Rapid and Reversible Migration of the Isothiocyanate Group around the Cyclopropene Ring

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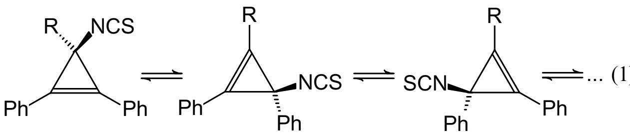
Rapid degenerate and non-degenerate intramolecular migrations of the isothiocyanate group around the cyclopropene ring have been studied by dynamic ^{1}H and ^{13}C NMR spectral methods and semiempirical PM3 calculations.

Few examples are known of degenerate and non-degenerate shifts of substituents in the cyclopropene ring along its perimeter. Among these are rapid chlorine[1] and azido group shifts[2] occurring *via* a dissociation-recombination mechanism ($G^{\ddagger}_{90\,°C}$ 13–15 kcal mol^{-1}),† high-energy barrier trimethylsilyl group migration (~ 35 kcal mol^{-1}),[3] slow 3,3 sigmatropic allyl[4] and indenyl (27–35 kcal mol^{-1})[5] shifts as well as hetero-Cope rearrangement of *S*-(1,2,3-triphenylcyclopropenyl)-*O*-ethyldithiocarbonate (18.4 kcal mol^{-1}).[6] Here we report on rapid degenerate and non-degenerate intramolecular isothiocyanate group migration around the cyclopropene ring in the corresponding derivatives of 1,2,3-triphenyl- **1**‡ and 1-(4-methoxyphenyl)-2,3-diphenylcyclopropene **2**.§



... (1)

1a,**2a** **1b**,**2b** **1c**,**2c**

1 R = Ph
2 R = 4-MeOC$_6$H$_4$

According to IR and ^{13}C NMR spectral data the reaction of 1,2,3-triphenyl- and 1-(4-methoxyphenyl)-2,3-diphenylcyclopropene bromides with potassium rhodanide (0.2 h, 81 °C, MeCN) leads to the corresponding covalent isothiocyanate derivatives **1** and **2**. IR spectra of these compounds in solid and in solution do not contain absorption bands in the 1400–1430 cm^{-1} range characteristic of the cyclopropene cations,[8] whereas in the spectral region of 1990–2190 cm^{-1} an intense, broad split absorption band appears relating to the –N=C=S valence vibration.[9] The ^{13}C NMR (75.5 MHz) spectra of **1** (see Figure 1) and **2** at room temperature display the signals at δ 131.26 (**1**, C$_6$D$_6$), 130.28 (**1**, CDCl$_3$), 128.67, 128.91 (**2**, CDCl$_3$, at +10 °C) ppm of the isothiocyanate quaternary carbons.[10] The ^{13}C thiocyanate signals are known to be observed in the interval of 110–114 ppm.[10] The signal of the cyclopropene sp^3 carbons in **1** and **2** are found at δ 47.09 (**1**, C$_6$D$_6$), 46.55 (**1**, CDCl$_3$) and 45.60, 47.75 (**2**, CDCl$_3$, 10 °C). Their downfield shift, as compared to other derivatives of cyclopropene, is due to the anisotropic influence of the –N=C=S group.[10] On raising the temperature the signals of **1a**–**c** (Figure 1) and **2a**–**c** broaden (10–40 °C) and coalesce (50–80 °C). No measurable dependence of the dynamic ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectral behaviour was observed when varying the concentration of the solutions in the range of 0.01–0.5 mol dm^{-3}, which indicates the intramolecular character of the rearrangements (1). From the line

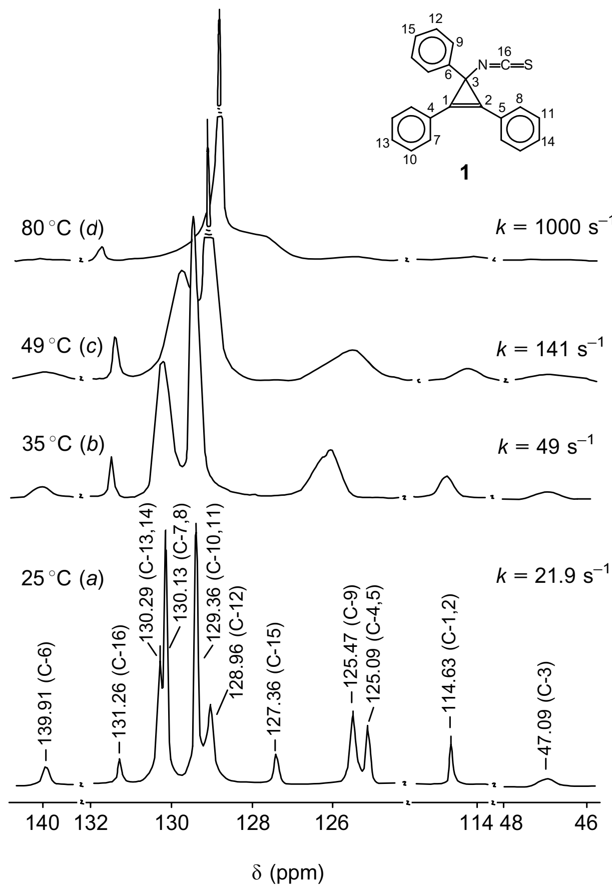


Figure 1 75.5 MHz ^{13}C NMR spectra of 3-isothiocyano-1,2,3-triphenylcyclopropene **1** in C$_6$D$_6$ solution at 25 °C (*a*), 35 °C (*b*), 49 °C (*c*) and 80 °C (*d*). The signals were assigned by use of monoresonance ^{13}C NMR spectra and APT methods. The solution signals have been removed from the spectra.

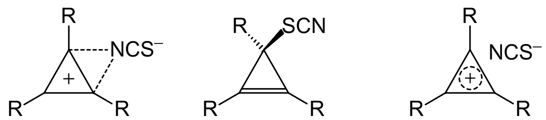
† 1 kcal = 4.184 J.

‡ *Characterization data for* **1** [colourless crystals (from acetonitrile)], m.p. 141–142 °C (lit.,[7] 138–140 °C), ^{1}H NMR (300 MHz, 25 °C), C$_6$D$_6$, δ 6.95–7.16 (9H, m, aromatic H), 7.39–7.44 (6H, m, aromatic H); CDCl$_3$, 7.39 (9H, br. m, aromatic H), 7.63 (6H, br. s, aromatic H). ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C), δ$_C$, 46.55 (C-3), 114.10 (C-1,2), 124.91 (C-4,5), 125.00 (C-9), 127.12 (C-15), 128.81 (C-12), 129.14 (C-10,11), 129.90 (C-7,8), 129.94 (C-13,14), 130.28 (C-16), 139.32 (C-6). IR (Nujol) ν/cm^{-1} 2190–1980 (N=C=S), 1840 (C$_{1-3}$-skeletal), 1610 (C=C), 1500, 1460, 1320, 1170, 1080, 1040, 970, 920. MS *m*/*z* 325 (21.9%) [C$_3$Ph$_3$NCS]$^+$ = [C$_3$Ph$_3$SCN]$^+$ = [M]$^+$.

§ *Characterization data for* **2** [colourless crystals (from acetonitrile)], m.p. 128–130 °C, ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C), δ 6.82–7.30 (8H, br. m, aromatic H), 7.38–7.53 (6H, br. m, aromatic H), 3.64 (3H, s, OMe). ^{13}C NMR (75.5 MHz, CDCl$_3$, 10 °C), δ$_c$, 45.60, 47.75 (C$_{sp3}$, ring); 55.00, 55.32 (C, OMe); 115.16–132.50 (CH, aromatic rings); 117.51, 118.42, 119.27, 127.81, 128.90, 136.23, 140.30, 144.30, 158.90, 161.16 (C-quaternary of the cyclopropene and aromatic rings); 128.67, 128.91 (C, NCS). IR (Nujol), ν/cm^{-1}, 2190–1990 (N=C=S), 1840 (C$_{1-3}$-skeletal), 1620, 1610 (C=C), 1410, 1300, 1180, 1020, 860. MS *m*/*z* 355 (18%) [C$_3$(4-MeOC$_6$H$_4$)Ph$_2$NCS]$^+$ = [C$_3$(4-MeOC$_6$H$_4$)Ph$_2$SCN]$^+$ = [M]$^+$. Compound **2** gave satisfactory elemental analysis..

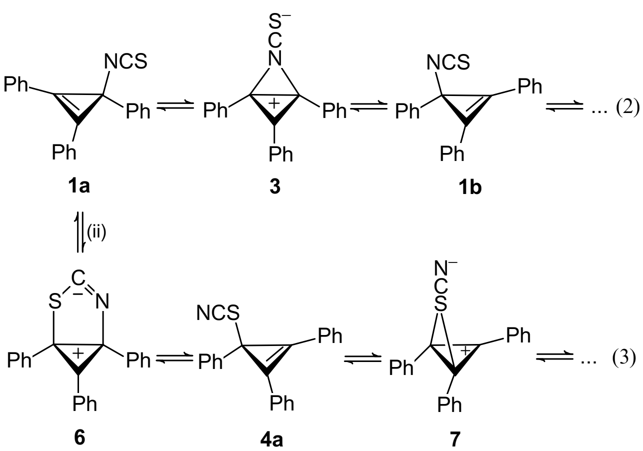
shape analysis of the ^{13}C NMR spectra in the temperature interval 10–80 °C the following kinetic parameters of the degenerate **1a** ⇄ **1b** ⇄ **1c** (C_6D_6, $G^{\ddagger}_{298}$ 15.6 kcal mol^{-1}, $H^{\ddagger}$ 14.3 ± 0.3 kcal mol^{-1}, $S^{\ddagger}$ −4.4 ± 0.4 e.u., k_{298} 21.9 s^{-1}; $CDCl_3$, $G^{\ddagger}_{298}$ 14.5 kcal mol^{-1}, $H^{\ddagger}$ 10.7 ± 0.3 kcal mol^{-1}, $S^{\ddagger}$ −12.8 ± 0.4 e.u., k_{298} 139 s^{-1}), **2b**→**2c** ($CDCl_3$, $G^{\ddagger}_{298}$ 14.7 kcal mol^{-1}, k_{298} 100 s^{-1}), and slightly non-degenerate **2a**→**2b** ($CDCl_3$, $G^{\ddagger}_{298}$ 14.9 kcal mol^{-1}, k_{298} 70.9 s^{-1}) and **2b**→**2a** ($CDCl_3$, $G^{\ddagger}_{298}$ 14.8 kcal mol^{-1}, k_{298} 83.2 s^{-1}) rearrangements have been calculated.

The migration of the isothiocyanate group over the cyclopropene ring may occur by three conceivable reaction paths: (i) 1,3 sigmatropic shift through the η^2 intermediate or transition state structure **3**; (ii) 3,3-hetero-Cope rearrangement occurring through unstable thiocyanate derivatives **4**; (iii) dissociation-recombination path with the formation of tightly-bound ion pair **5**.



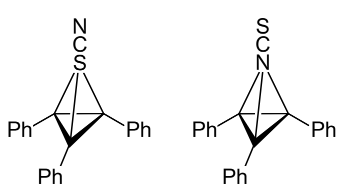
3 **4** **5**

Obviously, the overall kinetics may be governed by a mixture of all these mechanisms as was found to be the case for migration of the azido group around the periphery of the cycloheptatriene ring.[11]



In order to gain an insight into the role of the particular reaction pathways above, semiempirical PM3 calculations[13] of reaction (1) for compound **1** were perfomed.

The calculations reveal two stable isomeric ground state thiocyanate **4a** and isothiocyanate structures **1a** (see Table 1 and Figure 2). The former isomer **4a** is predicted to be 4.2 kcal mol^{-1} less stable than **1a** in the gas phase. The 1,3 shift reactions (2) and (3) occur through corresponding transition state (TS) η^2-structures **3** and **7**, the energy barriers to the migration in the gas phase being calculated as 47.2 and 31.4 kcal mol^{-1}, respectively. η^3-Structures **8** and **9** correspond to the top (critical point of the rank two) of the hill on the potential energy surfaces.



8 **9**

The interconversion of the isomers **1a** and **4a** proceeds by their hetero-Cope rearrangement through the TS structure **6** with energy barriers in the gas phase of 45.2 and 49.4 kcal mol^{-1} for migration of thiocyanate and isothiocyanate groups, respectively. When the effect of solvation was accounted for by use of the polarizable continuum model approach,[14] η^3-structures **8** and **9** which model tight ion pairs $C_3Ph_3^+ \cdots NCS^-$ become lower in energy than the η^2-structures **7** and **3**. This trend indicates that an increase in polarity of the solution may lead to rearrangement through a dissociation-recombination mechanism. Energy barriers of 15.9 and 26.7 kcal mol^{-1} were calculated for isothiocyanate and thiocyanate group random shifts in chloroform solution, respectively. On the contrary, no significant changes in the magnitude of the energy barrier are expected upon increasing the polarity of solution for interconversion of **1a** and **4a**.

Compound **4** is a minor component in the gas phase as indicated by the following low-intensity peaks in the mass spectra originated from fragmentation of the thiocyanate derivatives of type **4**: {*m*/*z* (%): **1**, 299 (0.4) [$C_3Ph_3SCN-CN$]$^+$; **2**, 329 (0.5) [$C_3(4\text{-}MeOC_6H_4)Ph_2SCN-CN$]$^+$}.

Thus, on the basis of the experimental study of the rearrangements of **1** and **2** and theoretical modelling of this reaction it may be concluded that the migration of the

Table 1 Heat of formation in the gas phase (ΔH_f/kcal mol^{-1}), in benzene (ΔH_f^{s1}/kcal mol^{-1}) and in chloroform (ΔH_f^{s2}/kcal mol^{-1}), calculated for structures **1**–**9** by semiempirical PM3 methods.

Heat of formation	1	3	4	6	7	8	9
ΔH_f	179.8	227.0	184.0	229.2	215.4	219.1	227.1
ΔH_f^{s1}	175.8	203.9	179.0	225.7	207.4	207.9	201.1
ΔH_f^{s2}	173.3	192.2	175.9	223.8	203.2	202.6	189.2

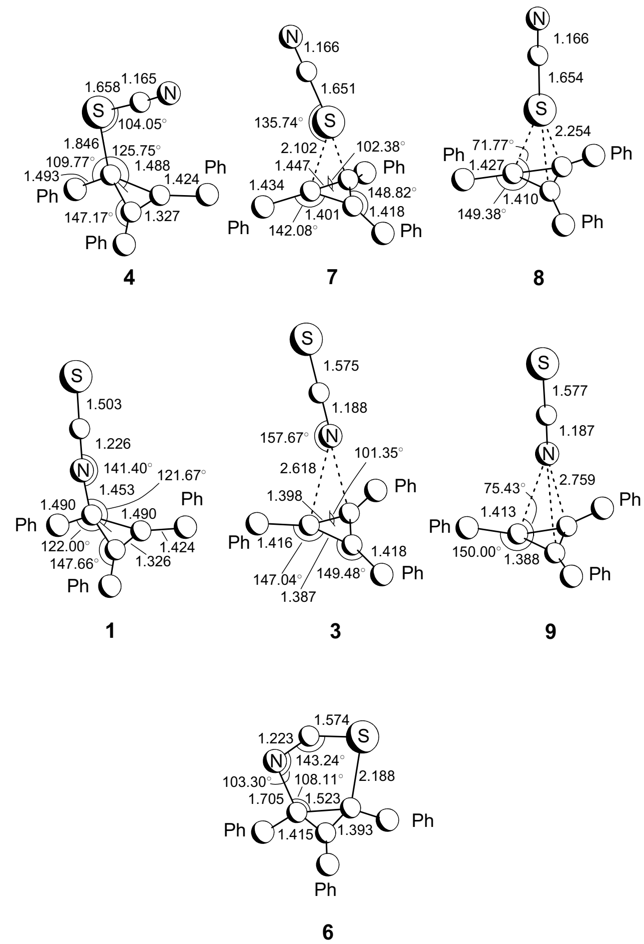


Figure 2 Geometric characteristics of the ground state structures **1a**, **4a** (R = Ph) and transition state structures **3**, **6**, **7** (R = Ph) and structures **8** and **9** (R = Ph) corresponding to the top of the hill on the PESs calculated by the PM3 method. The bond lengths are given in Å.

isothiocyanate group in 3-(1,2,3-triphenylcyclopropenyl)isothiocyanate **1** and the 4-methoxyphenyl derivative **2** occurs in polar solution *via* a dissociation-recombination mechanism with the intermediacy of tight ion pairs. However, in the gas-phase, all three mechanisms could be competitive.

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