Supporting Information

Ambident Reactivity of the Thiocyanate Anion Revisited: Can the Product Ratio be Explained by the HSAB Principle?

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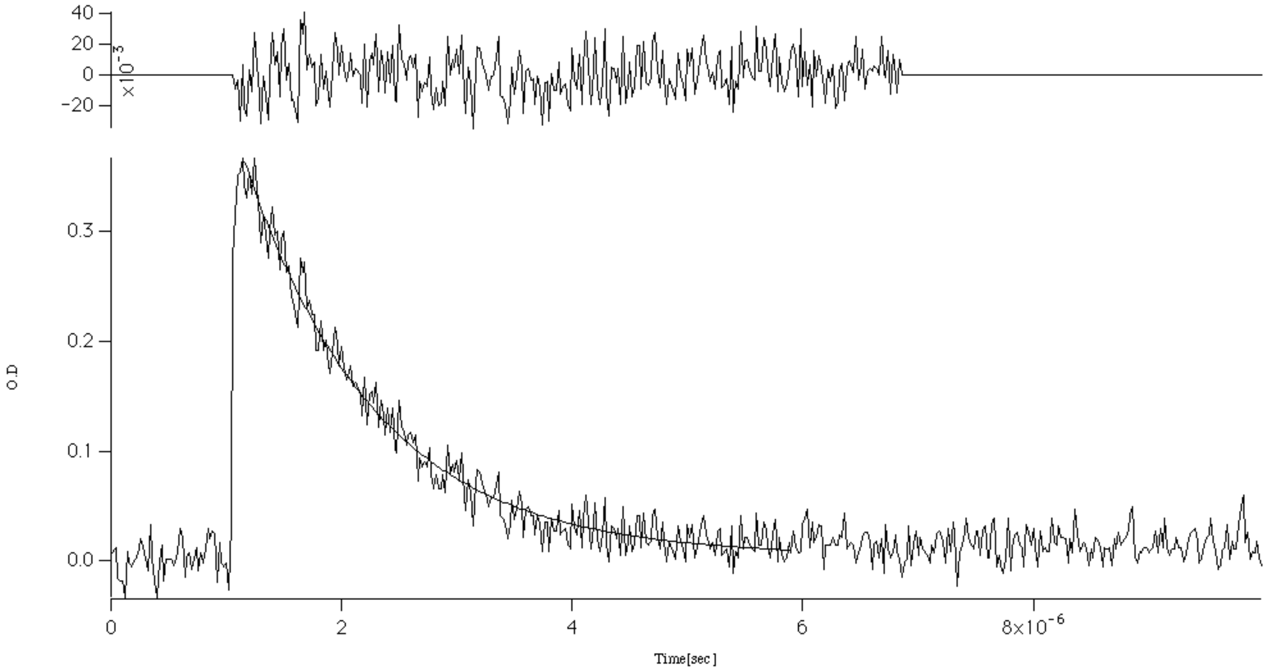
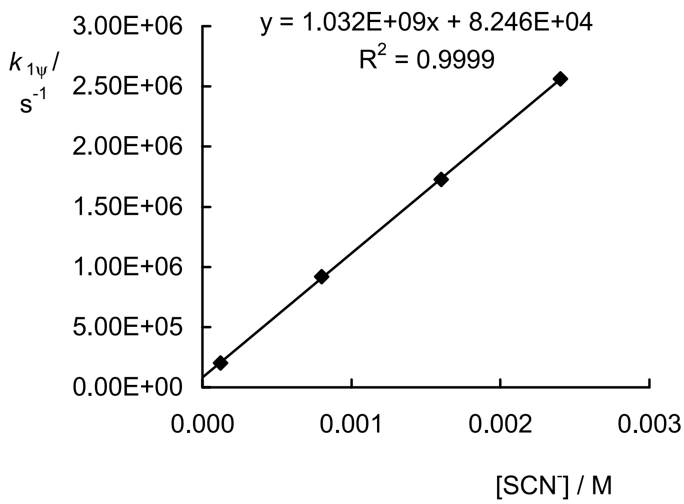


Figure S1. Example for the decay of **4** at 592 nm in the presence of 8.01×10^{-4} M SCN^- (single laser shot, acetonitrile, 20 °C) – Top: Quality of fit.

Table S1. Rate Constants for the Reaction of **4**-BF_4 (7.16×10^{-5} M) with $n$$Bu_4N^+SCN^-$ by Laser Flash (Solution Colorless before Irradiation).

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$ [a] / s^{-1}
lo27030211	1.20×10^{-4}	2.02×10^{5}
lo27030212	8.01×10^{-4}	9.18×10^{5}
lo27030213	1.60×10^{-3}	1.73×10^{6}
lo27030214	2.40×10^{-3}	2.56×10^{6}
lo27030215	4.00×10^{-3}	3.59×10^{6} [b]
lo27030216	6.01×10^{-3}	4.96×10^{6} [b]
lo27030217	1.20×10^{-2}	8.88×10^{6} [b]

[a] Attack at sulfur of SCN^-. [b] Not used for evaluation of k_S, see manuscript.



k_S (20 °C) = 1.03×10^{9} M^{-1} s^{-1}

k_{-S} (20 °C) = 8.25×10^{4} s^{-1}

$r^2 = 0.9999$

Formation of 5-SCN from 5 and SCN^- in acetonitrile at 20 °C

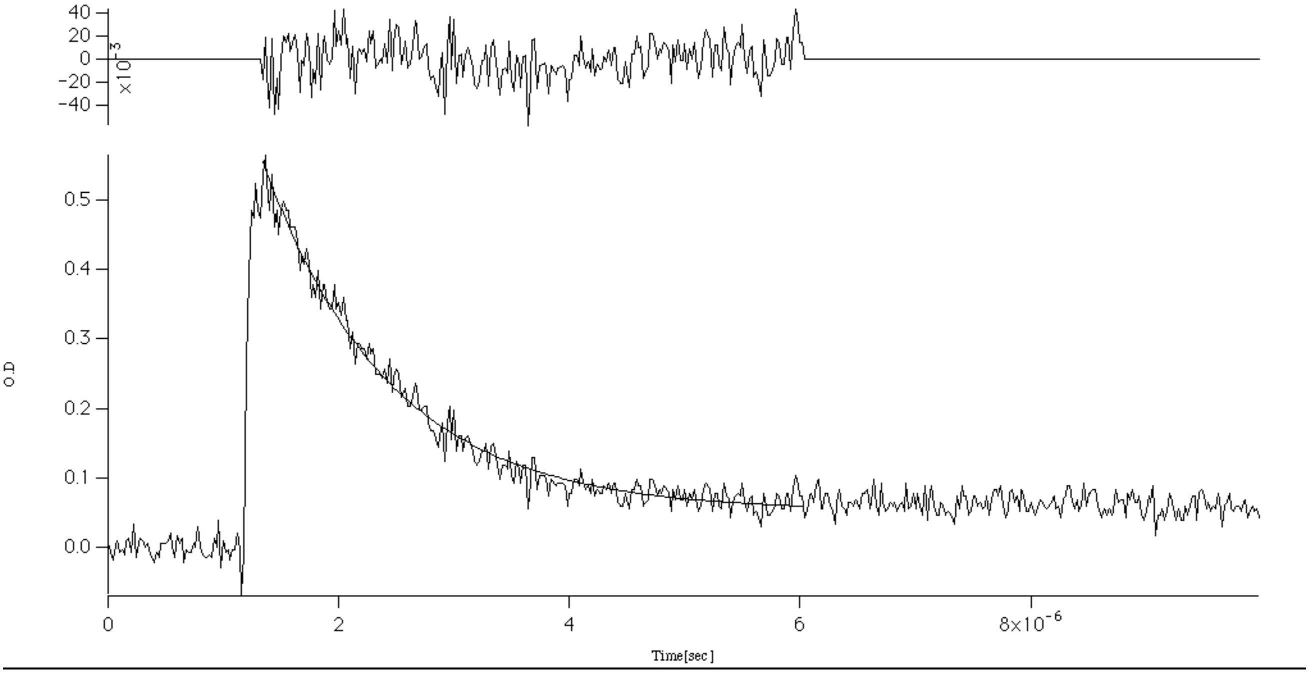
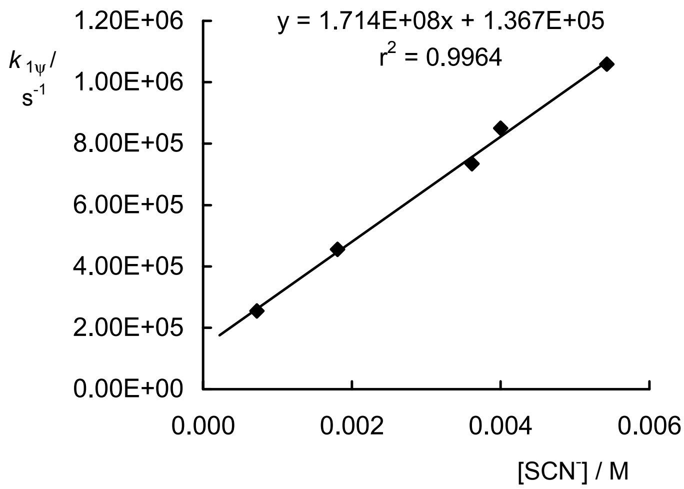


Figure S2. Example for the decay of **5** at 586 nm in the presence of 4.00×10^{-3} M SCN^- (single laser shot, acetonitrile, 20 °C) – Top: Quality of fit.

Table S2. Rate Constants for the Reaction of **5**-BF_4 (4.23×10^{-5} M) with $n Bu_4N^+SCN^-$ by Laser Flash (Solution Colorless before Irradiation).

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}{}^a$ / s^{-1}
lo28030201	4.00×10^{-3}	8.50×10^{5}
lo28030202	7.23×10^{-4}	2.54×10^{5}
lo28030203	1.81×10^{-3}	4.55×10^{5}
lo28030204	3.62×10^{-3}	7.34×10^{5}
lo28030205	5.43×10^{-3}	1.06×10^{6}
lo28030206	7.23×10^{-3}	1.28×10^{6} [b]
lo28030207	1.09×10^{-2}	1.78×10^{6} [b]
lo28030208	1.09×10^{-2}	1.71×10^{6} [b]
lo28030209	7.23×10^{-3}	1.32×10^{6} [b]

[a] Attack at sulfur of SCN^-. [b] Not used for evaluation of k_S, see manuscript.



k_S (20 °C) = 1.71×10^8 M^{-1} s^{-1}

k_{-S} (20 °C) = 1.37×10^5 s^{-1}

$r^2 = 0.9964$

Formation of 6-SCN from 6 and SCN⁻ in acetonitrile at 20 °C

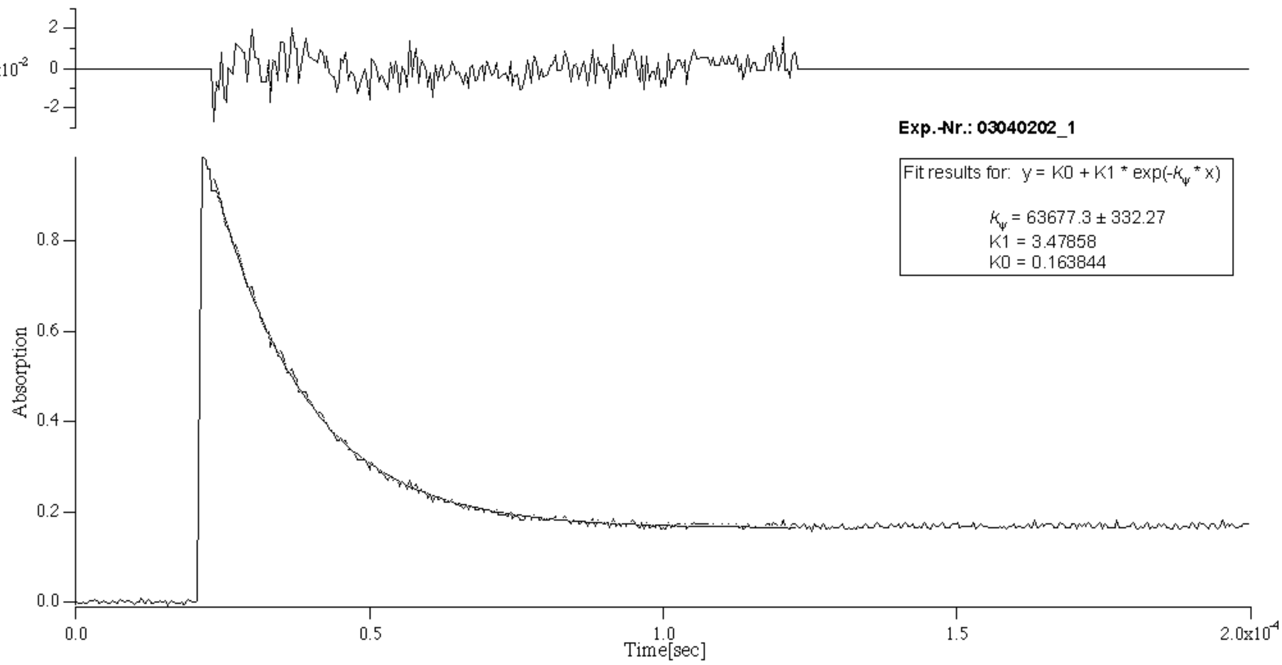
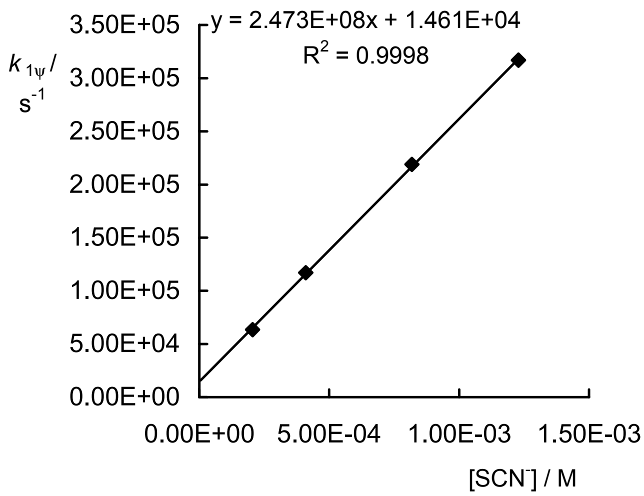


Figure S3. Example for the decay of **6** at 645 nm in the presence of 2.05×10^{-4} M SCN^- (single laser shot, acetonitrile, 20 °C) – Top: Quality of fit.

Table S3. Rate Constants for the Reaction of **6**-BF_4 (3.20×10^{-5} M) with $n Bu_4N^+SCN^-$ by Laser Flash (Solution Colorless before Irradiation).

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$[a] / s^{-1}
lo03040202	2.05×10^{-4}	6.35×10^{4}
lo03040203	4.09×10^{-4}	1.17×10^{5}
lo03040204	8.18×10^{-4}	2.19×10^{5}
lo03040205	1.23×10^{-3}	3.17×10^{5}
lo03040206	2.05×10^{-3}	4.71×10^{5} [b]
lo03040207	3.07×10^{-3}	6.42×10^{5} [b]

[a] Attack at sulfur of SCN^-. [b] Not used for evaluation of k_S, see manuscript.



k_S (20 °C) = 2.47×10^{8} M^{-1} s^{-1}

k_{-S} (20 °C) = 1.46×10^{4} s^{-1}

$r^2 = 0.9998$

Formation of 7-SCN from 7 and SCN⁻ in acetonitrile at 20 °C

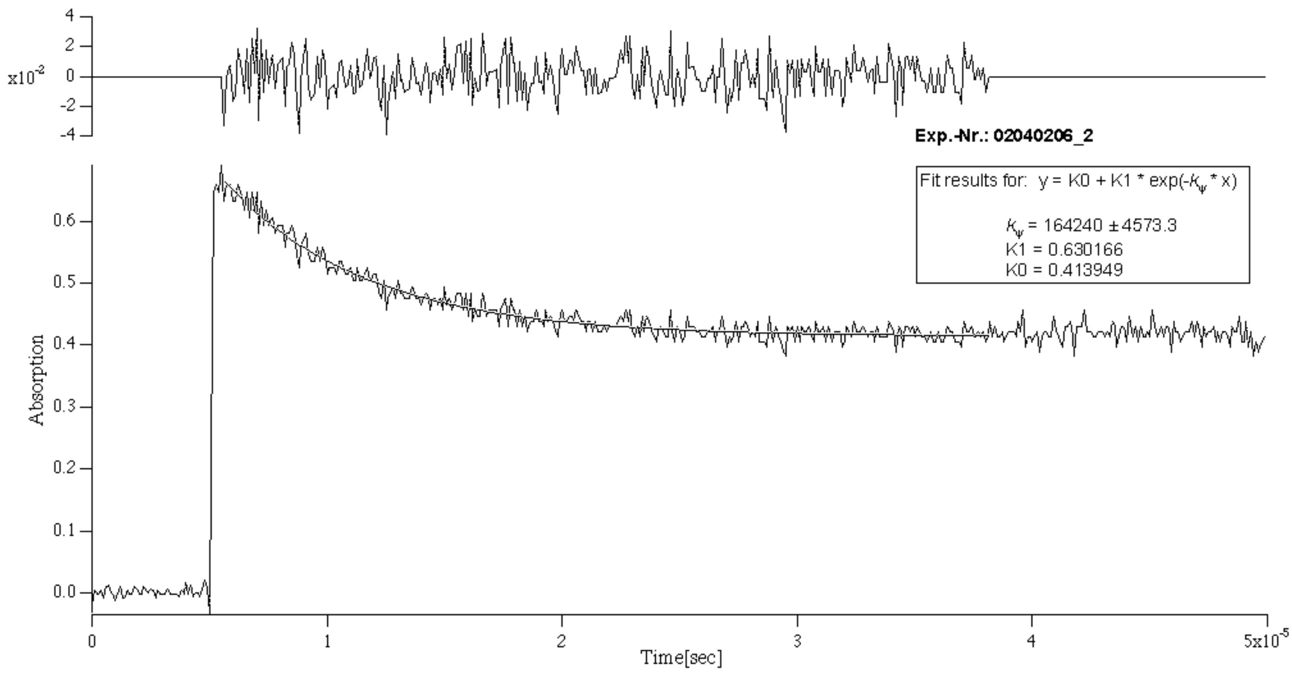
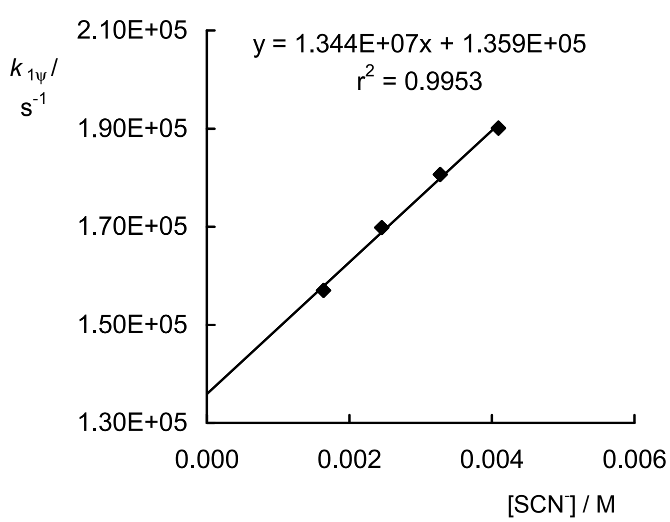


Figure S4. Example for the decay of **7** at 612 nm in the presence of 4.09×10^{-3} M SCN^- (single laser shot, acetonitrile, 20 °C) – Top: Quality of fit.

Table S4. Rate Constants for the Reaction of **7**-BF_4 (5.03×10^{-5} M) with $n$$Bu_4N^+SCN^-$ by Laser Flash.

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$ / s^{-1}
lo02040201	4.09×10^{-4}	2.65 ^{a,b}
lo02040202	8.18×10^{-4}	4.62 ^{a,b}
lo02040203	1.64×10^{-3}	1.57×10^{5} ^{b,c}
lo02040204	2.46×10^{-3}	1.70×10^{5} ^{c}
lo02040205	3.27×10^{-3}	1.81×10^{5} ^{c}
lo02040206	4.09×10^{-3}	1.90×10^{5} ^{c}
lo02040207	6.14×10^{-3}	2.04×10^{5} ^{c,d}

^{a} Only the slow reaction with nitrogen of SCN^- is observable, $k_N = k_\psi/[SCN^-]_0 = 6.48 \times 10^3$ and 5.85×10^3 M^{-1} s^{-1}, respectively. ^{b} At low $[SCN^-]$, **7**-NCS is partially ionized (blue solution!). ^{c} Attack at sulfur of SCN^-. ^{d} Not used for evaluation of k_S.



k_S (20 °C) = 1.34×10^7 M^{-1} s^{-1}

k_{-S} (20 °C) = 1.36×10^5 s^{-1}

$r^2 = 0.9953$

Formation of 8-SCN from 8 and SCN⁻ in acetonitrile at 20 °C

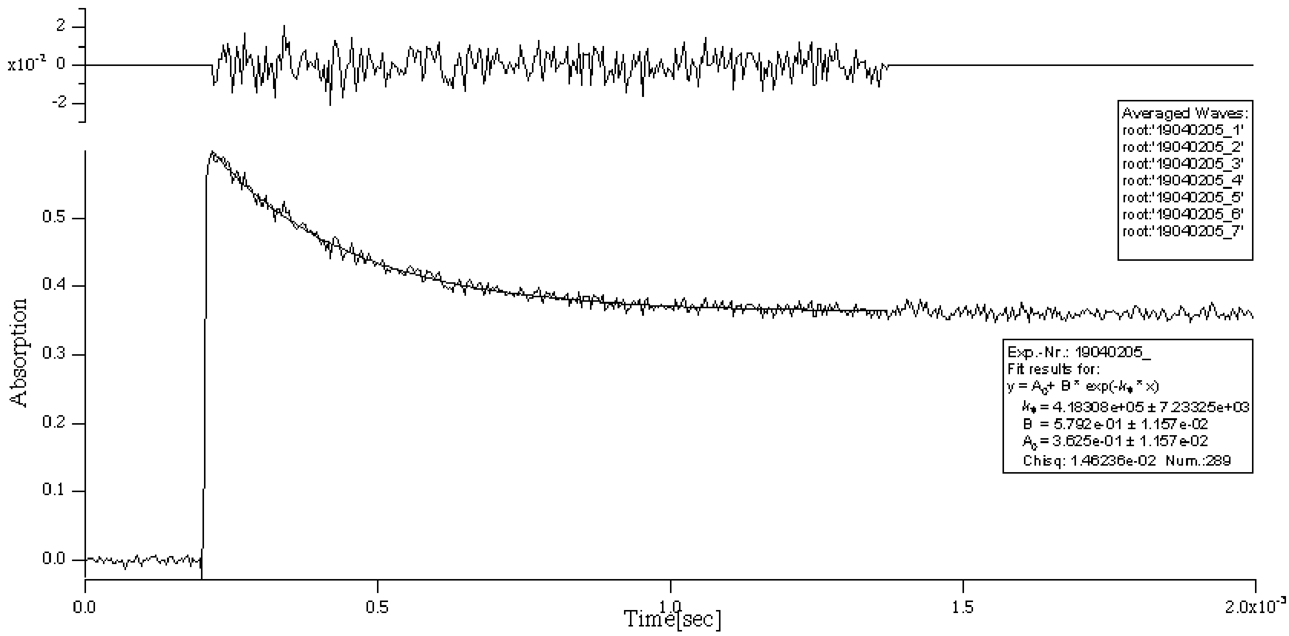
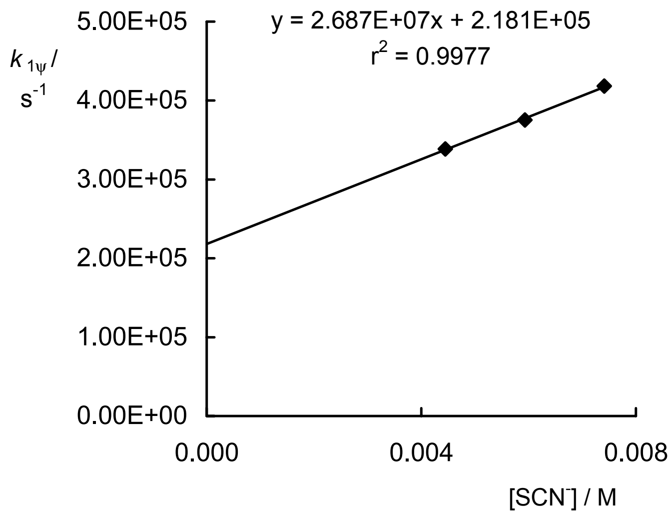


Figure S5. Example for the decay of **8** at 613 nm in the presence of 7.41×10^{-3} M SCN^- (averaged decay from 7 laser shots, acetonitrile, 20 °C) – Top: Quality of fit.

Table S5. Rate constants for the Reaction of **8**-BF_4 (2.48×10^{-5} M) with $n$$Bu_4N^+SCN^-$ by Laser Flash.

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$ / s^{-1}
lo19040201	7.41×10^{-4}	7.23 [a,b]
lo19040203	4.45×10^{-3} [c]	3.39×10^{5} [b,d]
lo19040204	5.93×10^{-3} [c]	3.75×10^{5} [b,d]
lo19040205	7.41×10^{-3} [c]	4.18×10^{5} [b,d]

[a] Only the slow reaction with nitrogen of SCN^- could be measured, $k_N = k_\psi/[SCN^-]_0 = 9.75 \times 10^3$ M^{-1} s^{-1} [b] Solutions are blue before irradiation. [c] Due to unfavorable equilibrium situation for sulfur attack, high concentrations of SCN^- have to be used in order to follow the fast decay. [d] Attack at sulfur of SCN^-.



k_S (20 °C) = 2.69×10^7 M^{-1} s^{-1}[a]

k_{-S} (20 °C) = 2.18×10^5 s^{-1}[a]

$r^2 = 0.9977$

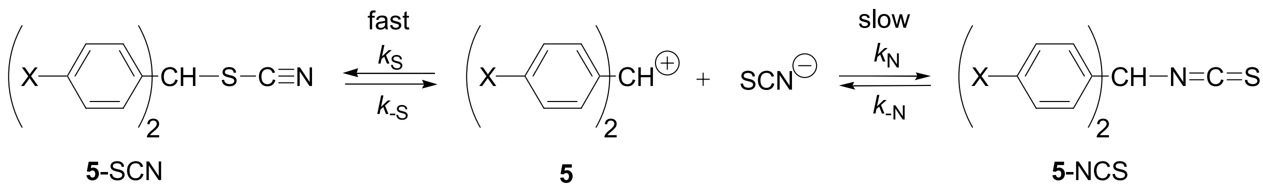
[a] Reliability of rate constants uncertain, because high concentrations (180–299 equiv.) of $n$$Bu_4N^+SCN^-$ have to be used to measure the fast decay of **8**. k_S also probably erroneous due to the curvature of the plot of $k_{1\Psi}/[SCN^-]_0$ observed in the reaction with **4**–**7** at high SCN^- concentrations. This may result in k_S values being too small for the reaction of **8** with sulfur of SCN^-.

Kinetic measurements by stopped-flow experiments

Formation of 5-NCS from 5 and SCN⁻ followed at 586 nm in acetonitrile at 20 °C

Because the formation of **5**-NCS was preceded by the reversible formation of considerable amounts of **5**-SCN during the mixing time of the stopped-flow apparatus (3 ms), the rate constants k_N and k_{-N} were derived from a numerical evaluation of the exponential decay of **5** based on the kinetic model in Scheme S1 using the software SPECFIT/32.[S1]

Scheme S1



The concentrations of **5**, **5**-SCN, and SCN^- after mixing were calculated as described on p S21 in the chapter "Equilibrium constants from stopped-flow experiments". The values for sulfur attack were taken as $k_S = 1.71 \times 10^8$ M^{-1} s^{-1} (obtained from the laser flash experiments, Table S2) and $k_{-S} = 3.36 \times 10^4$ M^{-1} s^{-1} (calculated from k_S and the equilibrium constant $K_S = 5110$ M^{-1} from Table S12). The numerical evaluation of the rate constants k_N and k_{-N} was then performed by least-squares fitting of the observed decays of the absorbances of **5** to the reaction model in Scheme S1.

Table S6. Rate Constants for the Reaction of **5**-BF_4 (1.37×10^{-5} M) with $n\mathrm{Bu_4N^+SCN^-}$ by Stopped-Flow.

Nr.	$[SCN^-]_0$ / M	k_N[a,b] / M^{-1} s^{-1}	k_{-N}[a,b] / s^{-1}
0907031b	4.02×10^{-5}	1.53×10^{5}	7.80×10^{-1}
0907032	8.04×10^{-5}	1.40×10^{5}	9.10×10^{-1}
0907032b	8.04×10^{-5}	1.57×10^{5}	7.59×10^{-1}
0907033	1.61×10^{-4}	1.52×10^{5}	9.88×10^{-1}
0907033b	1.61×10^{-4}	1.56×10^{5}	6.40×10^{-1}
0907034	2.41×10^{-4}	1.48×10^{5}	7.44×10^{-1}
0907035	3.22×10^{-4}	1.53×10^{5}	7.59×10^{-1}
0907036	4.02×10^{-4}	1.50×10^{5}	6.95×10^{-1}
0907037	6.03×10^{-4}	1.48×10^{5}	5.53×10^{-1}

[a] k_N and k_{-N} from numerical evaluation with the software Specfit/32, see above. [b] Attack at nitrogen of SCN^-.

k_N (20 °C) = $(1.51 \pm 0.04) \times 10^{5}$ M^{-1} s^{-1}

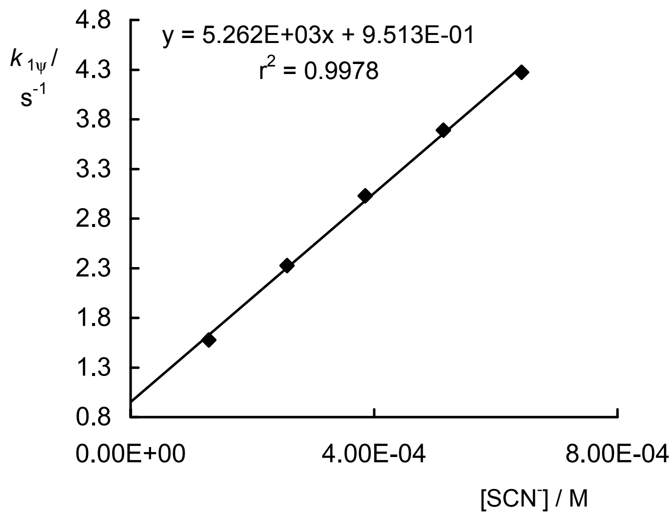
k_{-N} (20 °C) = $(7.59 \pm 1.17) \times 10^{-1}$ s^{-1}

Formation of 7-NCS from 7 and SCN^- followed at 620 nm in acetonitrile at 20 °C

Table S7. Rate Constants for the Reaction of **7**-BF_4 (1.47×10^{-5} M) with $n$$Bu_4N^+SCN^-$ by Stopped-Flow.[a]

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$[b] / s^{-1}
lo30070201	1.28×10^{-4}	1.58
lo30070202	2.57×10^{-4}	2.33
lo30070203	3.85×10^{-4}	3.03
lo30070204	5.14×10^{-4}	3.69
lo30070205	6.42×10^{-4}	4.27

[a] Reaction followed at 620 nm instead of λ_{max}. [b] Attack at nitrogen of SCN^-.



k_N (20 °C) = 5.26×10^3 M^{-1} s^{-1}

k_{-N} (20 °C) = 9.51×10^{-1} s^{-1}

$r^2 = 0.9978$

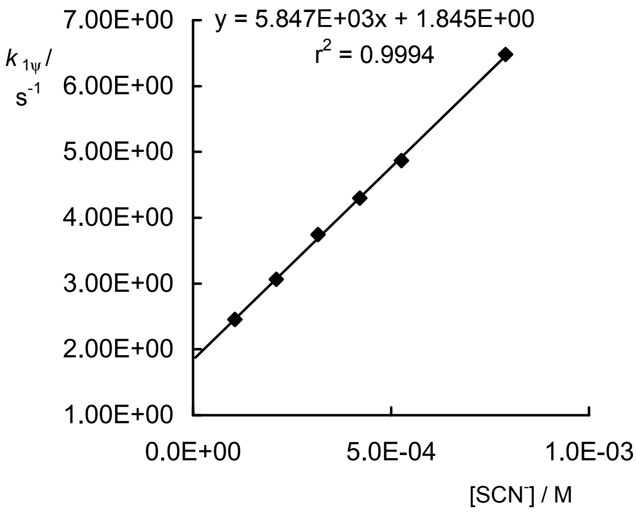
$K_N = k_N/k_{-N} = 5.53 \times 10^3$ M^{-1}

Formation of 8-NCS from 8 and SCN⁻ followed at 622 nm in acetonitrile at 20 °C

Table S8. Rate Constants for the Reaction of **8**-BF_4 (1.44×10^{-5} M) with $n$$Bu_4N^+SCN^-$ by Stopped-Flow.[a]

Nr.	$[SCN^-]_0$ / M	$k_{1\Psi}$[b]/ s^{-1}
lo26070201	1.05×10^{-4}	2.46
lo26070202	2.10×10^{-4}	3.07
lo26070203	3.16×10^{-4}	3.74
lo26070204	4.21×10^{-4}	4.30
lo26070205	5.26×10^{-4}	4.87
lo26070206	7.89×10^{-4}	6.48

[a] Reaction followed at 622 nm instead of λ_{max}. [b] Attack at nitrogen of SCN^-.



k_N (20 °C) = 5.85×10^3 M^{-1} s^{-1}

k_{-N} (20 °C) = 1.85 s^{-1}

r^2 = 0.9994

$K_N = k_N/k_{-N} = 3.17 \times 10^3$ M^{-1}

Equilibrium measurements

Equilibrium constants from laser flash experiments

The laser flash experiments allow one to calculate the equilibrium constants K_S for the fast and reversible attack of the sulfur of SCN^- at the benzhydryl cations **5**–**7** from the initial fast decay of the absorbance of the benzhydryl cations leading to an equilibrium. This reaction is followed by the much slower reaction at the nitrogen of SCN^- leading to complete decolorization. From the known molar absorption coefficients ε of **5**–**7** in acetonitrile and the width of the cell (1 cm), the concentration of the cation produced by irradiation with the laser $[Ar_2CH^+]_0$ was calculated according to eq. 2.

$$[Ar_2CH^+]_0 = A_0 / (d\ \varepsilon) \qquad (2)$$

From the absorbance A_{eq} at equilibrium, the concentration of the cation at equilibrium, $[Ar_2CH^+]_{eq}$, can be calculated by eq (3). Mass balance yields the concentration $[SCN^-]_{eq}$ according to eq. 4.

$$[Ar_2CH^+]_{eq} = (A_{eq}/A_0)\ [Ar_2CH^+]_0 \qquad (3)$$

$$[SCN^-]_{eq} = [SCN^-]_0 - ([Ar_2CH\text{-}SCN]_{eq} + [Ar_2CH\text{-}NCS]_{eq}) =$$

$$= [SCN^-]_0 - ([Ar_2CH^+BF_4^-]_0 - [Ar_2CH^+]_{eq}) \qquad (4)$$

The concentration of Ar_2CH-SCN at equilibrium can be derived from eq (5).

$$[Ar_2CH\text{-}SCN]_{eq} = [Ar_2CH^+]_0 - [Ar_2CH^+]_{eq} \qquad (5)$$

$[Ar_2CH^+BF_4^-]_0$ concentration of benzhydrylium tetrafluoroborate introduced.

$[SCN^-]_0$ starting concentration of $n Bu_4^+SCN^-$.

$[Ar_2CH^+]_0$ concentration of the benzhydrylium ion produced by the laser pulse from $[Ar_2CH\text{-}NCS]$.

$[Ar_2CH^+]_{eq}$ concentration of the benzhydrylium ion after formation of Ar_2CH-SCN reached equilibrium.

$[Ar_2CH\text{-}SCN]_{eq}$ equilibrium concentration of benzhydrylium thiocyanate.

$[Ar_2CH\text{-}NCS]_{eq}$ equilibrium concentration of benzhydrylium isothiocyanate.

Because the equilibrium constants K_S = $[Ar_2CH\text{-}SCN]_{eq}$ / ($[Ar_2CH^+]_{eq}$ $[SCN^-]_{eq}$) derived from laser flash experiments could not be obtained under rigorously anhydrous conditions, partial hydrolysis of **5**–**7** with formation of the corresponding benzhydrols cannot be excluded. Furthermore, partial destruction of the benzhydrylium systems may occur during the measurements, as discussed in the main article. Therefore, the K_S-values obtained in the laser flash experiments are considered to be less accurate than those derived in the stopped-flow experiments (see below).

Table S9. Equilibrium Constant for the Formation of **5**-SCN from **5** with SCN^- in Acetonitrile (Laser Flash, λ = 586 nm, 20 °C).

Molar absorption coefficient ε of **5**-BF_4 in CH_3CN at 593nm: **159199 M^{-1} cm^{-1}** Cell width: **1 cm**

Number	$[Ar_2CH^+BF_4^-]_0$ initial / M	$[SCN^-]_0$ initial / M	A_0 after laser pulse	$[Ar_2CH^+]_0$ after laser pulse	quantum yield / %	A_{eq}	$[Ar_2CH\text{-}SCN]_{eq}$ / M	$[Ar_2CH^+]_{eq}$ / M	$[SCN^-]_{eq}$ / M	K_S / M^{-1}
28030201_1	4.23E-05	4.00E-03	0.40	2.51E-06	5.94%	0.027069	2.343E-06	1.700E-07	3.958E-03	3.481E+03
28030201_2	4.23E-05	4.00E-03	0.55	3.45E-06	8.17%	0.051949	3.128E-06	3.263E-07	3.958E-03	2.422E+03
28030201_3	4.23E-05	4.00E-03	0.45	2.83E-06	6.68%	0.049087	2.518E-06	3.083E-07	3.958E-03	2.064E+03
28030201_4	4.23E-05	4.00E-03	0.50	3.14E-06	7.42%	0.046615	2.848E-06	2.928E-07	3.958E-03	2.457E+03
28030201_5	4.23E-05	4.00E-03	0.50	3.14E-06	7.42%	0.044606	2.861E-06	2.802E-07	3.958E-03	2.579E+03
28030202_2	4.23E-05	7.23E-04	0.52	3.27E-06	7.72%	0.181120	2.129E-06	1.138E-06	6.818E-04	2.744E+03
28030202_3	4.23E-05	7.23E-04	0.43	2.70E-06	6.39%	0.150260	1.757E-06	9.439E-07	6.816E-04	2.731E+03
28030202_4	4.23E-05	7.23E-04	0.31	1.95E-06	4.60%	0.111130	1.249E-06	6.981E-07	6.814E-04	2.626E+03
28030202_5	4.23E-05	7.23E-04	0.32	2.01E-06	4.75%	0.146620	1.089E-06	9.210E-07	6.816E-04	1.735E+03
28030202_6	4.23E-05	7.23E-04	0.40	2.51E-06	5.94%	0.136960	1.652E-06	8.603E-07	6.816E-04	2.818E+03
28030203_1	4.23E-05	1.81E-03	0.31	1.95E-06	4.60%	0.056966	1.589E-06	3.578E-07	1.768E-03	2.512E+03
28030203_2	4.23E-05	1.81E-03	0.39	2.45E-06	5.79%	0.069906	2.011E-06	4.391E-07	1.768E-03	2.590E+03
28030203_3	4.23E-05	1.81E-03	0.37	2.32E-06	5.49%	0.065328	1.914E-06	4.104E-07	1.768E-03	2.638E+03
28030203_4	4.23E-05	1.81E-03	0.37	2.32E-06	5.49%	0.070677	1.880E-06	4.440E-07	1.768E-03	2.395E+03
28030203_5	4.23E-05	1.81E-03	0.35	2.20E-06	5.20%	0.068234	1.770E-06	4.286E-07	1.768E-03	2.335E+03
28030203_6	4.23E-05	1.81E-03	0.33	2.07E-06	4.90%	0.063260	1.676E-06	3.974E-07	1.768E-03	2.385E+03
28030204_1	4.23E-05	3.62E-03	0.34	2.14E-06	5.05%	0.036028	1.909E-06	2.263E-07	3.578E-03	2.358E+03
28030204_2	4.23E-05	3.62E-03	0.40	2.51E-06	5.94%	0.045019	2.230E-06	2.828E-07	3.578E-03	2.204E+03
28030204_3	4.23E-05	3.62E-03	0.47	2.95E-06	6.98%	0.050364	2.636E-06	3.164E-07	3.578E-03	2.329E+03
28030204_4	4.23E-05	3.62E-03	0.40	2.51E-06	5.94%	0.033788	2.300E-06	2.122E-07	3.578E-03	3.029E+03
28030204_5	4.23E-05	3.62E-03	0.40	2.51E-06	5.94%	0.036530	2.283E-06	2.295E-07	3.578E-03	2.781E+03
28030204_6	4.23E-05	3.62E-03	0.48	3.02E-06	7.13%	0.051949	2.689E-06	3.263E-07	3.578E-03	2.303E+03
28030205_1	4.23E-05	5.43E-03	0.37	2.32E-06	5.49%	0.030092	2.135E-06	1.890E-07	5.388E-03	2.096E+03
28030205_2	4.23E-05	5.43E-03	0.44	2.76E-06	6.53%	0.036798	2.533E-06	2.311E-07	5.388E-03	2.034E+03
28030205_3	4.23E-05	5.43E-03	0.40	2.51E-06	5.94%	0.032804	2.307E-06	2.061E-07	5.388E-03	2.078E+03
28030205_4	4.23E-05	5.43E-03	0.50	3.14E-06	7.42%	0.036224	2.913E-06	2.275E-07	5.388E-03	2.376E+03
28030205_5	4.23E-05	5.43E-03	0.38	2.39E-06	5.64%	0.025828	2.225E-06	1.622E-07	5.388E-03	2.545E+03
28030205_6	4.23E-05	5.43E-03	0.40	2.51E-06	5.94%	0.039566	2.26E-06	2.49E-07	5.388E-03	1.691E+03

Average K_S over all laser-pulses: **2.441E+03 ± 3.65E+02** M^{-1}

$K_S(20\ °C) = (2.44 \pm 0.37) \times 10^3\ M^{-1}$

Table S10. Equilibrium Constant for the Formation of **6**-SCN from **6** with SCN^- in Acetonitrile (Laser Flash, λ = 645 nm, 20 °C).

Molar absorption coefficient ε of **6**-BF_4 in CH_3CN at 645nm: **91080 M^{-1} cm^{-1}** Cell width: **1 cm**

Number	$[Ar_2CH^+BF_4^-]_0$ initial / M	$[SCN^-]_0$ initial / M	A_0 after laser pulse	$[Ar_2CH^+]_0$ after laser pulse	quantum yield / %	A_{eq}	$[Ar_2CH\text{-}SCN]_{eq}$ / M	$[Ar_2CH^+]_{eq}$ / M	$[SCN^-]_{eq}$ / M	K_S / M^{-1}
03040201_1	6.40E-05	8.18E-05	0.86	9.44E-06	14.75%	0.514420	3.794E-06	5.648E-06	2.345E-05	2.865E+04
03040201_2	6.40E-05	8.18E-05	0.96	1.05E-05	16.47%	0.584040	4.128E-06	6.412E-06	2.421E-05	2.659E+04
03040201_3	6.40E-05	8.18E-05	0.90	9.88E-06	15.44%	0.575990	3.557E-06	6.324E-06	2.412E-05	2.332E+04
03040201_4	6.40E-05	8.18E-05	0.84	9.22E-06	14.41%	0.544800	3.241E-06	5.982E-06	2.378E-05	2.278E+04
03040201_5	6.40E-05	8.18E-05	0.92	1.01E-05	15.78%	0.598280	3.532E-06	6.569E-06	2.437E-05	2.207E+04
03040201_6	6.40E-05	8.18E-05	0.94	1.03E-05	16.13%	0.586390	3.882E-06	6.438E-06	2.424E-05	2.488E+04
03040202_1	3.20E-05	2.05E-04	1.00	1.10E-05	34.31%	0.163840	9.181E-06	1.799E-06	1.748E-04	2.920E+04
03040202_2	3.20E-05	2.05E-04	1.03	1.13E-05	35.34%	0.173130	9.408E-06	1.901E-06	1.749E-04	2.830E+04
03040202_3	3.20E-05	2.05E-04	1.00	1.10E-05	34.31%	0.162810	9.192E-06	1.788E-06	1.748E-04	2.942E+04
03040202_4	3.20E-05	2.05E-04	1.22	1.34E-05	41.86%	0.182930	1.139E-05	2.008E-06	1.750E-04	3.239E+04
03040202_5	3.20E-05	2.05E-04	1.00	1.10E-05	34.31%	0.166200	9.155E-06	1.825E-06	1.748E-04	2.870E+04
03040202_6	3.20E-05	2.05E-04	1.04	1.14E-05	35.68%	0.173080	9.518E-06	1.900E-06	1.749E-04	2.864E+04
03040203_1	3.20E-05	4.09E-04	0.98	1.08E-05	33.62%	0.081662	9.863E-06	8.966E-07	3.779E-04	2.911E+04
03040203_2	3.20E-05	4.09E-04	1.00	1.10E-05	34.31%	0.083604	1.006E-05	9.179E-07	3.779E-04	2.900E+04
03040203_3	3.20E-05	4.09E-04	1.00	1.10E-05	34.31%	0.082427	1.007E-05	9.050E-07	3.779E-04	2.946E+04
03040203_4	3.20E-05	4.09E-04	1.03	1.13E-05	35.34%	0.086098	1.036E-05	9.453E-07	3.779E-04	2.901E+04
03040203_5	3.20E-05	4.09E-04	1.00	1.10E-05	34.31%	0.088604	1.001E-05	9.728E-07	3.780E-04	2.721E+04
03040203_6	3.20E-05	4.09E-04	1.00	1.10E-05	34.31%	0.087606	1.002E-05	9.619E-07	3.780E-04	2.756E+04

Average *K* over all laser-pulses: **2.757E+04 ± 2.62E+03 M^{-1}**

K_S (20 °C) = $(2.76 \pm 0.26) \times 10^4$ M^{-1}

Table S11. Equilibrium Constant for the Formation of **7**-SCN from **7** with SCN^- in Acetonitrile; only Experiments at higher SCN^- Concentration used, where Initial Solutions were almost Colorless (Laser Flash, λ = 612 nm, 20 °C).

Molar absorption coefficient ε of **7**-BF_4 in CH_3CN at 612nm: **104075 M^{-1} cm^{-1}** Cell width: **1 cm**

Number	$[Ar_2CH^+BF_4^-]_0$ initial / M	$[SCN^-]_0$ initial / M	A_0 after laser pulse	$[Ar_2CH^+]_0$ after laser pulse	quantum yield / %	A_{eq}	$[Ar_2CH\text{-}SCN]_{eq}$ / M	$[Ar_2CH^+]_{eq}$ / M	$[SCN^-]_{eq}$ / M	K_S / M^{-1}
2040203_1	5.03E-05	1.64E-03	0.73	7.01E-06	13.94%	0.549420	1.735E-06	5.279E-06	1.595E-03	2.061E+02
2040203_2	5.03E-05	1.64E-03	0.69	6.63E-06	13.18%	0.512390	1.707E-06	4.923E-06	1.595E-03	2.174E+02
2040203_3	5.03E-05	1.64E-03	0.68	6.53E-06	12.99%	0.504570	1.686E-06	4.848E-06	1.595E-03	2.180E+02
2040203_4	5.03E-05	1.64E-03	0.72	6.92E-06	13.75%	0.560400	1.534E-06	5.385E-06	1.595E-03	1.785E+02
2040203_5	5.03E-05	1.64E-03	0.70	6.73E-06	13.37%	0.537650	1.560E-06	5.166E-06	1.595E-03	1.893E+02
2040203_6	5.03E-05	1.64E-03	0.69	6.63E-06	13.18%	0.523950	1.595E-06	5.034E-06	1.595E-03	1.987E+02
2040204_1	5.03E-05	2.46E-03	0.65	6.25E-06	12.42%	0.469190	1.737E-06	4.508E-06	2.414E-03	1.596E+02
2040204_2	5.03E-05	2.46E-03	0.68	6.53E-06	12.99%	0.485280	1.871E-06	4.663E-06	2.414E-03	1.662E+02
2040204_3	5.03E-05	2.46E-03	0.71	6.82E-06	13.56%	0.474190	2.266E-06	4.556E-06	2.414E-03	2.060E+02
2040204_4	5.03E-05	2.46E-03	0.68	6.53E-06	12.99%	0.440260	2.304E-06	4.230E-06	2.414E-03	2.256E+02
2040204_5	5.03E-05	2.46E-03	0.72	6.92E-06	13.75%	0.450170	2.593E-06	4.325E-06	2.414E-03	2.483E+02
2040204_6	5.03E-05	2.46E-03	0.76	7.30E-06	14.52%	0.446460	3.013E-06	4.290E-06	2.414E-03	2.909E+02
2040205_1	5.03E-05	3.27E-03	0.72	6.92E-06	13.75%	0.419150	2.891E-06	4.027E-06	3.224E-03	2.226E+02
2040205_2	5.03E-05	3.27E-03	0.73	7.01E-06	13.94%	0.413950	3.037E-06	3.977E-06	3.224E-03	2.368E+02
2040205_3	5.03E-05	3.27E-03	0.71	6.82E-06	13.56%	0.428190	2.708E-06	4.114E-06	3.224E-03	2.042E+02
2040205_4	5.03E-05	3.27E-03	0.70	6.73E-06	13.37%	0.419170	2.698E-06	4.028E-06	3.224E-03	2.078E+02
2040205_5	5.03E-05	3.27E-03	0.70	6.73E-06	13.37%	0.391200	2.967E-06	3.759E-06	3.223E-03	2.449E+02
2040205_6	5.03E-05	3.27E-03	0.70	6.73E-06	13.37%	0.429190	2.602E-06	4.124E-06	3.224E-03	1.957E+02
2040206_1	5.03E-05	4.09E-03	0.70	6.73E-06	13.37%	0.419650	2.694E-06	4.032E-06	4.044E-03	1.652E+02
2040206_2	5.03E-05	4.09E-03	0.67	6.44E-06	12.80%	0.460820	2.010E-06	4.428E-06	4.044E-03	1.122E+02
2040206_3	5.03E-05	4.09E-03	0.71	6.82E-06	13.56%	0.401380	2.965E-06	3.857E-06	4.044E-03	1.902E+02
2040206_4	5.03E-05	4.09E-03	0.69	6.63E-06	13.18%	0.433200	2.467E-06	4.162E-06	4.044E-03	1.466E+02
2040206_5	5.03E-05	4.09E-03	0.66	6.34E-06	12.61%	0.414380	2.360E-06	3.982E-06	4.044E-03	1.466E+02
2040206_6	5.03E-05	4.09E-03	0.66	6.34E-06	12.61%	0.407680	2.424E-06	3.917E-06	4.044E-03	1.531E+02

Average K_S over all laser-pulses: **1.971E+02 ± 3.87E+01** M^{-1}

K_S (20 °C) = $(1.97 \pm 0.39) \times 10^2$ M^{-1}

Equilibrium constants from stopped-flow experiments

The equilibrium constant K_S for the attack of sulfur of SCN^- at **5** can be calculated from stopped-flow experiments. During the mixing time of the stopped-flow instrument (3 ms) the rapid reaction of **5** with the sulfur of SCN^- reaches equilibrium, even before the stopped-flow instrument starts recording the absorbances. Thus A_0 is defined as the absorbance of a acetonitrile solution of **5**-BF_4 when mixed with an equal volume of pure acetonitrile. A_{eq} is the first recorded absorbance after mixing equal volumes of acetonitrile solutions of **5**-BF_4 and $n$$Bu_4N^+SCN^-$. The equilibrium constant K_S can then be derived from eq. 6 and eq. 7.

$$K_S = [Ar_2CH\text{-}SCN]_{eq} / ([Ar_2CH^+]_{eq} [SCN^-]_{eq}) =$$

$$= ([Ar_2CH^+BF_4^-]_0 - [Ar_2CH^+]_{eq}) / ([Ar_2CH^+]_{eq} ([SCN^-]_0 - [Ar_2CH^+BF_4^-]_0 + [Ar_2CH^+]_{eq})) \quad (6)$$

By substituting $[Ar_2CH^+]_{eq}$ with $(A_{eq}/A_0)[Ar_2CH^+BF_4^-]_0$ one obtains

$$K_S = (1 - A_{eq}/A_0) / (A_{eq}/A_0 ([SCN^-]_0 - (1 - A_{eq}/A_0) [Ar_2CH^+BF_4^-]_0)) \quad (7)$$

$[Ar_2CH^+BF_4^-]_0$ concentration of benzhydrylium tetrafluoroborate introduced.

$[SCN^-]_0$ starting concentration of $n$$Bu_4^+SCN^-$.

$[Ar_2CH^+]_{eq}$ concentration of the benzhydrylium ion after formation of Ar_2CH-SCN reached equilibrium (first recorded absorbance of the stopped-flow instrument).

$[Ar_2CH\text{-}SCN]_{eq}$ equilibrium concentration of benzhydrylium thiocyanate.

Table S12. Equilibrium Constant for the Formation of **5**-SCN from **5**-BF_4 with $n$$NBu_4^+SCN^-$ in Acetonitrile (Stopped-Flow, λ = 586 nm, 20 °C).

Nr.	$[Ar_2CH^+BF_4^-]_0$ / M	$[SCN^-]_0$ / M	A_0	A_{eq}	$[Ar_2CH^+]_{eq}$ / M	K_S / M^{-1}
0907031b	1.37×10^{-5}	4.02×10^{-5}	2.05	1.74	1.16×10^{-5}	4.67×10^{3}
0907032	1.37×10^{-5}	8.04×10^{-5}	2.05	1.52	1.01×10^{-5}	4.54×10^{3}
0907032b	1.37×10^{-5}	8.04×10^{-5}	2.05	1.48	9.87×10^{-6}	5.03×10^{3}
0907033	1.37×10^{-5}	1.61×10^{-4}	2.05	1.14	7.60×10^{-6}	5.16×10^{3}
0907033b	1.37×10^{-5}	1.61×10^{-4}	2.05	1.13	7.54×10^{-6}	5.27×10^{3}
0907034	1.37×10^{-5}	2.41×10^{-4}	2.05	0.95	6.30×10^{-6}	5.00×10^{3}
0907035	1.37×10^{-5}	3.22×10^{-4}	2.05	0.78	5.17×10^{-6}	5.26×10^{3}
0907036	1.37×10^{-5}	4.02×10^{-4}	2.05	0.66	4.37×10^{-6}	5.42×10^{3}
0907037	1.37×10^{-5}	6.03×10^{-4}	2.05	0.48	3.17×10^{-6}	5.60×10^{3}

K_S (20 °C) = $(5.11 \pm 0.32) \times 10^{3}$ M^{-1}

Equilibrium constants from conventional UV-vis experiments

For **7** and **8**, the equilibrium of the sulfur attack of SCN^- is far on the side of the ions and thus can be neglected. The equilibrium constants for the reaction with the nitrogen of SCN^- $K_N = [Ar_2CH\text{-}NCS]_{eq} / ([Ar_2CH^+]_{eq}\ [SCN^-]_{eq})$ in acetonitrile can be determined from the absorbance of Ar_2CH^+. In at least 3 separate experiments, the decrease of the absorbance of Ar_2CH^+ upon addition of various amounts of a $n\mathrm{Bu}_4N^+SCN^-$ solution was monitored at a J&M UV–vis diode array spectrometer. From the known concentrations $[Ar_2CH^+BF_4^-]_0$ and $[SCN^-]_0$, the equilibrium constant K_N can be calculated by eq. 8 and eq. 9.

$$K_N = [Ar_2CH\text{-}NCS]_{eq} / ([Ar_2CH^+]_{eq}\ [SCN^-]_{eq}) =$$

$$= ([Ar_2CH^+BF_4^-]_0 - [Ar_2CH^+]_{eq}) / ([Ar_2CH^+]_{eq}\ ([SCN^-]_0 - [Ar_2CH^+BF_4^-]_0 + [Ar_2CH^+]_{eq}) \qquad (8)$$

By substituting $[Ar_2CH^+]_{eq}$ with $(A_{eq}/A_0)[Ar_2CH^+BF_4^-]_0$ one obtains:

$$K_N = (1 - A_{eq}/A_0) / (A_{eq}/A_0\ ([SCN^-]_0 - (1 - A_{eq}/A_0)\ [Ar_2CH^+BF_4^-]_0)) \qquad (9)$$

$[Ar_2CH^+BF_4^-]_0$ concentration of benzhydrylium tetrafluoroborate introduced.

$[SCN^-]_0$ starting concentration of $n\mathrm{Bu}_4^+SCN^-$.

$[Ar_2CH^+]_{eq}$ concentration of the benzhydrylium ion after formation of Ar_2CH-NCS reached equilibrium.

$[Ar_2CH\text{-}NCS]_{eq}$ equilibrium concentration of the benzhydrylium isothiocyanate.

Table S13. Equilibrium Constant for the Formation of **7**-NCS from **7**-BF_4 with $n$$Bu_4N^+SCN^-$ in Acetonitrile (UV-vis Spectrometer, λ = 613 nm, 20 °C).

Nr.	$[Ar_2CH^+]_0$ / M	$[SCN^-]_0$ / M	A_0	A_{eq}	$[Ar_2CH^+]_{eq}$ / M	K_N[a] / M^{-1}
03040302a	2.12×10^{-5}	5.26×10^{-5}	1.18	0.82	1.47×10^{-5}	9.53×10^{3}
03040302b	2.10×10^{-5}	1.31×10^{-4}	1.18	0.54	9.72×10^{-6}	9.76×10^{3}
03040303	2.08×10^{-5}	2.58×10^{-4}	1.18	0.35	6.27×10^{-6}	9.50×10^{3}
03040304a	2.11×10^{-5}	1.31×10^{-4}	1.18	0.54	9.77×10^{-6}	9.69×10^{3}
03040304b	2.09×10^{-5}	2.60×10^{-4}	1.18	0.35	6.31×10^{-6}	9.45×10^{3}
03040305a	2.11×10^{-5}	1.31×10^{-4}	1.18	0.54	9.77×10^{-6}	9.70×10^{3}
03040305b	2.09×10^{-5}	2.60×10^{-4}	1.18	0.35	6.31×10^{-6}	9.44×10^{3}

[a] The values of K_N were calculated with more decimals of $[Ar_2CH^+]_0$, $[SCN^-]_0$, A_0 and A_{eq} than those indicated in this table. The use of the values of this table leads to slightly different values of K_N.

K_N (20 °C) = $(9.58 \pm 0.12) \times 10^3$ M^{-1}

Table S14. Equilibrium Constant for the Formation of **8**-NCS from **8**-BF_4 with $n$$Bu_4N^+SCN^-$ in Acetonitrile (UV-vis Spectrometer, λ = 613 nm, 20 °C).

Nr.	$[Ar_2CH^+]_0$ / M	$[SCN^-]_0$ / M	A_0	A_{eq}	$[Ar_2CH^+]_{eq}$ / M	K_N[a] / M^{-1}
1302032a	2.60×10^{-5}	1.07×10^{-4}	1.42	1.02	1.88×10^{-5}	3.82×10^{3}
1302032b	2.58×10^{-5}	2.12×10^{-4}	1.42	0.79	1.46×10^{-5}	3.80×10^{3}
1302033a	2.62×10^{-5}	2.70×10^{-4}	1.45	0.72	1.34×10^{-5}	3.76×10^{3}
1302033b	2.57×10^{-5}	5.29×10^{-4}	1.45	0.49	9.03×10^{-6}	3.61×10^{3}
1302034a	2.61×10^{-5}	2.69×10^{-4}	1.46	0.73	1.33×10^{-5}	3.77×10^{3}
1302034b	2.56×10^{-5}	5.27×10^{-4}	1.46	0.49	9.02×10^{-6}	3.61×10^{3}
1302035	2.57×10^{-5}	5.29×10^{-4}	1.48	0.50	9.11×10^{-6}	3.56×10^{3}

[a] The values of K_N were calculated with more decimals of $[Ar_2CH^+]_0$, $[SCN^-]_0$, A_0 and A_{eq} than those indicated in this table. The use of the values of this table leads to slightly different values of K_N.

K_N (20 °C) = $(3.70 \pm 0.10) \times 10^3$ M^{-1}

Analysis of bond lengths of SCN^-, Thiocyanates and Isothiocyanates

Table S15. Bond Lengths in pm of Organic Isothiocyanates C(sp^3)–N=C=S from Crystallographic Data (Search on the 13th March 2003 at the Cambridge Crystallographic Data Centre with the Limitation $R <$ 0.1).

CCD-number	C(sp^3)–N / pm	N=C / pm	C=S / pm	*R*-factor / %
YEKFEZ	144.5	116.8	155.6	4.00
XIGBOE	144.2	110.1	156.9	7.21
WIPFAC	141.5	110.6	154.2	5.05
VEDTIH	146.2	117.6	155.1	6.30
SARCIX	141.5	114.8	156.6	8.50
	(148.0)[a]	(107.3)[a]	(165.9)[a]	(8.50)[a]
NUYPOM	142.5	116.2	156.6	5.56
	146.0	115.2	154.7	5.56
JOYDEG	145.5	114.1	157.2	3.60
JAJVUL	144.8	112.5	157.3	8.40
FEHBEZ	143.0	115.3	158.6	6.10
CUQSIQ	145.7	114.8	157.5	3.53

[a] Values ignored due to obvious large deviations.

Averaged values: S=C: 156.4 ± 1.3 pm

C=N: 114.4 ± 2.3 pm

N–C(sp^3): 144.1 ± 1.7 pm

Table S16. Bond lengths in pm of Organic Thiocyanates C(sp^3)–S–C≡N from Crystallographic Data (search on the 13th March 2003 at the Cambridge Crystallographic Data Centre with the Limitation R < 0.1).

CCD-number	C(sp^3)–S	S–C≡	–C≡N	R-factor (%)
YACCAG	180.6	168.1	113.7	2.80
	183.2	170.5	112.3	2.80
UBIWOR	187.4	166.4	114.9	8.10
	187.4	166.4	114.9	8.10
TCYPRE	182.3	167.0	113.7	9.00
	181.2	160.1	119.4	9.00
TCNPNA	183.4	166.8	115.2	6.10
SARCET	185.3	164.5	116.5	8.70
PAGHIO	184.0	168.4	114.0	3.20
MEDTCN	180.8	167.6	119.4	7.30
LINPAZ	181.6	168.4	114.3	3.73
	181.8	167.0	116.0	3.73
KECSAM	181.5	168.1	112.9	5.20
KAVQUT	185.7	168.8	114.5	3.81
JUFLIF	184.5	169.1	114.6	5.20
GIMTUR	184.5	169.2	114.7	3.06
	184.7	168.8	115.3	3.06
GIMTOL	185.1	169.3	115.6	2.64
FEPWOM	183.5	169.3	114.6	4.00
FAGFUO	180.9	168.2	113.9	3.90
ETTHCY	179.7	162.5	117.9	4.70
DEHPAH	184.0	169.3	113.1	3.49
CIGGII	182.2	168.0	113.8	3.90
CASSAQ	181.6	164.6	116.9	6.20

Averaged values: S–C: 167.4 ± 2.3 pm

–C≡N: 115.0 ± 1.9 pm

C(sp^3)–S: 183.3 ± 2.3 pm

Because of the large number of hits for ionic thiocyanates in the Cambridge Crystallographic Data Centre, where coordination to transition metal centers can often not be excluded, we have selected crystal structures of alkali and ammonium thiocyanates as representatives of ionic thiocyanates.

Table S17. Bond Lengths of "Free" Thiocyanate Anions S–C≡N$^-$ from Crystallographic Data.

Compound	S–C	C≡N	R-Faktor (%)	reference
$NH_4^+SCN^-$	1.649	1.172	2.0	S2[a]
Na^+SCN^-	1.643	1.170	3.4	S3[b]
N,*N*-Dimethylpyrrolidinium thiocyanate	1.645	1.165	6.41	S4
$NMe_4^+SCN^- \cdot SO_2$	1.654	1.154	5.89	S5
Dihydrothiocyanate salt of 1,4,8,11-tetraazacyclotetradecane	1.607	1.145	7.10	S6
Hydrothiocyanate salt of racemic (6*RS*,7*RS*)-4-dimethylamino-6,7-diphenyl-bicyclo[2.2.2]octan-2-one	1.630	1.160	5.48	S7

[a] Values of conventional X-ray analysis taken. [b] Values of conventional X-ray analysis at 150 K taken.

Averaged values: S–C: 163.8 ± 1.6 pm

–C≡N: 116.1 ± 0.9 pm

References

(S1) SPECFIT/32 3.0 by Spectrum Software Associates is a software for analysis and simulation of complex reaction sequences.

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