1,7-Sigmatropic shifts of the phenylsulfanyl group along the perimeter of the cycloheptatriene ring

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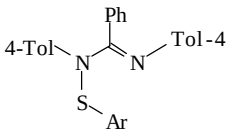
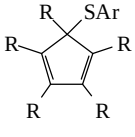
Rapid and reversible migrations of the phenylsulfanyl group around the seven-membered ring of 7-phenylsulfanylcyclohepta-1,3,5-triene have been proved to proceed through successive 1,7-sigmatropic shifts with an energy barrier ($\Delta G^{\neq}_{298}$) in the range of 19.5–20.1 kcal mol^{-1}.

Fast intramolecular 1,3-*N*,*N*'-migrations of arylsulfanyl groups in amidines **1** and 1,5-sigmatropic shifts of these groups over a five-membered cyclopentadiene ring **2** have been reported to occur with the energy barriers falling into the range ($\Delta G^{\neq}_{298}$) of 16.7–19.9[1] and 16.0–25.0[2,3] kcal mol^{-1}, respectively.



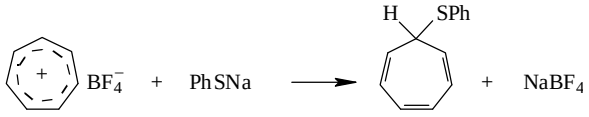
1



2

Ar = Ph, 2-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$;
R = CO_2Me (ref. 2), Me (ref. 3)

In this paper we describe fast intramolecular migrations of the phenylsulfanyl group along the perimeter of the seven-membered ring in the 7-phenylsulfanylcyclohepta-1,3,5-triene **3**. The compound **3**† has been obtained in 85% yield upon coupling tropylium tetrafluoroborate with sodium thiophenolate in acetonitrile (24 h, 22 °C) (Scheme 1).



3

Scheme 1

Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectral patterns of **3** which are in accord with the η^1-structure of this compound. The magnitude (6.8 Hz) of the $^3J_{HH}(H_1H_7)$ spin-spin coupling constant observed in the ^{1}H NMR spectrum (Figure 1) points to the quasi-axial position[4,5] of the phenylsulfanyl group in the boat-like conformation of the cycloheptatriene ring. The highest-field triplet signal obviously belongs to proton attached to the sp^3-hybridized carbon atom of the cycloheptatriene ring. An assignment of other proton signals in the ^{1}H NMR spectra of **3** has been made by using a 'double-resonance' technique, *i.e.* successive irradiation of the ring proton signals by an additional radiofrequency resulted in changes in their multiplicity. The ^{13}C NMR spectral signals were assigned on the basis of the characteristic values of carbon chemical shifts, the magnitudes of spin-spin coupling constants ^{1}H–^{13}C, an application of the APT technique and by means of heteronuclear correlation of the ^{13}C and ^{1}H chemical shifts (XHCORR). As Figure 1 portrays, on raising the temperature of a [$^2H_5$]nitrobenzene solution of **3** to 160 °C, reversible broadening and coalescence of proton signals of the cycloheptatriene ring occurs, whereas the positions of the aromatic ring proton signals are virtually unaffected by the temperature of solution. The unsymmetrical pattern of averaging proton signals of the cycloheptatriene ring allows one to rule out the dissociation–recombination mechanism established earlier in the case of isosulfanylcyano group migration in 5-isosulfanylcyanocyclohepta-1,3,5-triene.[6] It is worth noting that synchronous broadening of the H_7, H_1, H_6 and H_2, H_5 proton signals takes place, whereas the exchange broadening of the H_3, H_4 proton signals is two times slower (Figure 1). Similar spectral behaviour was also observed in the ^{13}C dynamic NMR spectra of **3**. Moreover, in the 2D ^{1}H and ^{13}C NMR EXSY spectrum of **3** (Figure 3) exchange cross

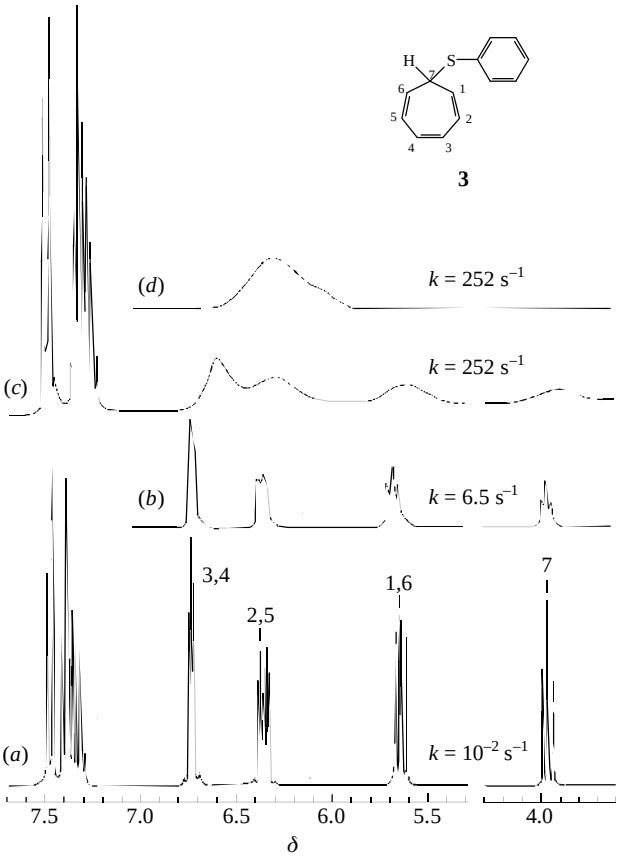


Figure 1 ^{1}H NMR (300 MHz) (*a*)–(*c*) and ^{1}H NMR (80MHz) (*d*) spectra of compound **3** in $C_6D_5NO_2$ at (*a*) 20 °C, (*b*) 100 °C, (*c*) 160 °C, (*d*) 160 °C.

† *Compound* **3**: colourless oil [purified by chromatography on silica gel column, eluent hexane–benzene (3:1), R_f 0.5]. ^{1}H NMR (300 MHz), C_6D_6: δ 3.74 (H, t, H_7), 5.38 (2H, m, $H_{1,6}$), 5.97 (2H, m, $H_{2,5}$), 6.34 (2H, m, $H_{3,4}$), ($^3J_{1,7}$ 6.8 Hz, $^3J_{1,2}$ 8.4 Hz, $^3J_{2,3}$ 3.5 Hz); 6.91–7.35 (5H, m, Ph). ^{13}C NMR (75.47 MHz), C_6D_6: δ 45.79 (C_7), 124.78 ($C_{1,6}$), 126.61 (C_{11}), 126.79 ($C_{2,5}$), 129.03 ($C_{10,12}$), 131.03 ($C_{9,13}$), 131.58 ($C_{3,4}$), 136.25 (C_8). IR (Nujol) ν/cm^{-1}: 1635, 1620–1605 (C=C), 1180 (S–C). Compound **3** gave satisfactory elemental analyses.

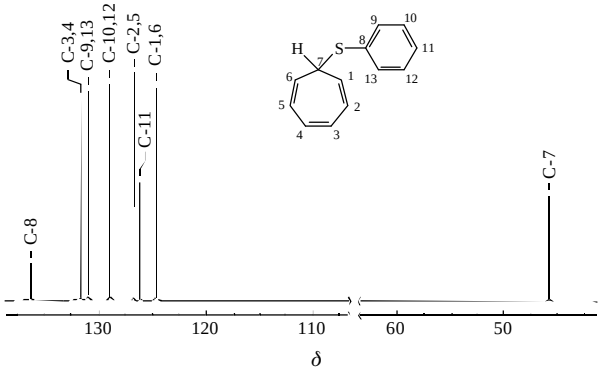


Figure 2 ^{13}C NMR (75.47MHz) spectrum of compound **3** in C_6D_6 at 22°C. Solvent signals are excluded from the spectra.

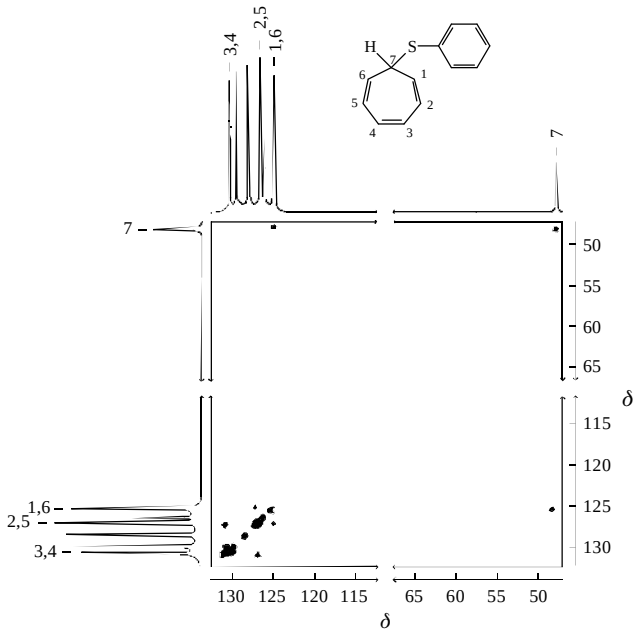
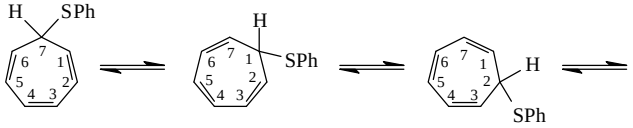


Figure 3 2D ^{13}C NMR (EXSY) spectrum of compound **3** in C_6D_6 at 15°C in the 42–132 ppm region. Solvent signals are excluded from the spectra.

peaks that correlate the positions 7–1,6 and 1,6–2,5 as well as 2,5–3,4 in the cycloheptatriene ring already appear at a temperature of 15 °C. Such temperature variable spectral patterns of **3** should be explained by the rapid reversible intramolecular‡ 1,2-shifts (1,7-sigmatropic shifts)[7] of the phenylsulfanyl group along the perimeter of the cycloheptatriene ring (Scheme 2).



Scheme 2

The same type of migration mechanism over the cycloheptatriene ring has been previously reported for $(\sigma\text{-}C_7H_7)Re(CO)_5$[8] and $C_7H_7SC(OEt)=S$.[9] On the contrary, the hydrogen atom,[10] methoxy[11] and triphenyltin groups[12] circumambulate the cycloheptatriene ring by successive 1,5-sigmatropic shifts. From line shape analysis of the ^{1}H and ^{13}C NMR spectra in the temperature interval 24–160 °C, the following kinetic parameters of the degenerate migrations of phenylsulfanyl group along the perimeter of the cycloheptatriene ring have been calculated using the DNMR-5 program: C_6D_6, $\Delta G^{\neq}_{298}$ 19.5 kcal mol^{-1}, $\Delta H^{\neq}$ 18.3±0.4 kcal mol^{-1}, $\Delta S^{\neq}$ –4.0±0.4 e.u., k_{298} 2.9×10^{-2} s^{-1}; $C_6D_5NO_2$, $\Delta G^{\neq}_{298}$ 20.1 kcal mol^{-1}, $\Delta H^{\neq}$ 18.5±0.3 kcal mol^{-1}, $\Delta S^{\neq}$ –5.5±0.4e.u., k_{298} 1.07×10^{-2} s^{-1}.

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‡ The rate of the observed dynamic process is not dependent on the concentration of the solution in the range 0.006–0.8 mol dm^{-3}.

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