(S3–C4) = 2.411Å, which is associated with the favorable **TS1** a new V(C4) monosynaptic basin integrating 0.31e appears over C4 carbon atom as a result of depopulation V(C4,N5) disynaptic basins from a sum of 4.61e into a sum of 4.21e. Emerging V(C4) monosynaptic basin in a very early point **P2**, compared with point **P5** located at the almost end of the IRC profile in which S3–C4 single bond beings to form, can be related to the presence of CCl3 substitution on C4. In other words, a highly electron withdrawing CCl3 group leads the *pseudoradical* C4 center to be stabilized and is allowed to form. At **P3** in which *d*(C1–N5) and *d*(S3–C4) are 2.027 and 2.264Å, respectively, while a re-depopulation of V(C1,N2) disynaptic basins leads to the formation of a new V(C1) monosynaptic basin integrating 0.15e over C1 carbon atom, a new Vʹʹ(S3) monosynaptic basin integrating 0.22e is allowed to be emerged over S3 sulfur atom. It should be noted that at **P3** while V(N2,S3) disynaptic basin is depopulated to 1.80e, the sum of V(S3) and Vʹ(S3) monosynaptic basins population is reduced to 5.11e. Consequently, the electronic density of Vʹʹ(S3) monosynaptic basin comes from depopulation of both V(N2,S3) disynaptic and, V(S3) and Vʹ(S3) monosynaptic basins. Therefore, at **P3** the two *pseudoradical* centers required for the subsequent S3–C4 single-bond formation have already been formed. At **P4**, *d*(C1–N5) = 1.813Å and *d*(S3–C4) = 2.116Å, the C1–N5 single bond beings to form characterized with the presence of a new V(C1,N5) disynaptic basin with an initial population of 1.13e. Finally, at **P5** for which *d*(C1–N5) and *d*(S3–C4) are, respectively, 1.649 and 2.008Å, the S3–C4 single bond starts to form by merging two Vʹʹ(S3) and V(C4) monosynaptic basins into a new V(S3,C4) disynaptic basin integrating 1.63e. It is noteworthy that when S3–C4 single bond beings to form, the V(C1,N5) disynaptic basin reaches to a population of 1.52e. If this value is compared with the corresponding value in cycloadduct **CA1**, 1.82e, one can easily be concluded that when formation of S3–C4 single bond beings, formation of C1–N5 single bond, started at **P4**, is almost completed by more than of 83% in clear agreement with the *two-stage* *one-step* molecular mechanism.



**Fig. S1.** MPWB1K/6-311G(d) IRC profile associated with the more favorable **TS1** of the studied 32CA reaction between **BNS1** and **TCAN2** including attractor positions of considered points **P1**-**P5** in the ELF topological analysis.



**Fig. S2.** Attractor positions for separate **BNS1** and **TCAN2**.

**References**

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**S3**

MPWB1K/6-311G(d) Cartesian coordinates of the optimized structures in the presence of toluene including thermochemical data for the species involved in the 32CA reaction between BNS1 and TCAN2.

**BNS1**

C –2.55630200 –1.19928000 0.00000800

C –1.17942600 –1.20812300 0.00000900

C –0.48788500 –0.00007300 0.00000600

C –1.17925900 1.20807300 0.00000900

C –2.55613700 1.19942100 0.00000800

C –3.24426300 0.00011800 0.00000600

H –3.09474300 –2.13248100 0.00000900

H –0.63503800 –2.13739600 0.00001100

H –0.63474300 2.13727100 0.00001100

H –3.09444900 2.13269700 0.00000900

H –4.32204200 0.00019300 0.00000700

C 0.92315400 –0.00017800 0.00001600

N 2.07265300 –0.00024600 0.00003500

S 3.68457200 0.00010500 –0.00004200

Zero-point correction= 0.104218 (Hartree/Particle)

Thermal correction to energy= 0.111622

Thermal correction to enthalpy= 0.112566

Thermal correction to Gibbs free energy= 0.070836

Sum of electronic and zero-point energies= –722.506005

Sum of electronic and thermal energies= –722.498601

Sum of electronic and thermal enthalpies= –722.497656

Sum of electronic and thermal free energies= –722.539386

Entropy= 87.827 cal/mol·K

**TCAN2**

C –0.02570100 –0.00010800 0.00020000

C –1.47578700 0.00007100 0.00385800

N –2.61596000 –0.00028900 0.00714400

Cl 0.53173000 –0.90555200 –1.40261500

Cl 0.54004800 –0.76066900 1.48334200

Cl 0.53532000 1.66635200 –0.08510100

Zero-point correction = 0.018250 (Hartree/Particle)

Thermal correction to energy = 0.024394

Thermal correction to enthalpy= 0.025338

Thermal correction to Gibbs free energy= –0.013137

Sum of electronic and zero-point energies= –1511.672188

Sum of electronic and thermal energies= –1511.666044

Sum of electronic and thermal enthalpies= –1511.665100

Sum of electronic and thermal free energies= –1511.703575

Entropy= 80.978 cal/mol·K

**TS1**

C –4.28193200 1.75837900 0.00002100

C –3.01688900 1.21186100 0.00002300

C –2.87552700 –0.16875300 –0.00000500

C –3.99610800 –0.99748200 –0.00003400

C –5.25173500 –0.43424200 –0.00003500

C –5.39643500 0.94153600 –0.00000700

H –4.39690400 2.82966900 0.00004300

H –2.13755000 1.82928700 0.00004400

H –3.87255000 –2.06759600 –0.00005500

H –6.12041200 –1.07181700 –0.00005700

H –6.38262400 1.37660800 –0.00000800

C –1.59448200 –0.78254900 –0.00000400

N –0.84684500 –1.68247500 –0.00000600

S 0.68550800 –2.14762800 –0.00000800

C 2.46957200 0.40297400 0.00000600

C 1.00240600 0.22179600 0.00000300

N –0.02485000 0.77768600 0.00000400

Cl 3.16441900 –0.33428400 1.44164100

Cl 2.82942000 2.13200700 0.00000200

Cl 3.16442900 –0.33429300 –1.44162000

Zero-point correction = 0.123494 (Hartree/Particle)

Thermal correction to energy= 0.137643

Thermal correction to enthalpy= 0.138587

Thermal correction to Gibbs free energy= 0.078169

Sum of electronic and zero-point energies= –2234.162019

Sum of electronic and thermal energies= –2234.147871

Sum of electronic and thermal enthalpies= –2234.146927

Sum of electronic and thermal free energies= –2234.207344

Entropy = 127.160 cal/mol·K

**TS2**

C –3.49677400 –0.57043500 1.19805500

C –2.32747600 0.15861700 1.20399700

C –1.74382900 0.52989000 0.00001700

C –2.32748500 0.15861600 –1.20395900

C –3.49678300 –0.57043500 –1.19800800

C –4.08124200 –0.93635400 0.00002600

H –3.95284400 –0.85383200 2.13238500

H –1.86422300 0.44448100 2.13368600

H –1.86423800 0.44448000 –2.13365200

H –3.95286000 –0.85383200 –2.13233400

H –4.99422500 –1.50940000 0.00002900

C –0.54824900 1.33293100 0.00001400

N –0.18232500 2.46793500 0.00001800

S 1.02484500 3.45077500 0.00001200

C 1.48331700 –0.93431400 –0.00001700

C 1.52010900 0.53887300 –0.00001300

N 2.31614900 1.40280200 –0.00001600

Cl 0.65293400 –1.50697600 1.44689700

Cl 3.12970900 –1.58746000 –0.00002700

Cl 0.65292100 –1.50696300 –1.44692800

Zero-point correction= 0.123884 (Hartree/Particle)

Thermal correction to energy= 0.137604

Thermal correction to enthalpy= 0.138548

Thermal correction to Gibbs free energy = 0.081629

Sum of electronic and zero-point energies = –2234.137195

Sum of electronic and thermal energies = –2234.123475

Sum of electronic and thermal enthalpies = –2234.122531

Sum of electronic and thermal free energies = –2234.179450

Entropy= 119.797

**CA1**

C –4.14903900 –1.68684600 0.00001200

C –2.83823300 –1.25531900 –0.00000300

C –2.55647200 0.10235000 –0.00001300

C –3.59588100 1.02134800 –0.00000900

C –4.90251200 0.58553000 0.00000300

C –5.18208900 –0.76952800 0.00001400

H –4.36357900 –2.74336600 0.00002200

H –2.02613600 –1.96297200 –0.00000300

H –3.36682100 2.07418500 –0.00001700

H –5.70697100 1.30316100 0.00000500

H –6.20532200 –1.10970300 0.00002500

C –1.17117600 0.56995900 –0.00002700

N –0.88039300 1.84111900 –0.00002300

S 0.73845000 2.01824700 –0.00002500

C 2.29837100 –0.35706200 0.00001200

C 0.96788000 0.33052300 –0.00000600

N –0.14159100 –0.31682900 –0.00001000

Cl 2.43536500 –1.36042600 –1.44053000

Cl 2.43533700 –1.36043400 1.44055100

Cl 3.58708700 0.85209400 0.00002100

Zero-point correction = 0.127861 (Hartree/Particle)

Thermal correction to energy = 0.140786

Thermal correction to enthalpy = 0.141731

Thermal correction to Gibbs free energy = 0.085421

Sum of electronic and zero-point energies = –2234.266938

Sum of electronic and thermal energies = –2234.254013

Sum of electronic and thermal enthalpies = –2234.253068

Sum of electronic and thermal free energies = –2234.309378

Entropy= 118.514 cal/mol·K

**CA2**

C –3.18613500 –1.33534700 0.80007000

C –1.94277300 –0.73967900 0.84932100

C –1.67987500 0.38728100 0.08766200

C –2.68360400 0.91745300 –0.70982400

C –3.92214700 0.31497400 –0.76488400

C –4.17600500 –0.81464900 –0.01048200

H –3.38107700 –2.20896600 1.40077800

H –1.18293200 –1.14982900 1.49151400

H –2.48068800 1.80338300 –1.28885800

H –4.69170800 0.72930200 –1.39590600

H –5.14477700 –1.28619500 –0.05047000

C –0.39409700 1.09826400 0.13327100

N –0.42261300 2.40092900 0.23444000

S 1.09244000 2.96344700 0.23336100

C 1.42982700 –0.80948300 –0.11325800

C 0.95534100 0.61085900 0.03367500

N 1.85036000 1.54863500 0.08843100

Cl 1.43072000 –1.59191200 1.48461700

Cl 3.07063500 –0.86115100 –0.74363100

Cl 0.38127500 –1.70739700 –1.21064700

Zero-point correction = 0.127809 (Hartree/Particle)

Thermal correction to energy = 0.140562

Thermal correction to enthalpy = 0.141506

Thermal correction to Gibbs free energy = 0.086719

Sum of electronic and zero-point energies = –2234.247920

Sum of electronic and thermal energies = –2234.235167

Sum of electronic and thermal enthalpies = –2234.234223

Sum of electronic and thermal free energies = –2234.289010

Entropy = 115.308 cal/mol·K

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