

Fluxional Behaviour of 7-Cyclohepta-1,3,5-trienyl Ethoxydithiocarbonate

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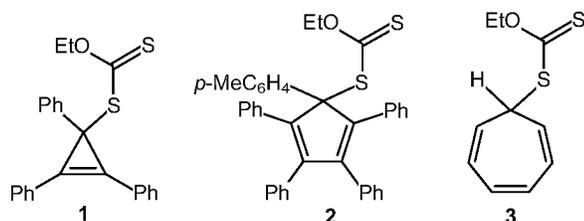
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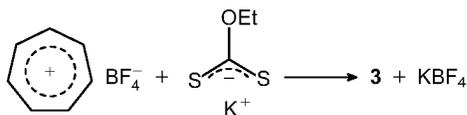
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Fast and reversible migrations of the ethoxydithiocarbonate group along the perimeter of the cycloheptatriene ring of **3** have been found to occur through a series of successive 1,7-sigmatropic shifts with an energy barrier in the range 17.4–17.9 kcal mol⁻¹.

Circumambulatory rearrangements of dithioacyloxy groups around the cyclopropene¹ and cyclopentadiene² rings have been found to occur through 3,3-sigmatropic shift reaction pathways with energy barriers of 17.8 and 24 kcal mol⁻¹ for compounds **1** and **2**, respectively.



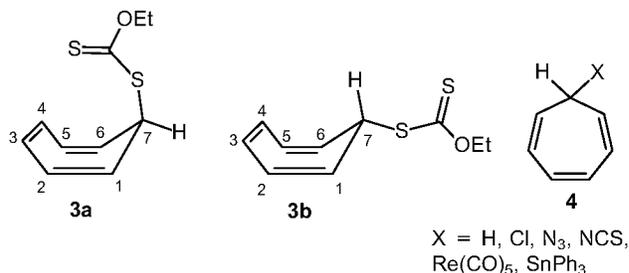
Here we report on the observation of fast and reversible intramolecular migrations of the ethoxydithiocarbonate group along the perimeter of the seven-membered cycloheptatriene ring in 7-cyclohepta-1,3,5-trienyl ethoxydithiocarbonate **3**. Compound **3** has been prepared in 95% yield by coupling tropylium tetrafluoroborate with potassium ethyl xanthogenate in acetonitrile solution (4 h, 0 °C) (Scheme 1).



Scheme 1

The η^1 -structure of compound **3** with the ethoxydithiocarbonate group in the quasi-axial position **3a** is witnessed by its ¹H and ¹³C NMR spectra shown in Fig. 1.

The ¹H NMR spectral pattern of **3** is similar to those of



(σ -C₇H₇)Re(CO)₅³ and (σ -C₇H₇)SnPh₃,⁴ although in the case of **3** four multiplets of ring proton signals (H₁–H₇) are shifted downfield and their assignment is slightly different (δ H₇ < δ H_{1,6} < δ H_{2,5} < δ H_{3,4}). The magnitude of the ³J_{HH}(H₁H₇) spin-spin coupling observed in the ¹H NMR spectrum of **3** (7.9 Hz) is indicative of the preferred quasi-axial position of the ethoxydithiocarbonate group in the boat-like cycloheptatriene ring. This is justified by comparison with the ³J_{HH}(H₁H₇) spin-spin constant reported for the triphenyltin cycloheptatriene, for which a conformation similar to **3a** was proved by use of single crystal X-ray structural analysis.⁵

Organic and organometallic derivatives of the general type **4** cycloheptatrienes were found by earlier NMR spectral studies to display fluxional behaviour due to displacements of substituents X around the seven-membered ring. The reaction mechanism that governs these displacements depends strongly on the origin of the migrant. Whereas the hydrogen atom,⁶ methoxy⁷ and triphenyltin groups⁸ circumambulate the cycloheptatriene ring by successive suprafacial 1,5-sigmatropic shifts, migration of pentacarbonyl rhenium occurs through antarafacial 1,7-sigmatropic shifts and a 3,3-sigmatropic shift accompanied by a 1,7-shift is characteristic of the migration of the azide group in **4**. A random shift associated with dissociation into the ion pair of tropylium cation and thiocyanate anion occurs in the corresponding thiocyanate **4**.⁹ The dissociation-recombination mechanism also contributes to the kinetics of azide migration, the relative contributions of each particular reaction pathway being determined by the polarity of the solvent in use.¹⁰

The temperature-variable ¹H NMR spectrum of **3a** (Fig. 1) exhibits a dynamic process of averaging of all ring proton signals related to displacement of the ethoxydithiocarbonate group over the ring. The unsymmetrical averaging pattern clearly points against the dissociation-recombination mecha-

[†] Compound **3**: yellowish oil [purified by chromatography on silica gel column, eluent hexane–benzene (2:1), R_f 0.8]. ¹H NMR (300 MHz), C₆D₆, δ 0.75 (3H, t, J 7.1 Hz, Me), 4.14 (2H, q, ³J 7.1 Hz, CH₂), 4.95 (1H, t, H₇), 5.61 (2H, m, H_{1,6}), 6.01 (2H, m, H_{2,5}), 6.27 (2H, m, H_{3,4}), (³J_{1,7} 7.9 Hz, ³J_{1,2} 9.1 Hz, ³J_{2,3} 3.9 Hz); C₆D₅CD₃, δ 0.99 (3H, t, ³J 7.1 Hz, Me), 4.28 (2H, q, ³J 7.1 Hz, CH₂), 4.94 (1H, t, H₇), 5.59 (2H, m, H_{1,6}), 6.04 (2H, m, H_{2,5}), 6.32 (2H, m, H_{3,4}), (³J_{1,7} 7.9 Hz, ³J_{1,2} 9.4 Hz, ³J_{2,3} 3.6 Hz). ¹³C NMR (75.47 MHz), C₆D₆, δ 13.57 (Me), 47.71 (C₇), 69.57 (CH₂), 122.70 (C_{1,6}), 129.09 (C_{2,5}), 132.05 (C_{3,4}), 214.93 (C=S); C₆D₅CD₃, δ 13.57 (Me), 47.49 (C₇), 69.41 (CH₂), 122.58 (C_{1,6}), 128.90 (C_{2,5}), 131.89 (C_{3,4}), 214.50 (C=S). IR (Nujol) v/cm⁻¹ 1630, 1610 (C=C); 1260 (C=S). Compound **3** gave satisfactory elemental analyses.

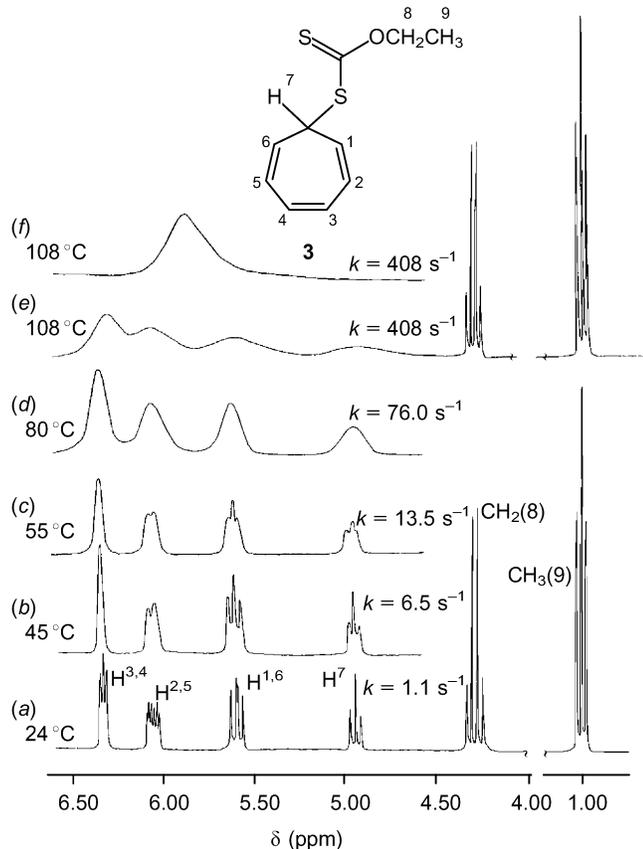


Fig. 1 ^1H NMR (300 MHz) (a)–(e) and ^1H NMR (80 MHz) (f) spectra of compound **3** in $[\text{}^2\text{H}_8]\text{toluene}$ at (a) 24 °C, (b) 45 °C, (c) 55 °C, (d) 80 °C, (e) 108 °C, (f) 108 °C.

nism that would involve formation of the intermediate tropylium cation-ethoxydithiocarbonate anion ion pair. As Fig. 1 shows, on raising the temperature of the solution synchronous broadening of the signals belonging to the $\text{H}_7, \text{H}_1, \text{H}_6$ and H_2, H_5 protons begins, whereas exchange broadening of the signals of the H_3, H_4 protons is two times lower. Similar spectral behaviour of the ^{13}C nuclei signals in the respective positions of the seven-membered ring has been observed in the ^{13}C dynamic NMR spectrum of **3a** in solution. Such temperature-variable spectral patterns have been recognized as good evidence in favour of the successive 1,2-shift (1,7-sigmatropic shift) mechanism of circumambulatory rearrangements over the cycloheptatriene ring.¹¹ A preferred 1,2-shift of the ethoxydithiocarbonate group is also confirmed by the 2D ^1H NMR EXSY spectrum of **3a** which exhibits the presence of exchange cross-peaks between the pairs of $\text{H}_7\text{--}\text{H}_1, \text{H}_6$ and $\text{H}_1, \text{H}_6\text{--}\text{H}_2, \text{H}_5$ as well as of $\text{H}_2, \text{H}_5\text{--}\text{H}_3, \text{H}_4$ signals even at a solution temperature of 27 °C. From line shape analysis of the ^1H and ^{13}C NMR spectra in the temperature interval 24–108 °C, the following kinetic parameters of the degenerate migrations of the ethoxydithiocarbonate group along the perimeter of the cycloheptatriene ring have been calculated using the DNMR-3 program: C_6D_6 , G_{298}^\ddagger 17.9 kcal mol $^{-1}$, H^\ddagger 16.9 \pm 0.3 kcal mol $^{-1}$, S^\ddagger -3.3 ± 0.4 e.u., k_{298} 0.45 s $^{-1}$; $\text{C}_6\text{D}_5\text{CD}_3$, G_{298}^\ddagger 17.4 kcal mol $^{-1}$, H^\ddagger 15.4 \pm 0.2 kcal mol $^{-1}$, S^\ddagger -6.6 ± 0.3 e.u., k_{298} 1.1 s $^{-1}$. The rate of the observed dynamic process is not dependent on the concentration of the solution in the range 0.007–0.7 mol dm $^{-3}$.

Since mechanistic studies using dynamic NMR spectroscopy can disclose only the type of permutational mechanism, an alternative 2,3-sigmatropic shift mechanism accompanied by successive or simultaneous 1,3-hydrogen shifts cannot be, *a priori*, ruled out. However, it seems to be highly energy unfavourable, as stems from the comparison of the energy barriers calculated for various pathways of circumambulatory rearrangements of heteroallyl groups over the cycloheptatriene ring.^{12†}

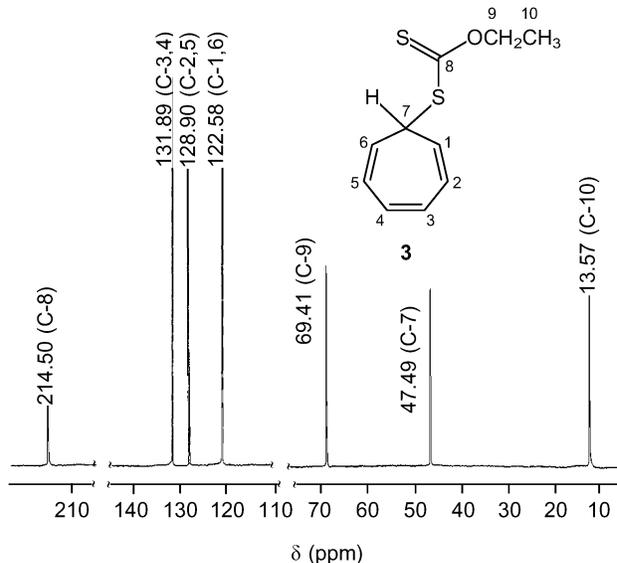


Fig. 2 ^{13}C NMR (75.47 MHz) spectrum of compound **3** in $[\text{}^2\text{H}_8]\text{toluene}$ at 24 °C. The solvent signals are excluded from the spectra.

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[†]Two additional dynamic processes are known to be typical of the type **4** compounds. Cycloheptatriene ring inversion is expected to occur at a much higher rate (in the case of cycloheptatriene itself the energy barrier against boat inversion is as low as 6.1 kcal mol $^{-1}$, whereas introduction of such a bulky substituent as the *tert*-butyl group increases the barrier up to 14.8 kcal mol $^{-1}$ in CS_2 solvent).¹³ This process would not lead to averaging of ring proton and carbon signals. The possibility exists, however, of low-energy barrier valence cycloheptatriene–norcaradiene tautomerization preceding the subsequent circumambulation of the cyclopropane ring thus formed. In this case the overall energy barrier will be sufficiently higher than that observed, *cf.* refs. 6 and 12.