Structure and rearrangements of 7-(1,2,3,4,5,6,7-heptaphenylcycloheptatrienyl) isocyanate, isothiocyanate and isoselenocyanate

Galina A. Dushenko,*[a] Igor E. Mikhailov,[a] Adolf Zschunke,[b] Gunter Reck,[b] Burkhard Schulz[b] and Vladimir I. Minkin[a]

[a] *Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation. Fax: +7 8632 28 5667; e-mail: mikhail@ipoc.rnd.runnet.ru*

[b] *Federal Institute for Materials Research and Testing, D-12200 Berlin, Germany. Fax: +4 9306 392 5972*

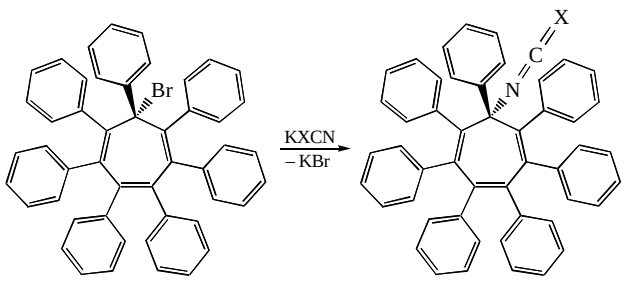
In 7-(1,2,3,4,5,6,7-heptaphenylcycloheptatrienyl) isothiocyanate and isoselenocyanate, migration of isothiocyanate and isoselenocyanate groups along the perimeter of the seven-membered ring occurs *via* an intramolecular dissociation–recombination mechanism with high free energy barriers ($\Delta G^{\neq}_{298}$) of 24.3 and 22.4 kcal mol^{-1}, respectively.

Recently, we have shown that migration of the isothiocyanate group in the three-membered ring of 3-(1,2,3-triphenylcyclopropenyl) isothiocyanate occurs *via* a dissociation–recombination mechanism ($\Delta G^{\neq}_{298\,K}$ = 14.5–15.6 kcal mol^{-1}), while circumambulation of selenocyanate ($\Delta G^{\neq}_{298\,K}$ = 16.7 kcal mol^{-1}) and isoselenocyanate ($\Delta G^{\neq}_{408\,K}$ = 22 kcal mol^{-1}) groups along the periphery of the pentaphenylcyclopentadiene ring proceeds as a series of 1,5-, and 3,3-sigmatropic shifts, respectively.[1–3]

To examine the effect of the size of a conjugated carbocycle on the migratory ability of –NCX (X = O, S or Se) groups, we have synthesised isocyanate, isothiocyanate and isoselenocyanate derivatives of heptaphenylcycloheptatriene and studied their structure and fluxional behaviour by dynamic ^{13}C and ^{1}H NMR techniques and X-ray diffraction analysis. Parent 1,2,3,4,5,6,7-heptaphenylcycloheptatriene (C_7Ph_7H)[4] has been found to possess a structure with an axial position of the phenyl substituent at the sp^3 carbon in the boat conformation of the cycloheptatriene ring.[5] Few examples are known of substituent rearrangements in this system. Among these are an irreversible high-energy-barrier 1,5-sigmatropic shift of a phenyl group (300 °C, 45 min) in C_7Ph_7H and a hydrogen migration in the same compound ($\Delta G^{\neq}_{298\,K}$ ~ 25 kcal mol^{-1}), which exhibits a high energy barrier because of the necessity of the flipping seven-membered ring to arrange the hydrogen axially.[5,6]

7-(1,2,3,4,5,6,7-Heptaphenylcycloheptatrienyl) isocyanate, isothiocyanate and isoselenocyanate **1**–**3** have been obtained by treatment of 7-bromo-1,2,3,4,5,6,7-heptaphenylcycloheptatriene[4] with equimolar amounts of potassium cyanate, thiocyanate or selenocyanate, respectively, in an acetonitrile solution (Scheme 1).† No cyanate, thiocyanate or selenocyanate isomers of **1**–**3** have been isolated.

The structure of isothiocyanate **2** has been determined by X-ray diffraction analysis (Figure 1).‡ The molecule of **2** possesses a boat-like conformation of the cycloheptatriene ring. The dihedral angles between the planes of the cycloheptatriene ring [C(6)–C(7)–C(1)/C(1)–C(2)–C(5)–C(6) 55.4(2)° and C(1)–C(2)–C(5)–C(6)/C(2)–C(3)–C(4)–C(5) 35.2(1)°] show that the bending of the sp^3 carbon is larger than that in cycloheptatriene C_7H_8 (36°); this minimises sterical interactions between the phenyl groups.[5] The isothiocyanate substituent occupies the pseudo-equatorial position, while the phenyl ring is arranged at the more sterically favoured pseudo-axial site. All phenyl rings are twisted relative to the central cycloheptatriene ring (the corresponding dihedral angles vary from 41.26 to 87.08°, Figure 1).



1–**3**

1 X = O
2 X = S
3 X = Se

Scheme 1

† *Compounds* **1**–**3**. Potassium cyanate (thiocyanate or selenocyanate) (5 mmol) was added to a suspension of 7-bromo-1,2,3,4,5,6,7-heptaphenylcycloheptatriene (5 mmol) in acetonitrile (100 ml). The mixture was stirred for 0.5 h at 25 °C. The precipitated KBr was separated using a hot-air filter funnel, and the solvent was evaporated *in vacuo*. The residue was recrystallised from acetonitrile. Yields 92–94%.

1: yellow crystals, mp 242–243 °C. IR (vaseline oil, ν/cm^{-1}): 2255, 1610, 1570, 1490, 1465. MS, *m*/*z*: 666 (51.3%) $[Ph_7C_7NCOH{=}MH]^+$, 665 (100) $[Ph_7C_7NCO = M]^+$, 649 (0.4) $[M – O]^+$, 648 (0.9) $[M – OH]^+$, 637 (9.6) $[M – CO]^+$, 636 (7.1) $[M – HCO]^+$, 623 (13.9) $[M – NCO = Ph_7C_7]^+$, 622 (8.2) $[Ph_7C_7 – H]^+$, 588 (10.3) $[M – Ph]^+$, 560 (42.4) $[M – Ph – CO]^+$, 546 (33.4) $[Ph_7C_7 – Ph = Ph_6C_7]^+$, 545 (69.7) $[Ph_6C_7 – H]^+$, 534 (30.6) $[Ph_6C_7 – C = Ph_6C_6]^+$, 467 (9.0) $[Ph_7C_7 – 2C_6H_6]^+$, 367 (6.0) $[Ph_5C_5 – C_6H_6]^+$, 267 (2.8) $[Ph_3C_3]^+$, 91 (3.4) $[C_7H_7]^+$, 77 (11.9) $[C_6H_5]^+$.

2: yellow crystals, mp 263–265 °C (decomp.). IR (vaseline oil, ν/cm^{-1}): 2125, 1600, 1575, 1490, 1475. MS, *m*/*z*: 682 (27.3%) $[Ph_7C_7NCSH = MH]^+$, 681 (51.1) $[Ph_7C_7NCS = M]^+$, 649 (2.3) $[M – S]^+$, 648 (3.9) $[M - SH]^+$, 624 (29.4) $[MH – NCS = Ph_7C_7H]^+$, 623 (51.2) $[Ph_7C_7]^+$, 622 (25.1) $[Ph_7C_7 – H]^+$, 604 (2.5) $[M – Ph]^+$, 546 (46.1) $[Ph_7C_7 – Ph = Ph_6C_7]^+$, 545 (100) $[Ph_6C_7 – H]^+$, 534 (2.4) $[Ph_6C_7 – C = Ph_6C_6]^+$, 467 (10.3) $[Ph_7C_7 – 2C_6H_6]^+$, 367 (7.0) $[Ph_5C_5 – C_6H_6]^+$, 267 (3.6) $[Ph_3C_3]^+$, 103 (21.1) $[PhCN]^+$, 91 (3.4) $[C_7H_7]^+$, 77 (11.9) $[C_6H_5]^+$.

3: yellow crystals, mp 269–270 °C (decomp.). IR (vaseline oil, ν/cm^{-1}): 2050, 1600, 1580, 1490, 1470. MS, *m*/*z*: 729 (1.6%) $[Ph_7C_7NCSeH = MH]^+$, 728 (3.0) $[Ph_7C_7NCSe = M]^+$, 702 (0.8) $[Ph_7C_7SeCN – CN]^+$, 701 (0.8) $[Ph_7C_7SeCN – HCN]^+$, 650 (16.4) $[M – C_6H_6]^+$, 649 (31.6) $[M – Se]^+$, 648 (9.8) $[M – SeH]^+$, 623 (90.7) $[M – NCSe = Ph_7C_7]^+$, 622 (63.0) $[Ph_7C_7 – H]^+$, 572 (16.6) $[M – 2C_6H_6]^+$, 571 (16.0) $[M – Se – C_6H_6]^+$, 546 (58.9) $[Ph_7C_7 – Ph = Ph_6C_7]^+$, 545 (100) $[Ph_6C_7 – H]^+$, 534 (3.8) $[Ph_6C_7 – C = Ph_6C_6]^+$, 467 (18.3) $[Ph_7C_7 – 2C_6H_6]^+$, 367 (18.0) $[Ph_5C_5 – C_6H_6]^+$, 267 (10.6) $[Ph_3C_3]^+$, 194 (15.3) $[PhCNCSe]^+$, 105 (7.4) $[NCSe]^+$, 91 (37.1) $[C_7H_7]^+$, 77 (55.6) $[C_6H_5]^+$.

‡ *Crystal data for* **2**. $C_{50}H_{35}NS·0.5C_6H_6$, monoclinic, space group $P2_1/n$, a = 19.126(4) Å, b = 11.349(5) Å, c = 18.952(4) Å, β = 100.18(2)°, V = = 4049(2) Å^3, Z = 4, d_{calc} = 1.183 g cm^3. The X-ray diffraction experiments were carried out on an Enraf Nonius CAD-4 diffractometer [T = 293(2) K, graphite-monochromated MoKα radiation, λ = 0.71069 Å, $\theta/2\theta$ scan technique, $3° < 2\theta < 40°$]. The structure was solved by direct methods using SHEXS-97 (G. Scheldrick, University of Göttingen, 1990). Independent reflections: 3754. Refinement method: full-matrix least-squares (SHELXL-97, G. Sheldrick, University of Göttingen, 1997), data/parameters 3754/497, goodness-of-fit 1.035, final R indices [$I > 2\sigma(I)$] R_1 = 0.0353, wR_2 = 0.0993; R indices (all data) R_1 = 0.0418, wR_2 = 0.1040, Δf_{max} = = 0.087 e Å^{-3}. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement using the riding model. Atomic coordinates, bond lengts, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/54.

Table 1 Kinetic and activation parameters of rotation of the phenyl rings at $C_{1,6}$ in **1**–**3.**

Compound	Solvent	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$ (e.u.)	k_{298}/s^{-1}	$\Delta G^{\neq}_{298\ K}$/ kcal mol^{-1}
1, X = O	C_6D_6	12.6±0.3	–10.9±0.9	14.1	15.9
2, X = S	[$^2H_8$]toluene	13.1±0.4	–8.8±1.1	17.8	15.7
3, X = Se	[$^2H_8$]toluene	13.2±0.3	–8.9±0.9	15.1	15.8

The structure of compounds **1**–**3** has been confirmed by IR and NMR spectroscopy and mass spectrometry. In the IR spectra of compounds **1**–**3**, broad absorption peaks characteristic of the –N=C=O, –N=C=S and –N=C=Se stretching vibration region[7] were observed at 2255, 2125 and 2050 cm^{-1}, respectively. In the ^{13}C NMR spectra of compounds **1**–**3**§ in C_6D_6, the –N=C=O, –N=C=S (Figure 2) and –N=C=Se carbon signals appear in their characteristic regions[8,9] at δ 124.75, 138.30 and 133.00 ppm, respectively. No carbon signals of the C_7Ph_7–XCN (X = O, S or Se) isomers of **1**–**3** were detected in the characteristic regions of δ 110–113 ppm.[8,9]

The *o*- and *m*-carbon atoms of the phenyl rings at $C_{1,6}$ of the cycloheptatriene ring are magnetically nonequivalent at 20 °C. With increasing temperature of the solutions of **1**–**3**, these two pairs of signals broaden, coalesce and become narrow at 75 °C (Figure 2). Such a spectral behaviour indicates the hindered rotation of these rings. From line shape analysis of the indicator signals of the *o*- and *m*-carbons of the rings at $C_{1,6}$ in the dynamic ^{13}C NMR spectra (25–90 °C), the kinetic and activation parameters of the hindered rotation of the phenyl rings at $C_{1,6}$ in **1**–**3** have been calculated using the DNMR-5 program[10] (Table 1).

The shape of the cycloheptatriene ring signals as well as *para*- and *ipso*-aromatic carbon signals are almost unaffected by the temperature of solutions in the range from –70 to +100 °C (C_6D_6, [$^2H_8$]toluene). The hindered rotation of the phenyl rings at $C_{2,5}$ and $C_{3,4}$ for compounds **1**–**3** can also be detected at low temperatures in the ^{13}C NMR spectra. It manifests itself in considerable broadening of the *ortho*- and *meta*-carbons in these rings ($T < -10$ °C for Ph at $C_{2,5}$, $\Delta G^{\neq}_{223\ K} \approx$ $\approx$ 12 kcal mol^{-1}; $T < -50$ °C for Ph at $C_{3,4}$, $\Delta G^{\neq} < 9$ kcal mol^{-1}). Note that in C_7Ph_7H the rotation barriers for the phenyl rings at $C_{1,6}$ ($C_{3,4}$) and $C_{2,5}$ were evaluated as $\approx$ 9 and 11 kcal mol^{-1}, respectively.[5] An increase in the barrier for the hindered rotation of the phenyl rings at $C_{1,6}$ in **1**–**3** can be explained by the additional overcrowding of the heptaphenylcycloheptatriene ring by –NCX substituents.

The ^{1}H and ^{13}C NMR spectral signals of compounds **1**–**3** were assigned on the basis of the characteristic values of

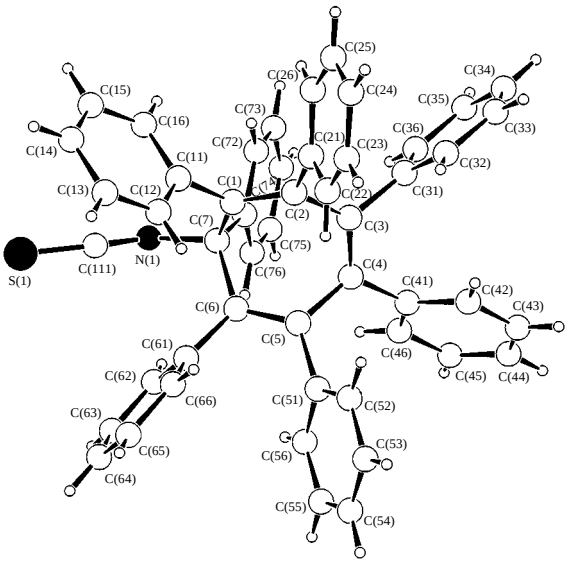
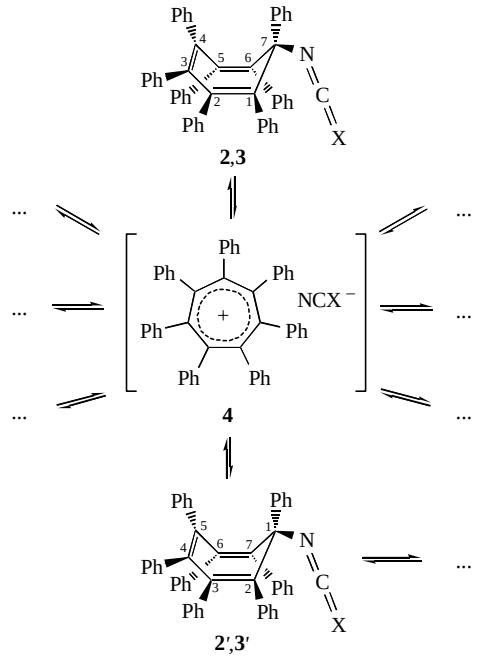


Figure 1 The molecular structure of compound **2**. Selected bond lengths/Å: N(1)–C(7) 1.457(3), N(1)–C(111) 1.148(3), S(1)–C(111) 1.575(3), C(1)–C(7) 1.537(3), C(6)–C(7) 1.536, C(7)–C(71) 1.539, C(1)–C(11) 1.487(3), C(2)–C(21) 1.499(3); selected bond angles/°: C(111)–N(1)–C(7) 165.1(2), N(1)–C(111)–S(1) 177.1(2), N(1)–C(7)–C(6) 108.84(16), N(1)–C(7)–C(1) 108.42(17), N(1)–C(7)–C(71) 104.06(15), C(1)–C(7)–C(6) 104.53(15). Dihedral angles between the cycloheptatriene ring and the phenyl rings/°: [C(1)–C(2)–C(3)–C(4)–C(5)–C(6)–C(7)]/[C(11)–C(12)–C(13)–C(14)–C(15)–C(16)] 74.65(8), [C(1)–C(7)]/[C(21)–C(26)] 68.97(8), [C(1)–C(7)]/[C(31)–C(36)] 87.08(8), [C(1)–C(7)]/[C(41)–C(46)] 41.26(9), [C(1)–C(7)]/[C(51)–C(56)] 58.28(8), [C(1)–C(7)]/[C(61)–C(66)] 86.80(9), [C(1)–C(7)]/[C(71)–C(76)] 78.92(8).



2 X = S
3 X = Se

Scheme 2

§ **1**: ^{1}H NMR (300 MHz, 20 °C, C_6D_6) δ: 6.36 (dd, 4H, *ortho*, Ph at $C_{3,4}$, *J* 6.9 and 1.6 Hz), 6.54–6.64 (m, 6H, *meta*, *para*, Ph at $C_{3,4}$), 6.76–6.80, 6.88–6.93, 7.02–7.08 (m, 18H, Ph at $C_{1,6}$ and $C_{2,5}$), 7.24 (tq, 1H, *para*, Ph at C_7, *J* 7.5 and 1.2 Hz), 7.40 (dd, 2H, *meta*, Ph at C_7, *J* 8.3 and 7.5 Hz), 7.61 (dd, 2H, *ortho*, Ph at $C_{1,6}$, *J* 7.8 and 1.5 Hz), 8.23 (dd, 2H, *ortho*, Ph at C_7, *J* 7.2 and 1.6 Hz). ^{13}C NMR (75.47 MHz, 20 °C, C_6D_6) δ: 72.73 (C_7), 126.09 (*para*, Ph at $C_{3,4}$), 126.56 (*para*, Ph at $C_{2,5}$), 126.73 (*meta*, Ph at $C_{3,4}$), 126.75 (*para*, Ph at $C_{1,6}$), 127.34 (*ortho*, Ph at C_7), 127.52 (*meta*, Ph at $C_{2,5}$), 127.54, 127.87 (*meta*, Ph at $C_{1,6}$), 128.72 (*para*, Ph at C_7), 129.39 (*meta*, Ph at C_7), 131.45 (*ortho*, Ph at $C_{2,5}$), 131.59 (*ortho*, Ph at $C_{3,4}$), 131.76, 131.87 (*ortho*, Ph at $C_{1,6}$), 124.75 (NCO), 139.41, 140.03, 141.10 (*ipso*, Ph at C_{1-6}), 137.77, 143.51, 144.03 (C_{1-6}), 146.65 (*ipso*, Ph at C_7).

2: ^{1}H NMR (300 MHz, 20 °C, [$^2H_8$]toluene) δ: 6.29 (dd, 4H, *ortho*, Ph at $C_{3,4}$, *J* 7.0 and 1.5 Hz), 6.48–6.59 (m, 6H, *meta*, *para*, Ph at $C_{3,4}$), 6.71–6.80, 6.83–6.88, 6.95–7.15 (m, 18H, Ph at $C_{2,5}$ and $C_{1,6}$), 7.24 (tq, 1H, *para*, Ph at C_7, *J* 7.5 and 1.2 Hz) 7.41 (dd, 2H, *meta*, Ph at C_7, *J* 8.2 and 7.5 Hz), 7.66 (dd, 2H, *ortho*, Ph at $C_{1,6}$, *J* 7.8 and 1.5 Hz), 8.21 (dd, 2H, *ortho*, Ph at C_7, *J* 7.2 and 1.5 Hz). ^{13}C NMR (75.47 MHz, 20 °C, C_6D_6) δ: 76.44 (C_7), 126.06 (*para*, Ph at $C_{3,4}$), 126.61 (*para*, Ph at $C_{2,5}$), 126.66 (*meta*, Ph at $C_{3,4}$), 126.85 (*para*, Ph at $C_{1,6}$), 127.40 (*ortho*, Ph at C_7), 127.49 (*meta*, Ph at $C_{2,5}$), 127.60, 127.78 (*meta*, Ph at $C_{1,6}$), 129.04 (*para*, Ph at C_7), 129.36 (*meta*, Ph at C_7), 131.32 (*ortho*, Ph at $C_{2,5}$), 131.42 (*ortho*, Ph at $C_{3,4}$), 131.57, 131.67 (*ortho*, Ph at $C_{1,6}$), 138.30 (NCS), 137.69, 141.81, 143.95 (C_{1-6}), 138.94, 139.77, 140.65 (*ipso*, Ph at C_{1-6}), 144.35 (*ipso*, Ph at C_7).

3: ^{1}H NMR (300 MHz, 20 °C, [$^2H_8$]toluene) δ: 5.91 (dd, 4H, *ortho*, Ph at $C_{3,4}$, *J* 6.8 and 1.6 Hz), 6.14–6.19 (m, 6H, *meta*, *para*, Ph at $C_{3,4}$), 6.37–6.53, 6.57–6.65, 6.73–6.82 (m, 18H, Ph at $C_{1,6}$ and $C_{2,5}$), 6.87 (tq, 1H, *para*, Ph at C_7, *J* 7.5 and 1.2 Hz) 7.03 (dd, 2H, *meta*, Ph at C_7, *J* 8.2 and 7.5 Hz), 7.31 (dd, 2H, *ortho*, Ph at $C_{1,6}$, *J* 7.8 and 1.5 Hz), 7.84 (dd, 2H, *ortho*, Ph at C_7, *J* 7.2 and 1.5 Hz). ^{13}C NMR (75.47 MHz, 20 °C, C_6D_6) δ: 77.19 (C_7), 126.10 (*para*, Ph at $C_{3,4}$), 126.64 (*para*, Ph at $C_{2,5}$), 126.68 (*meta*, Ph at $C_{3,4}$), 126.98 (*para*, Ph at $C_{1,6}$), 127.50 (*meta*, Ph at $C_{2,5}$), 127.55 (*ortho*, Ph at C_7), 127.78, 127.83 (*meta*, Ph at $C_{1,6}$), 129.23 (*para*, Ph at C_7), 129.43 (*meta*, Ph at C_7), 131.32 (*ortho*, Ph at $C_{2,5}$), 131.42 (*ortho*, Ph at $C_{3,4}$), 131.58, 131.64 (*ortho*, Ph at $C_{1,6}$), 133.00 (NCSe), 138.59, 139.71, 140.55 (*ipso*, Ph at C_{1-6}), 137.78, 141.20, 143.44 (C_{1-6}), 143.97 (*ipso*, Ph at C_7).

Table 2 Kinetic and activation parameters of –NCX group migrations in **2** and **3**.

Compound	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$ (e.u.)	k_{298}/s^{-1}	$\Delta G^{\neq}_{298}$/ kcal mol^{-1}
2, X = S	26.5±0.4	+7.3±1.0	8.9×10^{-6}	24.3
3, X = Se	22.9±0.3	+1.8±0.9	2.2×10^{-4}	22.4

chemical shifts and the integral intensities, the application of the APT techniques and by means of monoresonance ^{13}C spectra, heteronuclear correlation of the ^{1}H and ^{13}C chemical shifts (XHCOORR), ^{1}H–^{1}H COSY and NOE measurements (see footnote;§ Figures 2 and 3). The assignments are consistent with those reported previously for heptaphenylcycloheptatriene.[5] The NOE experiments pointed to the notable interaction between the *ortho*-protons of the rings at $C_{3,4}$ and C_7 thus confirming a pseudo-axial position of the phenyl ring at C_7 of **1**–**3**. The proton signals of a single phenyl ring at C_7 of **1**–**3** (Figure 3) are shifted relative to those of the rings at $C_{3,4}$ and found in the most downfield part of the ^{1}H NMR spectra, whereas the proton signals of the rings at $C_{3,4}$ are detected in the most upfield part. The proton signals of the phenyl rings at $C_{2,5}$ and $C_{1,6}$ are partially overlapped; one of the *o*-protons (which are nonequivalent at ≤ 25 °C) of the rings at $C_{1,6}$ appears separately as a doublet of doublet signal at δ 7.66–7.31 ppm. As the temperature of [$^{2}H_5$]nitrobenzene solutions of **1**–**3** was increased from 25 to 100 °C (Figure 3), broadening and coalescence of signals of both nonequivalent *o*- and *m*-protons of the rings at $C_{1,6}$ were observed. At 140–180 °C for **2** and at 120–160 °C for **3**, synchronous reversible broadening and coalescence of the proton signals of all the phenyl rings take place, indicating a random dissociation–recombination mechanism[11] of displacement

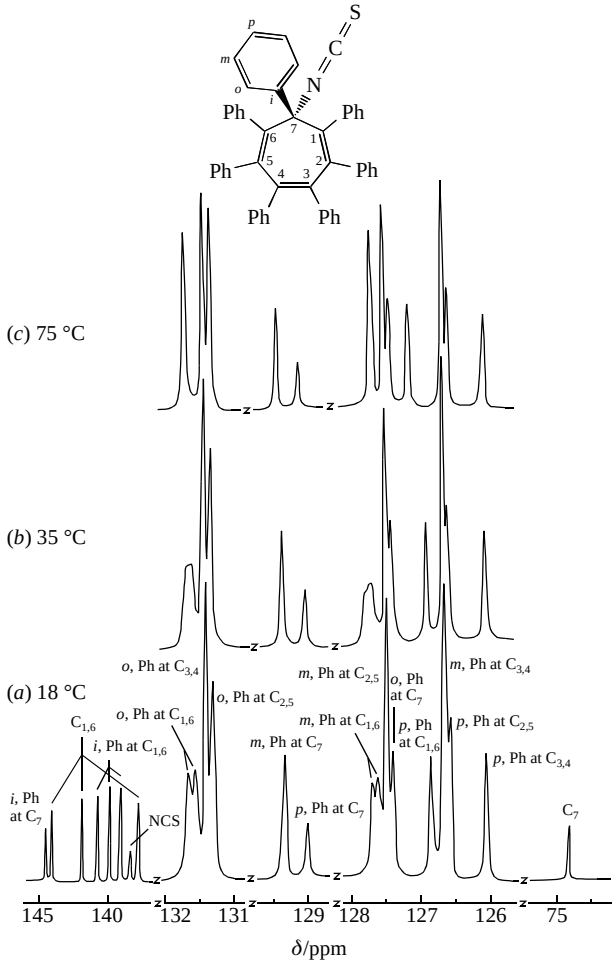


Figure 2 ^{13}C NMR (75.47 MHz) spectra of **2** in C_6D_6 at (*a*) 18 °C, (*b*) 35 °C, (*c*) 75 °C. Spectra (*b*) and (*c*) are given in the region 126–132 ppm; the pattern of the rest spectral parts is not changed at these temperatures. Solvent signals are excluded from the spectra.

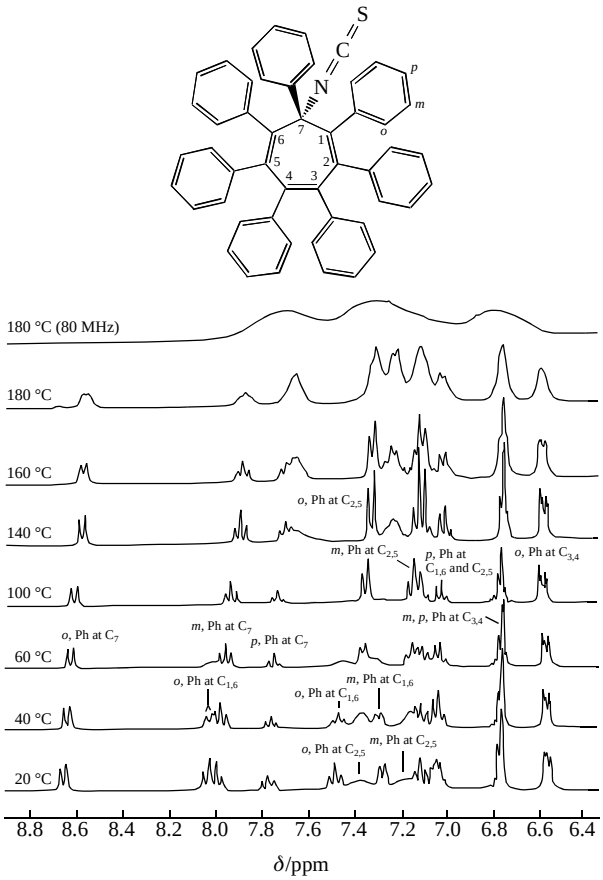


Figure 3 ^{1}H NMR (300 MHz) spectra of **2** in [$^{2}H_5$]nitrobenzene at 20, 40, 60, 100, 140, 160, 180 °C and 180 °C (80 MHz). Solvent signals are excluded from the spectra.

of isothiocyanate and isoselenocyanate groups along the perimeter of the seven-membered ring (**2**,**3** = **2′**,**3′** = …; Scheme 2). Upon varying the concentration of solutions (*c* 0.003–0.3 mol dm^{-3}) of **2** and **3**, no changes in the dynamic NMR spectral patterns were observed. This proves the intramolecular tight ion pair mechanism of the migrations.

For isocyanate derivative **1**, the NMR spectra did not show any temperature dependence up to 180 °C. Such a spectral behaviour indicates the stereochemical rigidity of **1** on the characteristic NMR time scale ($\Delta G^{\neq}_{298\ K} > 25$ kcal mol^{-1}).

By comparison of the experimental line shape of the indicator proton signals of the phenyl rings at C_{1-7} in the dynamic ^{1}H NMR spectra (120–180 °C) with the theoretical shape the kinetic parameters of the –NCX (X = S or Se) group migrations in **2** and **3** in [$^{2}H_5$]nitrobenzene solutions have been calculated using the DNMR-5 program.[10] The activation parameters have been calculated from the ln *k*/*T*–1/*T* relationship for eight temperature measurements (Table 2).

The –NCO and –NCS group migrations along the periphery of the unsubstituted cycloheptatriene ring in cycloheptatrienyl isocyanate and isothiocyanate is known[9,12,13] to occur *via* tight ion pair reaction paths with low free activation barriers $\Delta G^{\neq}$ of 16.5 and 14.8 kcal mol^{-1}, respectively. An increase in the energy barriers of the –NCX group migrations over the heptaphenylcycloheptatriene ring as compared to those for the unsubstituted seven-membered ring is most probably caused by steric hindrances created by the phenyl substituents in the $C_7Ph_7^+$ cation, which is formed in intermediate **4** of the rearrangement.¶

¶ A similar increase of the energy barrier against a boat inversion of the seven-membered ring in C_7Ph_7H ($\Delta G^{\neq} \geq 25$ kcal mol^{-1}) due to sterical hindrances, as compared to that for unsubstituted cyloheptatriene C_7H_6 ($\Delta G^{\neq}$ 6.1 kcal mol^{-1}) was observed earlier.[5,14] The high barrier of the boat inversion in the heptaphenylcycloheptatriene system restricts the symmetry-allowed suprafacial sigmatropic shifts of substituents, which can occur when migrants are axially positioned.

In the case of compound **3**, a minor component of the selenocyanate species (Ph_7C_7SeCN) was detected in the gas phase by the appearance of low-intensity peaks in the mass spectrum, originated from fragmentation of this species: *m*/*z* (%), 702 (0.8) $[Ph_7C_7SeCN - CN]^+$ and 701 (0.8) $[Ph_7C_7SeCN - HCN]^+$, unlike compounds **1** and **2**.† This fact points to the principal possibility of an additional competitive mechanism for the isoselenocyanate group migration in the seven-membered ring of **3** in the gas phase.

Thus, the migratory ability of –NCX groups decreases in proportion to the increase in the ring size of the perphenylcyclopolyene $Ph_3C_3 > Ph_5C_5 > Ph_7C_7$ due to changes in the mechanism of the circumambulations in the cyclopentadiene derivatives and a lower stability of the sterically overcrowded $Ph_7C_7^+$ cation in **4** as compared to the $Ph_3C_3^+$ cation in the ion-pair transition state of the migrations over the cyclopropene ring.

This work was supported by the Russian Foundation for Basic Research (grant no. 98-03-33062) and by the programme 'Russian Universities: Fundamental Research' (grant no. 4058).

References

1 G. A. Dushenko, I. E. Mikhailov, I. V. Dorogan, R. M. Minyaev, A. Zschunke and V. I. Minkin, *Mendeleev Commun*., 1995, 213.
2 G. A. Dushenko, I. E. Mikhailov, A. Zschunke, N. Hakam, C. Mugge, R. V. Skachkov and V. I. Minkin, *Mendeleev Commun*., 1995, 182.
3 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, O. E. Kompan and A. Zschunke, *Izv. Akad. Nauk, Ser. Khim*., 1998, 913 (*Russ. Chem. Bull.*, 1998, **47**, 884).
4 M. A. Battiste, *Chem. Ind. (London)*, 1961, 550.
5 L. S. F. Chao, H. K. Gupta, D. W. Hughes, J. F. Britten, S. S. Rigby, A. D. Bain and M. J. McGlinchey, *Organometallics*, 1995, **14**, 1139.
6 J. A. Harvey and M. A. Ogliaruso, *J. Org. Chem*., 1976, **41**, 3374.
7 B. H. Williams and I. Fleming, in *Spectroskopische Metoden in der Organischen Chemie*, G. Thieme Verlag, Stuttgart, 1971 (in German).
8 G. C. Levy and G. L. Nelson, in *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley–Interscience, New York, 1972.
9 M. Feigel, H. Kessler and A. Walter, *Chem. Ber.*, 1978, **111**, 2947.
10 D. S. Stephenson and G. Binsch, *J. Magn. Reson*., 1978, **32**, 145.
11 B. E. Mann, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, A. G. F. Stone and E. Abel, Pergamon Press, New York, 1982, vol. 3, ch. 20, p. 90.
12 H. Kessler and M. Feigel, *Acc. Chem. Res.*, 1982, **15**, 2.
13 H. Kessler, *Chimia*, 1973, **27**, 444.
14 M. Oki, *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH, Weinheim, 1985, pp. 310, 374.

Received: 28th May 1999; Com. 99/1492