New insight into experimental and theoretical properties of some *para*-like substituted 2-azidothiophenes

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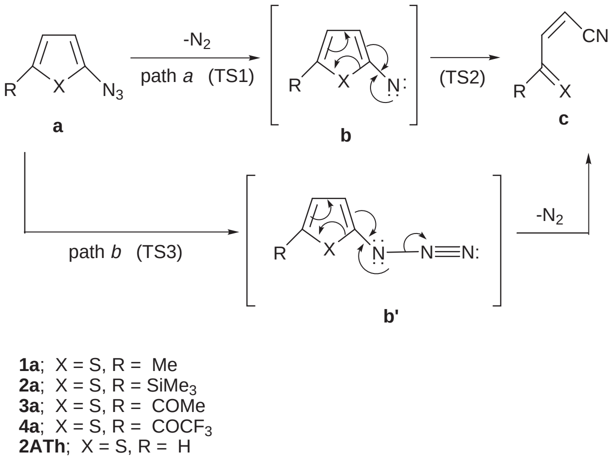
The *para*-like substituent effect on the thermolysis of a number of 5-substituted (-Me, -SiMe$_3$, -COMe, COCF$_3$) 2-azidothiophenes **1a**–**4a** is investigated experimentally and at the AM1 and RHF/6-31G* + ZPE levels of theory. Calculated structures located along the reaction coordinate from the reactant azides **1a**–**4a** show that the extrusion of the N$_2$ molecule is the rate determining step of the process and leads to neutral ring-opened 4-cyano-1-heterodiene products **1c**–**4c** in a concerted manner. The activating 5-methyl substituent of **1a** causes rate enhancement with respect to the 2-azidothiophene (**2ATh**), whereas decreasing rates are observed in the cases of the deactivating 5-COMe and 5-COCF$_3$ groups, **3a** and **4a**. Theoretical results provide a reasonable description of the *para*-like substituent effects on the dissociation, giving electronic structural changes and the corresponding energies involved, as practical support to the experimental data.

Introduction

Thermal azido-dissociation into molecular nitrogen of five-membered 2-azidoheteroaryls containing one heteroatom generally results in the cleavage of the original heteroaryl ring affording useful nitrilic hetero-1,3-diene products type **c** (Scheme 1, R = H). Other products can also be formed depending on the number (and the position) of heteroatoms in the ring.[1] This reaction has been exploited for application in synthesis[1,2] but the details of the mechanism involved represent an intriguing question. The significantly low activation energies of thermally induced ring-cleavages of 2-azido-5-oxofurans,[3] 5-azidotriazoles[4] and 5-azidopyrazoles[5] have been explained either by valence-bond contributors to the presumed nitrene intermediates[3,5] or by concerted processes.[4,5b]



Scheme 1

Further findings on the thermolysis of isomeric α-azido- and β-azido-thiophenes[6] (and the benzo derivatives[7]), and α-azido- and β-azido-selenophenes,[8] suggested that the dissociation of the α-azidoheteroaryls is likely to proceed *via* a low-energy process involving concerted ring-opening and dinitrogen loss (path *b*; **b′**, Scheme 1), rather than *via* singlet nitrene (path *a*; **b**, R = H, X = S, Se; Scheme 1). This observation is also supported by theoretical studies of a number of simple five membered α-azidoheteroaryls,[9,10] which also furnished clear evidence for the absence of a discrete nitrene on the reaction path.[10]

Substituent effects on the thermolysis of aryl azides have been much investigated over the last 20 years.[1,11] Conversely, studies on the conjugative effects exerted by substituents on the unimolecular decomposition of azidothiophenes (or other azidoheteroaryls) are limited.[12] An effort to synthesize 5-methyl- (**1a**) and 5-(trimethylsilyl)-2-azidothiophene (**2a**) showed that the stability of 2-azidothiophene (**2ATh**) is markedly depressed by a 5-methyl substitutent, whereas it is slightly enhanced by a trimethylsilyl one.[13] In addition, a number of isomeric oxo-substituted azidothiophenes, including 5-acetyl- (**3a**) and 5-(2,2,2-trifluoroacetyl)-2-azidothiophene (**4a**), have been prepared by selective azido transfer bifunctionalization of dibromothiophenes *via* the corresponding 2-lithium derivatives and tosyl azide.[14]

We were prompted to extend our thermal–kinetic study to *para*-like substituted 2-azidothiophenes by measuring thermal-rates and determining activation parameters for the dissociation of **1a**–**4a** (R = Me, SiMe$_3$, COMe, COCF$_3$, X = S; Scheme 1). The role of various substituents, together with our previous results obtained with **2ATh**,[6,10] on the evolution of the peculiar low-energy unimolecular process, is illustrated by means of calculations performed at AM1 and RHF/6-31G* levels of theory. These gas phase theoretical studies are carried out in an attempt to locate the most significant topological structures, intermediates and TS(s), and related energies as practical support to the experimental data.

Results and discussion

Thermal–kinetic dissociation of azides 1a–4a

The 2-azidothiophenes **1a**–**4a** have been prepared as previously described and were characterized by ^{1}H-, ^{13}C-NMR, IR and mass spectra.[13,14] Thermal decompositions of **1a**–**4a** were carried out in an inert solvent such as *p*-chlorotoluene † following the usual procedure described elsewhere.[6] The reaction mixtures were monitored as a function of time following the

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† Previous experiments indicated that inert solvents such as toluene, xylenes, chlorotoluenes and degassed mineral oil do not cause significant changes in rates.[11c]

Table 1 Rate constants and activation parameters for thermolysis of 5-X substituted 2-azidothiophenes[a]

5-X	T/°C	k/10^{-4} s^{-1}	E_a/kJ mol^{-1}	S_a/J K^{-1} mol^{-1} [b]
H	32.5	0.21 ± 0.01		
	54.0	2.62 ± 0.07	94.1 ± 0.4	−34.3 ± 2.9
	80.0	30.8 ± 0.11		
$SiMe_3$	46.0	0.42 ± 0.01		
	60.0	2.33 ± 0.05	108.8 ± 1.2	2.1 ± 2.1
	78.0	16.38 ± 0.10		
$COCH_3$	55.0	0.22 ± 0.01		
	75.4	2.43 ± 0.06	111.3 ± 1.2	−3.8 ± 2.5
	103.0	40.7 ± 0.12		
$COCF_3$	60.0	0.15 ± 0.01		
	89.6	4.31 ± 0.06	114.2 ± 0.8	−4.2 ± 2.1
	111.0	35.4 ± 0.12		

[a] In *p*-chlorotoluene solution. [b] At 60 °C.

reduction of the strong IR asymmetric band of the azido group (*ca.* 2100 cm^{-1}). The azide **1a** showed a very high rate constant at 60 °C; $k = 9.02 \times 10^{-4}$ s^{-1}, which meant we were unable to determine experimentally activation energies.

The results obtained with azidothiophenes **2a**–**4a**, collected in Table 1, show first-order kinetic rates compatible with a unimolecular process. The electrical effects of various substituents on the reaction rate at 60 °C fall in the range of relative rates from 1 for **4a** to 60 for **1a**. In order to address these effects on reaction rates the set of σ_p constants (Me −0.17, $SiMe_3$ −0.07, COMe 0.50 and $COCF_3$ 0.80) are selected from various types of Hammett substituent constants.[15a] The correlation of reaction rates ($\log k_{uni}$) against σ_p values gives: $\log k = -3.48 - 1.72\sigma_p$. This correlation has the datum point for the trimethylsilyl (TMS) group fitting badly and the resulting correlation coefficient r is 0.971 ($n = 5$). By elimination of the TMS data the correlation would be: $\log k = -3.37 - 1.88\sigma_p$, $r = 0.997$ ($n = 4$). This variance might be ascribed to the uncertainty in the reliability of the appropriate σ_p value, due to entangled effects (field/inductive, resonance and hyperconjugative) acting between silicon d orbitals and directly bonded aromatic,[16a] vinyl[16b] and carbonyl[16c] π-electron systems.[16d]

As expected, the fit of the data results improved when suitable substituent constants[15a] are employed containing positive R terms value for the TMS group, due to its small $+I$ and $-M$ effects. In fact, the simplest correlation of the rates by using σ_R (Me −0.13, $SiMe_3$ 0.05, COMe 0.16 and $COCF_3$ 0.27) constants‡ gives a better fit: $\log k = -3.51 - 4.75\sigma_R$ ($n = 5$, $r = 0.981$). The observed increased negative magnitude of the reaction constant and the satisfactory fit of the data indicate that the same mechanism, mainly affected by resonance with little contribution from field effects, operates throughout the course of the reaction.

The dissection of σ_p into field/inductive (σ_I: Me 0.01, $SiMe_3$ 0.01, COMe 0.33 and $COCF_3$ 0.54) and resonance (R^+: Me −0.32, $SiMe_3$ −0.01, COMe 0.14§ and $COCF_3$ 0.31) terms gives a satisfactory fit: $\log k = -3.34 - 4.75\sigma_I - 0.997R^+$ ($n = 5$, $r = 0.985$). The correlations have been performed with the BSTFT, which is a general purpose fitting program. A multiple linear regression analysis has been selected. The resulting reaction constant (−0.997) is slightly smaller than that (−1.48) reported by Dyall *et al.* for the thermolysis of activated azidobenzenes.[11c] Moreover, both are considerably smaller than those reported for the reaction of *N*-phenylnitrenium–Lewis acid complexes in aromatic side-chains, which were obtained by using similar substituent constants σ^+ and σ_P (−6.0 for $AlCl_3$[17] and −6.69 for BF_3[18]).

In the light of the results obtained by relating the temperature dependence of the rate coefficient to the experimental activation energy we can argue that the substituent effect on the thermolysis of the azido group is real, in spite of small differences in magnitude determined for **2a**–**4a** (Table 1). In these instances the observed increment of both the E_a and the S_a energy values, which become close to zero with respect to the S_a value for **2ATh**, suggests that the presence of a conjugate deactivating group stabilizes the reactant azides, and produces detectable differences in geometries and charge distributions in the transition states.

NMR Study of the substituent effect

^{1}H- and ^{13}C-NMR data for compounds **3a**, **4a**[14] and **2ATh**[6] have been reported elsewhere, however, proton and carbon shifts of azidothiophenes (**1a**–**4a** and **2ATh**) measured from the resonance of tetramethylsilane (TMS) are collected in Tables 2 and 3, respectively. Negative SCS δ_H and δ_C values (in parentheses) are defined as an upfield shift relative to the corresponding δ_H or δ_C values measured for **2ATh**. The previously reported C-3 and C-5 carbon shifts of **2ATh** were scrambled.[6] Satisfactory linearity of the SCS values in cross-correlation between equivalent carbon atoms of the phenyl azide (and some 2-azidoselenophene) has already been obtained.[19] Moreover, a general concordance in the δ_H and δ_C trend is found with those reported by Gronowitz *et al.* for a series of substituted thiophenes.[20]

The increasing electron-withdrawing effect for the series X = $SiMe_3$, COMe and $COCF_3$ of **2a**–**4a** is reflected in the progressive deshielding of ring protons, especially those adjacent to the substituent. Conversely, both the protons H-3 and H-4, for which a methyl-coupling ^4J constant of 1.1 Hz was observed, are shifted upfield in compound **1a**.

Considering that the degree of C(2)–N(1) bond order, depending in turn on the carbon charge, is the most important factor influencing the C-2 chemical shifts, we examined the δ_C values of the azides **1a**–**4a** relative to the equivalent δ_C values of **2ATh**. The electrical effects exerted by the substituent on the carbon shifts, especially at the C-2, are evidenced by the resulting SCS reported in Table 3 (ppm relative to **2ATh** in parentheses). As expected for the electron-withdrawing substituted thiophene ring all the carbon atoms of compounds **3a** and **4a** are shifted downfield. In contrast, the higher electron density on the C-2, C-3 and C-4 carbon atoms of **1a** causes shielding. The C-2 SCS values can be used to estimate the *para effects* by relationship with the above employed σ_R constants.[15] The very good fit obtained: SCS = $1.40 + 43.40\sigma_R$ ($n = 5$, $r = 0.992$), indicates that variation of electron densities upon C-2 (and in the thiophene ring) mainly depends on the *para*-like resonance exerted by substituents.[21]

Computational method and results

There is no question that assisted dissociations of aromatic azides exist.[1b] The question is whether theoretical studies, locating the most significant topological structures on the potential energy surface (PES) and the corresponding energy barrier, might be used to recognize borderline cases. Calculations are carried out by using a MacSpartan plus 1.1.7 program,[22] which runs on a Macintosh 9600 PPC (300 MHz 604e) with 64 MB of memory. AM1[23] and RHF/6-31G*[24] levels of theory were used to obtain reactant and product structures (and conformations), as well as energies and charge distributions along the entire reaction coordinates. Molecular geometries have been fully optimized, without geometrical constraints, at the RHF/6-31G* level and further confirmed as stationary points by harmonic frequency analysis. This procedure also provides corrections for zero point vibrational energies (ZPE). Significant geometrical parameters and net atomic charges (Mulliken) for reactant

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‡ The σ_R measures the ability to delocalize π electrons into or out of an aromatic ring and should be appropriate whenever resonance effects predominate in the reaction site or for NMR chemical shifts of substituted benzenes.

§ This value has been obtained by applying equation 20 from p. 187 of ref. 15(*a*)

Table 2 ^1H NMR data for 5-X substituted 2-azidothiophenes[a]

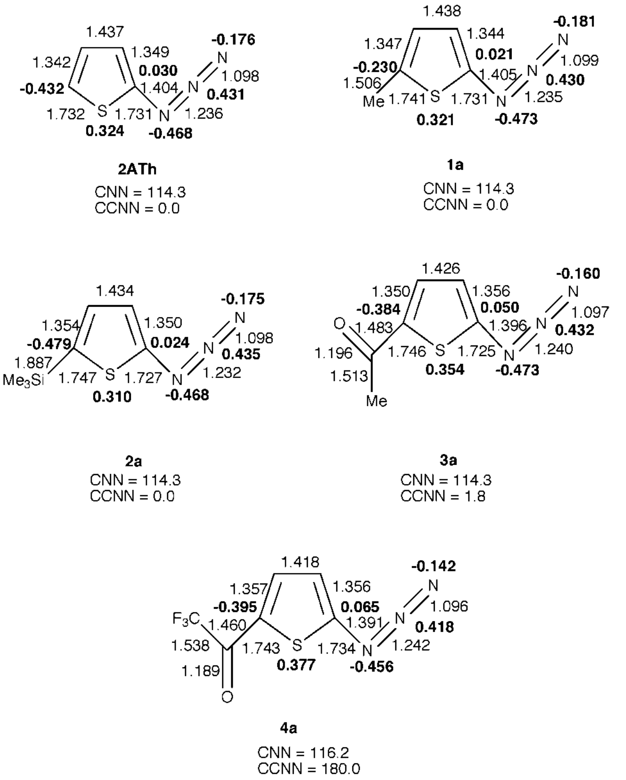
5-X	H-3[b]	H-4	H-5	CH_3	J_{HH}/Hz	J/Hz
H	6.60	6.83	6.90			
Me	6.41(−0.19)	6.51(−0.32)	—	2.43	3.7	1.1[c]
$SiMe_3$	6.61(0.01)	6.95(0.12)	—	0.30	3.7	
$COCH_3$	6.63(0.03)	7.48(0.65)	—	2.49	4.3	
$COCF_3$	6.76(0.16)	7.77(0.94)	—		4.4	1.5[d]

[a] In order to obtain as far as possible uniform and reliable δ_H the ^1H spectra are recorded for dilute solutions (*ca.* 10%, wt) in $CDCl_3$ and TMS as internal standard. [b] δ_H in ppm ($\Delta H_n = \delta_{H(substrate)} - \delta_{H(2ATh)}$). [c] $J_{Me,H-4}$. [d] $J_{F,H-4}$.

Table 3 ^{13}C NMR data for 5-X substituted 2-azidothiophenes[a]

5-X	C-2[b]	C-3	C-4	C-5	C=O	CH_3	J_{CH-3}/Hz	J_{CH-4}/Hz	J_{CH-5}/Hz
H	143.2	116.0	127.3	119.8			177.1	170.8	190.3
Me	139.6(−3.6)	115.5(−0.5)	124.7(−2.6)	134.2(14.4)	—	15.7	168.4	171.8	
$SiMe_3$	147.3(4.1)	117.2(1.2)	134.0(6.7)	134.9(15.1)		−0.1[c]	168.6	172.1	
COMe	151.6(8.4)	116.6(0.6)	133.0(5.4)	138.2(18.4)	190.1	26.1	171.2	168.6	
$COCF_3$	156.6(13.3)	117.7(1.7)	137.5(10.2)	129.7(9.9)	172.8	116.6[d]	173.4	172.0	

[a] In ppm relative to TMS (*ca.* wt 10%). [b] δ_C in ppm ($\Delta C_n = \delta_{C(substrate)} - \delta_{C(2ATh)}$). [c] $SiMe_3$. [d] CF_3.



2ATh
CNN = 114.3
CCNN = 0.0

1a
CNN = 114.3
CCNN = 0.0

2a
CNN = 114.3
CCNN = 0.0

3a
CNN = 114.3
CCNN = 1.8

4a
CNN = 116.2
CCNN = 180.0

Fig. 1 RHF/6-31G* optimized structures, significant distances in Å and Mulliken net charge (bold) for initial reactants **2ATh**, **1a**–**4a**.

azides **1a**–**4a** and **2ATh**, calculated at the RHF/6-31G* level, are reported in Fig. 1.

To evaluate more efficiently the energetics of the reaction paths *a* and *b* (Scheme 1), semi-empirical AM1 models, obtained by expansion (0.05 Å) along the coordinate of the N(1)–N(2) bond, were initially used. This also provided a guess at both the favoured equilibrium geometry and matrix of the second order energy derivatives for the *ab initio* calculations.

As previously calculated,[10] the thermolysis of **2ATh** has been shown to proceed *via* transition structure(s) corresponding to the break of the N(1)–N(2) bond concerted with the ring cleavage process to **2AThc** (path *b*, R = H, Scheme 1). Similarly, in the present calculations using the RHF/6-31G* basis set we located a first order saddle point connecting the minima for the reactant **2ATh** and the cisoid conformation of **2AThc** plus N_2 on the PES. The frequency calculations of the given transition structure produce one imaginary frequency, as required for the transition structure. The calculated activation barrier for the corresponding reaction is −0.09785 hartrees. When added to the zero point energy, scaled by 0.89, it produces a relative energy of -270.9 kJ mol^{-1}. The path *a* depicted in Scheme 1 (R = H) has already been discarded because an attempt to minimize the structure **2AThb** leads to the ring-opened **2AThc**.

The most important component of the transition vector in the case of azide **1a** corresponds again to the concerted breaking of the N(1)–N(2) and C(2)–S bonds finally leading to 4-cyano-2-methyl-1-thiabuta-1,3-diene **1c**. In fact, we located a first order saddle point connecting the minima of the reactant **1a** and the product **1c** + N_2, which is confirmed by vibrational transition structures. The evolution of the reaction is very fast showing the breaking of the N(1)–N(2) bond at a bond length of 1.639 Å (compared to 1.235 Å of the reactant azide). By comparison the reaction of **2ATh** showed the breaking of the N(2)–N(2) bond at a bond length of 1.840 Å (with respect to 1.236 Å of the reactant azide). The progress of the pathway *b* appears mainly affected by the greater polarization produced on the N(1)–N(2) bond in the structure(s) **1a**,**b′** (R = Me) by the electron-donor supply. Thus, the energy barrier for the dissociation and concerted ring cleavage of **1a** shows an energy decrement with respect to **2ATh** (-49.3 kJ mol^{-1}).

It is interesting to note that the evolution of the reaction through the path *b*, depicted by the structure **b′** where n- and π-electron pairs are uniformly spread over the unsaturated thiophene carbons and azido nitrogen atoms, proceeds simultaneously breaking and makes an alternating sequence of σ and π bonds. This process types the concerted topology of the transition state for five-membered heteroarylnitrenes (and carbenes) described by Herges.[25]

Table 4 reports relative energies and activation barriers for gas phase thermolyses of **1a**–**4a** and **2ATh**. Optimized structures of **1c**–**4c** and **2AThc**, arising by the dissociation and ring cleavage of the corresponding azides are reported in Fig. 2.

The contribution of the trimethylsilyl substituent to the resonance in aromatic substrates is generally predicted in terms of d/π interactions exerted by the silicon atom in the π-electron systems.[16] Thus, little stabilization of the reactant azide **2a** with respect to **2ATh** is expected on the basis of the slightly deactivating influence of the silyl group. The progress of the reaction is slow when compared to that of the azide **1a**, whereas results are comparable to those for **2ATh**, showing the breaking of the N(1)–N(2) bond at bond length of 1.784 Å (1.232 Å for the starting azide). However, the calculated energy barrier for

Table 4 Relative energies of the main structures involved in the thermolysis in the gas phase of azidothiophenes optimized at RHF/6-31G* level

Structures	HF/hartrees[a]	ZPE/kJ mol^{-1}[b]	E_a/kJ mol^{-1}[c]
$\mathbf{N_2}$	−108.94395	14.6	
2ATh	−713.96765	176.8	
2AThc	−605.12155	148.0	−270.9 (0.0)
1a	−753.00494	245.4	
1c	−644.17662	214.0	−320.2 (−49.3)
2a	−1121.19520	398.3	
2c	−1012.33903	373.7	−240.3 (30.6)
3a	−865.74172	262.5	
3c	−756.87661	243.3	−211.1 (59.8)
4a	−1162.31356	215.7	
4c	−1053.41021	188.9	−118.7 (152.2)

[a] Single point calculations at RHF/6-31G* on the gas phase geometries. [b] Zero point vibrational energies scaled by 0.89. [c] Activation energies (+ZPE) relative to the **2ATh** are in parentheses.

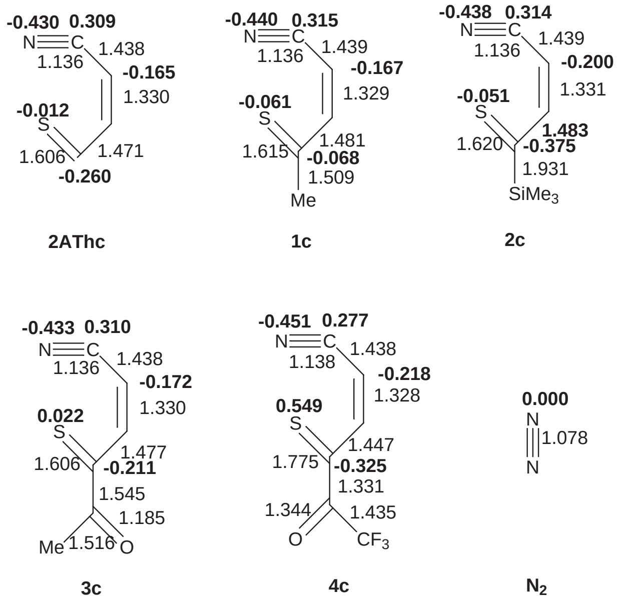


Fig. 2 RHF/6-31G* optimized structures, significant distances in Å and Mulliken net charge (bold) for **2AThc**, **1c**–**4c**.

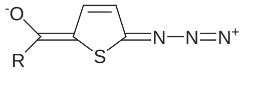
the dissociation of **2a** shows a small increment in energy with respect to **2ATh** (30.5 kJ mol^{-1}).

In contrast with the thermolysis of **2ATh**, **2a** and especially **1a**, discussed above the strong electron-withdrawing *para*-substituents in **3a** and **4a** provide valuable stabilization of the reactant azides. In these instances the transition vector corresponds again to the concerted breaking of the N(1)–N(2) and C(2)–S bonds, but the evolution of the reaction is slower. The breaking of the N(1)–N(2) bond occurs at a bond length of 1.930 and 2.064 Å respectively (1.242 and 1.240 Å for the starting azides). Finally, higher energy barriers are required with respect to **2ATh** (59.8 and 152.2 kJ mol^{-1}, respectively).

Although the energies are calculated in the gas phase, a qualitative approach to the electrical effect of the *para*-like substituents in the evolution of the reaction could be obtained by plotting relative energy barriers, determined with respect to that of **2ATh**, against σ_R values. Satisfactory linear correlation of the data has been obtained by this relationship: $\Delta E_{\text{uni}} = 4.88 + 482.33\sigma_R$ ($n = 5$, $r = 0.980$) suggesting that resonance effects are called into play.

In the light of these experimental and theoretical results obtained with the thermolysis of *para*-like substituted 2-azidothiophenes **1a**–**4a**, the ring opening generally proceeds concertedly with the elimination of molecular nitrogen. The electrical effects exerted by activating $+I$ and $+M$ substituents largely favour the low-energy process mainly by stabilization of the reactive structure **b′** supplied by the electron-donor. In particular, as expected the vibrational frequencies at the transition state, where the triatomic asymmetric stretch predominates, are close in energy to those of destabilized reactant azides. Inactive or weakly deactivating $+I$ and $-M$ substituents, like the trimethylsilyl group, provide a valuable electronic stabilization of the ground state N(1)–N(2) bond probably partially counterbalanced by σ-inductive effects caused by the low electronegativity of the silicon atom.

Finally, strongly deactivating $-I$ and $-M$ substituents such as a keto-carbonyl group coplanar with the ring of **3a** and **4a** may generate quinoidal structures **A**, which provide larger



A ; R = Me, CF_3

stabilization of the reactant azides by spreading electron charges. In spite of the fact that the quinoidal structures are characterized by alternant delocalized chemical bonding, the five membered ring aromaticity remains virtually unchanged and the vibrational energy of the azido group increase by slight variations in symmetry. The resulting higher molecular complexity, *e.g.* with respect to **1a**, corresponds to enhanced vibrational frequencies at the transition state rather than the reactant molecule, reflecting the greater force constant at the global maximum on the PES.[26]

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