Supporting Information for

Uncaging Carbon Disulfide. Delivery Platforms for Potential Pharmacological Applications: A Mechanistic Approach.

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Contents:

Experimental descriptions of substrate syntheses:

Note: *Carbon disulfide is toxic at high exposures, and long periods of modest exposure have been associated with a number of health conditions. Handle and store CS_2 and CS_2-generating compounds with care.*

Materials and Analytical Instrumentation: Except where noted, starting materials were used without further purification. Diisopropylamine (≥99.5%), imidazole (≥99%), ammonium pyrrolidinyldithiocarbamate (~99%), pyrrole (98%), calcium hydride, potassium metal and potassium bromide (FT-IR grade) were purchased from Sigma Aldrich. Carbon disulfide (ACS Reagent Grade, ≥99.9%), morpholine (Alfa Aesar, 99%), potassium hydroxide, and sodium hydroxide were purchased from Fisher Scientific. Pyrrole (98%) was purchased from Sigma and distillated before use under reduced pressure in the presence of calcium hydride (Sigma) as reported in literature.[1] HPLC grade methanol, dichloromethane, acetone, and chloroform were from VWR, acetonitrile was from Fisher Scientific, and absolute ethanol was from Rossville. Nanopure water (≥18 megohm) was obtained from a Barnstead Nanopure II system and used in all syntheses. Dry DMF in a Sure-seal bottle was purchased from Sigma-Aldrich.

Electronic absorption spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Infrared spectra in KBr pellets were recorded with a Bio-Rad FTS-60 SPC3200 FTIR spectrophotometer, while IR spectra in solutions and solid powders were recorded with a Bruker ALPHA Platinum ATR FTIR with a single reflection diamond. NMR spectra were obtained on a Varian 500 MHz spectrometer in deuterated solvents from Cambridge Isotope Laboratories, Inc. Mass spectrometry for charged species was conducted on a Waters Micromass QTOF2 mass spectrometer with an electrospray ionization source (ESI, negative mode). Elemental analyses (C,H,N) were conducted at the UCSB MSI Analytical Lab with a thermal conductivity method using a Control Equipment Corporation 440HA Elemental Analyzer.

Syntheses of Dithiocarbamates (DTCs). *Sodium and potassium diisopropylammonium diisopropyldithiocarbamate:* The sodium salt Na[DIDTC] was prepared by a modification of a published procedure.[2] A round bottom flask was charged with 30 mL of Et_2O and 10 mL of CS_2, cooled to 0 – 5 °C with an ice bath and purged with inert gas. With rapid stirring, finely ground NaOH (1.0 g, 25 mmol) was added to a flask. Sufficient water was added to solubilize the hydroxide (~ 2 mL). To this solution, 5 mL diisopropylamine (3.61 g, 35.7 mmol) was added over a two min. period, during which the solution rapidly became light yellow and cloudy. This mixture was stirred for an additional 1 h after which the solid product was collected by filtration and washed with cold Et_2O. The product was recrystallized from a saturated acetonitrile/methanolic solution by slow diffusion of Et_2O and dried *in vacuo*. The typical yield was 75-89%. The compounds were stored in a freezer. Elemental analysis (calculated for $C_7H_{14}NS_2Na \cdot 2.5\ H_2O$): C, 33.8 (34.41); H, 7.46 (7.84); N, 5.61 (5.73). (~2.5 waters were present in the crystal lattice according to thermal gravimetric analysis (TGA), others have reported as high as 5 H_2O's).[2,3] UV/Vis spectrum λ_{max} 261 (ε = 1.15 x $10^4\ M^{-1}\,cm^{-1}$) and 286 nm (ε = 1.1 x $10^4\ M^{-1}\,cm^{-1}$) in pH 7.4 deoxygenated water. Infrared spectrum (ATR, cm^{-1}): 3300 (*v*, O–H), 2920, 2968 (*v*, C–H), 1615-1700 (δ, O–H), 1470 (*v*, C–N), 1356, 1431 (*v*, CH_3), 1294 (*v*, N–C), 1137 (*ρ*, CH_3), 941 (*v*, C–S). ^{1}HNMR (CD_3OD): *δ* 6.25 (*broad*, singlet, 1H), 3.86 (*broad*, singlet, 1H), 1.70 (*broad*, singlet, 6H), 1.21 (*broad*, singlet, 6H).

The diisopropylammonium salt [$^i Pr_2H_2N$][DIDTC] was prepared in a similar manner. A round bottom flask in an ice bath (0 – 5 °C) was charged with 30 mL of Et_2O and purged with a gentle flow of argon. To the flask was added 10 mL of CS_2 (166 mmol) and then 5 mL of diisopropylamine (35.7 mmol). The solution was allowed to react for 2 h, producing a pale-yellow precipitate that was collected by filtration and washed with cold Et_2O. The yield was 56%. Crystals suitable for x-ray diffraction studies were obtained by infusion of Et_2O into an carbon disulfide/acetonitrile (1:4)

solution of this compound at −20 °C. The volume of the unit cell and the crystallographic parameters were the same as those published previously.[4] Infrared spectrum (ATR, cm^{-1}): 2970 (ν(C-H), m); 2818 – 2429 (ν(N-H, quartenary amine), w); 1552 (δ(NH_2, quartenary amine), w); 1469 (ν(-N-C=S), m); 1432 (ν(-N=C-S-), m); 1391 and 1362 (ν(-C-CH_3), m); 1282 (ν(N-CS_2), s), 1197 and 1143 ((ν(C-N), s); 1028 (ν$(CS_2)_{asym}$, s); 944 (ν$(CS_2)_{sym}$, s); 903 – 786 (ν(C-S), m).[5-7] Elemental analysis: C, 55.92 (56.06); H, 11.04 (10.86); N, 10.05 (10.06).

The potassium salt, K[$(iPr)_2NCS_2$], was prepared from the diisopropylammonium salt [$^{i}Pr_2H_2N$][$(iPr)_2NCS_2$]. The diisopropylammonium salt (9.0 mmol) was solubilized in a THF solution of potassium tert-butoxide (*t*-butO^-K^+) (9.0 mmol) under argon atmosphere (glove box). The solution was stirred for more 30 min and then all the solution was dried under vacuum. The white solid obtained was stirred in Et_2O, filtered and washed with Et_2O. The yield was 61%. Crystals suitable for x-ray diffraction studies were obtained by infusion of Et_2O into an acetonitrile solution of the compound at –20 °C. The crystals were kept in solution until the X-ray analysis. When out of solution the crystals back to the original amorphous solid. Infrared spectrum (ATR, cm^{-1}): 3294 (ν(O-H), s); 2972 (ν(C-H), m); 1605 (δ(H_2O), m); 1476 (ν(-N-C=S), m); 1437 (ν(-N=C-S-), m); 1370 and 1358 (ν(-C-CH_3), m); 1299 (ν(N-CS_2), s), 1196 and 1142 ((ν(C-N), s); 1032 (ν$(CS_2)_{asym}$, s); 940 (ν$(CS_2)_{sym}$, s); 907 – 786 (ν(C-S), m).[5-7] ^{1}HNMR (CD_3CN): δ 6.48 (*broad*, singlet, 1H), 3.78 (*broad*, singlet, 1H), 1.70 (*broad*, singlet, 6H), 1.11 (*broad*, singlet, 6H). Elemental analysis (calculated for K[$(iPr)_2NCS_2$]·1/4H_2O): C, 38.32 (38.20); H, 6.22 (6.59); N, 6.29 (6.37).

Ammonium morpholinedithiocarbamate (NH_4[MorDTC]): The procedure was analogous to that used to prepare NH_4[AnDTC]. To an argon-purged flask, 5 mL morpholine (4.97 g, 57.0 mM) was added dropwise to an ice-cold mixture of prepared from 12 mL of 8 M ammonium hydroxide, 4 mL of CS_2 (5.06 g, 67 mM) and 10 mL of diethyl ether with stirring. The solution turned slightly yellow, and a white powder immediately began to precipitate. The vessel was allowed to return to room temperature over the course of 2-6 h. Addition of 5-10 mL of Et_2O precipitated the product further. The solid was collected by filtration, washed with cold ethanol, and dried *in vacuo*. It is sparingly soluble in other than water, including acetonitrile and alcohols. Elemental analysis (calculated for $C_5H_{12}N_2S_2$): C, 33.82 (33.31); H, 6.56 (6.71); N, 15.38 (15.54). UV/Vis spectrum λ_{max} 263 (ε = 1.5 x 10^4 M^{-1} cm^{-1}) and 286 nm (ε = 1.4 x 10^4 M^{-1} cm^{-1}) in pH 7.4 water. ^{1}HNMR (D_2O): δ 4.28 (m, 4H), 3.64 (m, 4H); ^{13}CNMR (D_2O): δ 211.5 (CS_2), 68.7 (-N-CH_2-), 55.1 (-O-CH_2-). These data agree well with those reported elsewhere.[8,9]

Potassium imidazoledithiocarbamate (K[ImDTC]). Imidazole (7.3 mmol) was dissolved in 1.2 mL of nanopure water containing KOH (7.3 mmol). The water was then removed using a rotary evaporator followed by drying in a vacuum oven at 100 °C for 2 h. The resulting dry pink solid was then rapidly added to a round bottom flask containing 5 mL of dry acetonitrile at −40 °C. Under stirring, CS_2 (0.53 mL, 8.76 mmol) was added dropwise, and the solution color immediately turned orange followed in few minutes by precipitation of a yellow solid. After 30 min reaction, the solution was filtered, and the solid product was washed with chloroform and dried under vacuum overnight. The yield was 53%. Elemental analysis (calculated for $C_4H_3N_2S_2K$): C: 26.15 (26.35), H: 1.66 (1.66), N: 15.14 (15.37). UV/Vis spectrum λ_{max} 255 (ε = 6.36 x 10^3 M^{-1} cm^{-1}), 280 nm (ε = 9.38 x 10^3 M^{-1} cm^{-1}) and 353 nm (ε = 1.24 x 10^4 M^{-1} cm^{-1}) in acetonitrile. Infrared spectrum (ATR, cm^{-1}): 3158 – 3110 (ν(C-H), w); 1524 (ν(C=N), m); 1464 (ν(C=C), m); 1310 (ν(C-N), s); 1201 (ν(N-CS_2), s); 1070 (δ(C-H), s); 1014 (ν$(CS_2)_{asym}$, s); 830 (ν$(CS_2)_{sym}$, s); 742 (ν(C-S), m). ^{1}HNMR (CD_3CN): δ 6.80 (triplet, 1H), 8.15 (triplet, 1H), 8.74 (*broad*, triplet, 1H). Crystals suitable for X-ray analysis were grown by infusion of diethyl ether in an acetonitrile solution of the compound at −20 °C.

Potassium pyrroledithiocarbamate (K[PyrDTC]). Potassium pyrrolyldithiocarbamate was prepared as described by Bereman.[10] Pyrrole (15.0 mmol), recently distillated, was added to 30 mL of dry THF. Potassium metal (15.0 mmol) was added to the solution and the mixture was allowed to

react for 36 h. The solution was cooled to −78 °C and 1.08 mL (18 mmol) of CS_2 were added dropwise for 30 min. The solution was kept under stirring for 60 minutes, after which, cold hexanes (−20 °C) was added to the solution to precipitate a bright yellow solid in high yield (85%). The compound obtained is highly hygroscopic and air sensitive, and must be handled in a glove box under inert atmosphere and low humidity. Elemental analyses did not give good results probably due exposure to the environment on the analysis. Nevetheless, the compound is stable for days in deoxygenated aqueous solutions. UV/Vis spectrum λ_{max} 297 (ε = 1.29 x 10^4 M^{-1} cm^{-1}), 343 nm (ε = 6.30 x 10^3 M^{-1} cm^{-1}) in deoxygenated nanopure water; Infrared spectrum (ATR, cm^{-1}): 3371 (ν(O-H), s); 3153 – 3096 (ν(C-H), w); 1607 (δ(H_2O), m); 1447 (ν(C=C), m); 1291 (ν(C-N), s); 1237 (ν(N-CS_2), s); 1072 (δ(C-H), s); 1001 (ν$(CS_2)_{asym}$, s); 811 (ν$(CS_2)_{sym}$, s); 744 (ν(C-S), m).[5] ^{1}HNMR (D_2O): δ 6.34 (triplet, 2H), 8.04 (triplet, 2H) Crystals suitable for X-ray analysis were grown by slow evaporation of a saturated water solution of the compound under vacuum.

Models for acid and buffer catalyzed decay of diisopropyldithiocarbamate ($DIDTC^-$).

For simplicity, we will use the following terms:

$DTC^- = DIDTC^-$ $\quad$ DTCH = DIDTCH $\quad$ R_2NH = diisopropyl amine

BH = buffer conjugate acid; B^- = buffer conjugate base, $[B]_{tot}$ = total buffer concentration

Key equilibria:

$$DTCH \overset{K_a}{\rightleftharpoons} DTC^- + H^+ \qquad K_a = [DTC^-][H+]/[DTCH]$$

$$BH \overset{K_a^B}{\rightleftharpoons} B^- + H^+ \qquad K_a^B = [B^-][H^+]/[BH]$$

Note: The pK_a's of $H_2PO_4^-$ and MOPS are reported to be 7.165 and 7.044, respectively, at 37 °C.[11]

Acid (only) catalyzed decay

$$DTC^- + H^+ \overset{K_a^{-1}}{\rightleftharpoons} DTCH$$

$$DTCH \xrightarrow{k_1} CS_2 + R_2NH$$

$$\mathbf{d[P]/dt = k_1[DTCH] = k_{obs}[DTC]_{tot}}$$

$$[DTC]_{tot} = [DTCH] + [DTC^-] = [DTCH]\,(1 + K_a[H^+]^{-1}) = K_a\,[DTC^-]\,(K_a + [H^+])$$

$$[DTCH] = [DTC]_{tot}\,[H^+]/(K_a + [H^+])$$

therefore:

$$\frac{d[P]}{dt} = k_1[\text{DTCH}] = \frac{k_1\,[\text{H}^+][\text{DTC}]_{\text{tot}}}{K_a + [\text{H}^+]}$$

and:

$$k_{obs} = \frac{k_1\,[\text{H}^+]}{K_a + [\text{H}^+]} \qquad \textbf{(eq. A)}$$

From the k_{obs} versus pH curve over the pH range 2.0 to 7.8 (Figure 7 in text), the pK_a is estimated to be 4.6 and k_1 is 0.37 s^{-1} based on the limiting k_{obs} values at low pH.

for the pH range 6.5-7.8, $K_a >> [\text{H}^+]$, *thus:* $\boldsymbol{k_{obs} = k_1 K_a^{-1}[\text{H}+]}$

Add a buffer catalyzed rate — simple general acid catalysis

$$\text{DTC}^- + \text{BH} \xrightarrow{k_{ga}} \text{CS}_2 + \text{R}_2\text{NH} + \text{B}^-$$

then

$$\frac{d[P]}{dt} = k_1[\text{DTCH}] + k_{ga}[DTC^-][\text{BH}] = \frac{(k_1\,[\text{H}^+] + k_{ga}K_a[\text{BH}])[\text{DTC}]_{\text{tot}}}{K_a + [\text{H}^+]}$$

However: for the pH range 6.5-7.8, $K_a >> [\text{H}^+]$

thus: $\boldsymbol{k_{obs} = k_1 K_a^{-1}[\text{H}^+] + k_{ga}\,[\text{BH}]}$

where $[\text{BH}] = [\text{B}]_{\text{tot}}[\text{H}+]\,/([\text{H}^+] + K_a^B)$,

giving:

$$k_{obs} = k_1 K_a^{-1}[\text{H}^+] + \frac{k_{ga}[\text{H}^+][\text{B}]_{\text{tot}}}{K_a^B + [\text{H}^+]} \qquad \textbf{(eq. B)}$$

Thus: a plot of k_{obs} vs $[\text{B}]_{\text{tot}}$ at constant pH should be linear

intercept = $k_1 K_a^{-1}[\text{H}^+]$ and slope = $k_{ga}[\text{H}^+]/([\text{H}^+] + K_a^B)$

In this context, k_{obs} values for $DIDTC^-$ decay in the MOPS buffer at pH 7.4, k_{obs} vs $[\text{B}]_{\text{tot}}$ gave a linear plot with intercept = 9.1 x 10^{-4} s^{-1} and slope = 0.0123 M^{-1} s^{-1}

Thus for $[\text{H}^+]$ = 3.98 x 10^{-8} M and K_a^B(MOPS) = 9.04 x 10^{-8} M at 37 °C *,

(i) $k_1 K_a^{-1}$ = 2.29 x 10^4 M^{-1} s^{-1}

given that a limiting value of 0.37 s^{-1} was determined for k_1 at low pH this gives an

estimate for K_a = 1.62 x 10^{-5} M, or pKa (DIDTCH) = 4.79

(ii) $k_{ga}[H^+] / ([H^+] + K_a^B) = 0.0123\ s^{-1}\ M^{-1}$

Therefore, this gives

k_{ga} = 0.040 $M^{-1}\ s^{-1}$ for the conjugate acid of MOPS buffer

In contrast, the curvature in the k_{obs} vs. $[B]_{tot}$ plots for phosphate imply a saturation effect at higher buffer concentrations.

Fitting the k_{obs} versus $[B]_{tot}$ data for phosphate buffers at different pH values.

In attempts to fit the phosphate data we have tested two models, with BH = $H_2PO_4^-$ and B^- = HPO_4^{2-} and $[B]_{tot} \sim [BH] + [B^-]$

I. The first is a mechanism where the buffer catalysis step involves proton transfer to the DTC nitrogen within a complex between $H_2PO_4^-$ and DIDTC$^-$.

$$DTC^- + BH \underset{}{\overset{K_B}{\rightleftharpoons}} DTCBH$$ (where DTCBH is a complex between BH and DIDTC$^-$)

$$DTCBH \xrightarrow{k_2} CS_2 + R_2NH + B^-$$

$$d[P]/dt = k_1 K_a^{-1}[H^+][DTC^-] + k_2[DTCBH] = (k_1 K_a^{-1}[H^+] + k_2 K_B[BH])\,[DTC^-]$$

$$[DTC]_{tot} = [DTC^-] + [DTCH] + [DTCBH]$$

at near neutral pH:

$$[DTC]_{tot} = [DTC^-] + [DTCBH] = [DTC^-] + K_B[DTC^-]\,[BH] = [DTC^-]\,(1 + K_B[BH])$$

$$[DTC^-] = [DTC]_{tot} / (1 + K_B[BH])$$

therefore:

$$\frac{d[P]}{dt} = \frac{(k_1 K_a^{-1}\,[H^+] + k_2 K_B[BH])[DTC]_{tot}}{1 + K_B[BH]}$$

and

$$k_{obs} = \frac{k_1 K_a^{-1}\,[H^+] + k_2 K_B[BH]}{1 + K_B[BH]}$$

However: [BH] is a function of pH

$$BH \overset{K_a^B}{\rightleftharpoons} B^- + H^+ \quad \text{where } K_a^B = 6.84 \times 10^{-8}\ \text{M for } H_2PO_4^- \text{ at } 37\ ^oC.[11]$$

$$[B]_{tot} = [BH] + [B^-] = [BH] + K_a^B[BH][H^+]^{-1} = [BH](1 + K_a^B[H^+]^{-1})$$

$$[BH] = [B]_{tot}/(1 + K_a^B[H^+]^{-1}) = [B]_{tot}([H^+]/([H^+] + K_a^B))$$

Taking into account the pH dependence of [BH] leads to the following equation

$$k_{obs} = \left(\frac{k_1 K_a^{-1}[H^+] + \left(\frac{k_2 K_B[H^+]}{[H^+] + K_a^B}\right)[B]_{tot}}{K_a^B + [H^+] + K_B[H^+][B]_{tot}}\right)(K_a^B + [H^+]) \qquad \textbf{(eq. C)}$$

The following constants are known for the above:

$k_1 =$ 0.37 s^{-1} (from limiting rate at low pH)

$K_a =$ 2.5 x 10^{-5} M (from k_{obs} vs. pH data, see text Figure 7)

$K_a^B =$ 6.84 x 10^{-8} M[11]

$[H^+]$ (5 sets of k_{obs} data as a function of $[B]_{tot}$ for pH values 6.5, 6.8, 7.0, 7.4 & 7.8)

The equation above could be numerically fit to the k_{obs} values at each pH using OriginPro 8.5 (OriginLab software) to determine best values of K_B and k_2. However, these values (which should have been constants) varied considerably although the product k_2K_B was nearly constant. Nonetheless, we used the K_B and k_2 values obtained from the pH 7.4 data (26 M and 0.27 s^{-1}, which were near the average values from the 5 pH experiments) with eq. C to recalculate the curves for data sets at the 5 pH values. This attempt (as well as those with other K_B and k_2 values) *did not give reasonable fits for the k_{obs} vs $[B]_{tot}$ plots for all five pH values.*

II. The second prospective mechanism involves proton transfer to the DIDTC$^-$ nitrogen from $H_2PO_4^-$ but inhibition of DIDTC$^-$ decay by formation of a complex with HPO_4^{2-}.

In this model the following reactions lead to products:

$$DTCH \xrightarrow{k_1} CS_2 + R_2NH$$

$$DTC^- + BH \xrightarrow{k_{ga}} CS_2 + R_2NH + B^-$$

while one reaction does not

$$DTC^- + B^- \overset{K_C}{\rightleftharpoons} C \longrightarrow \text{no reaction}$$

This gives

$$d[P]/dt = (k_1 K_a^{-1}[H^+] + k_{ga}[BH])\,[DTC^-]$$

Although not reactive, the complex C affects the concentrations of the other species

$$[DTC]_{tot} = [DTC^-] + [DTCH] + [C] = (1 + K_a^{-1}[H^+] + K_c[B^-])[DTC^-]$$

$$= (1 + K_c[B^-])[DTC^-] \qquad \text{given that } 1 >> K_a^{-1}[H^+]$$

thus: $[DTC^-] = [DTC]_{tot}/(1 + K_c[B^-])$

Thereby giving

$$d[P]/dt = (k_1 K_a^{-1}[H^+] + k_{ga}[BH])\,[DTC]_{tot}/(1 + K_c[B^-])$$

since: $[BH]_{tot} >> [DTC]_{tot}$, the formation of C has little effect on [BH] or $[B^-]$

Therefore: $[BH] = [B]_{tot}([H^+]/([H^+] + K_a^B))$ and $[B^-] = K_a^B[B]_{tot}/([H+] + K_a^B)$

Giving:

$$\frac{d[P]}{dt} = (k_1 K_a^{-1}[H^+] + \frac{k_{ga}[H^+][B]_{tot}}{K_a^B + [H^+]})(\frac{K_a^B + [H^+]}{K_a^B + [H^+] + K_a^B K_C[B]_{tot}})[DTC]_{tot}$$

and

$$k_{obs} = (k_1 K_a^{-1}[H^+] + \frac{k_{ga}[H^+][B]_{tot}}{K_a^B + [H^+]})(\frac{K_a^B + [H^+]}{K_a^B + [H^+] + K_a^B K_C[B]_{tot}})$$

given that the following constants are known for the above:

$k_1 = 0.37\ s^{-1}$ (from limiting rate at low pH)

$K_a = 2.5 \times 10^{-5}$ M (from k_{obs} vs. pH data, see text)

$K_a^B = 6.84 \times 10^{-8}$ M

$[H^+]$ (5 sets of k_{obs} data as a function of $[B]_{tot}$ for pH values 6.5, 6.8, 7.0, 7.4 & 7.8)

The equation above could be numerically fit to the k_{obs} values at each pH using OriginPro 8.5 k_{ga} (OriginLab software) to determine best values of K_C and k_{ga}. The calculated values of k_{ga} were remarkably constant, varying by only about $\pm$10%. A wider range was seen for the calculated K_C values, although the K_c for the four higher pH values were more tightly grouped with an average variation of $\pm$20%. Figure S10 shows the fits of the calculated k_{obs} values to the experimental ones using the average k_{ga} value 0.27 $M^{-1}\ s^{-1}$ and the average K_c value 26 M^{-1} determined for the four sets of experiments at the higher pH's. *The fits of the experimental data to eq. D are reasonable for all 5 pH values.*

Notably, the k_{ga} value for the general acid catalysis of DIDTC- decay by $H_2PO_4^-$ estimated in this way for the reactions in phosphate buffer is nearly 7 times as large as that determined for the conjugate acid of the MOPS buffer.

Figures

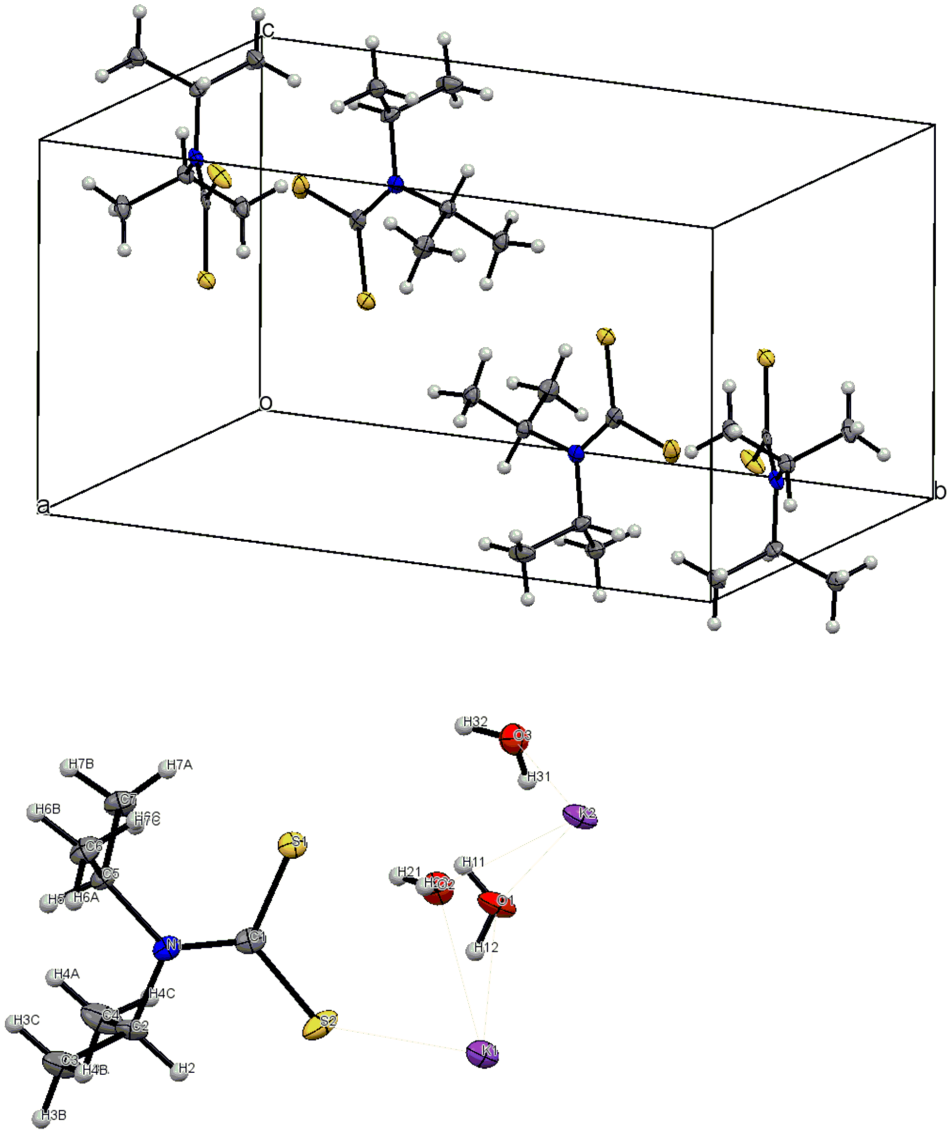


Figure S1. X-ray structure packing diagram (upper) and asymmetric unit (bottom) of potassium diisopropyldithiocarbamate, K[DIDTC]. Thermal ellipsoids are drawn at 50% probability. Water molecules and potassium cation were omitted in the packing representation for clarity (CCDC # 1557062)

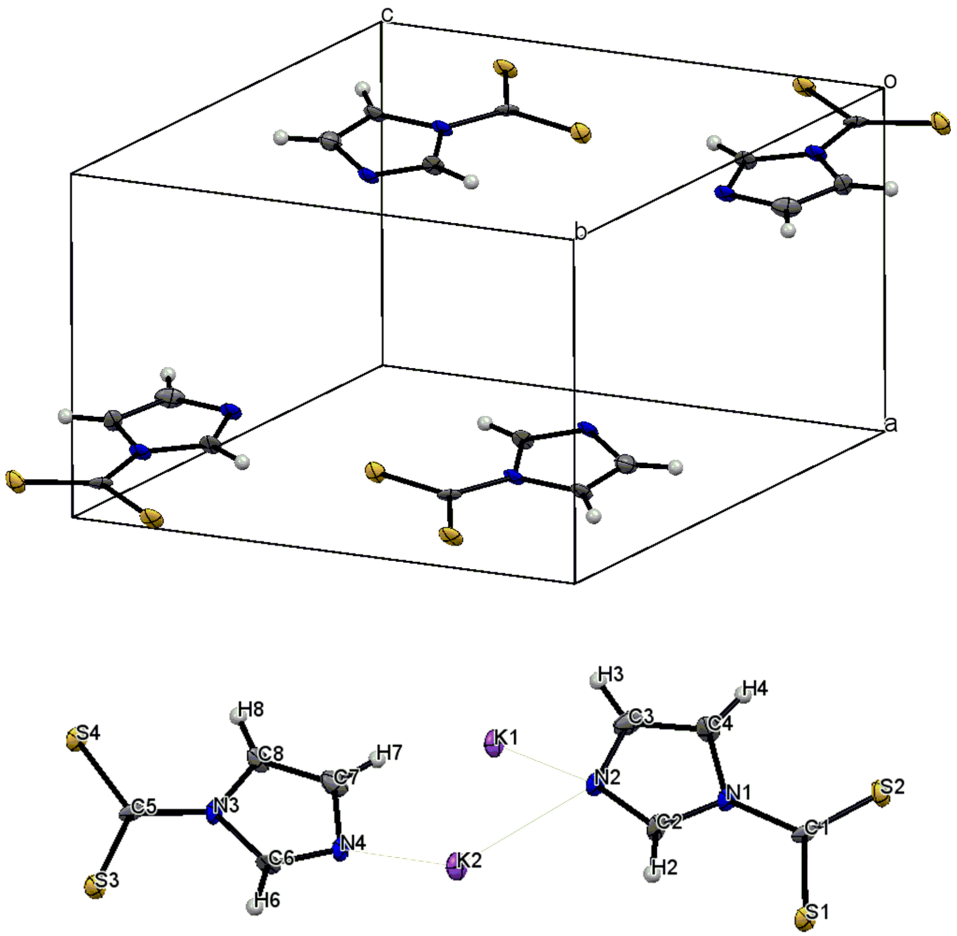


Figure S2. X-ray structure packing diagram (upper) and asymmetric unit (bottom) of potassium imidazoledithiocarbamate (K[ImDTC]). Thermal ellipsoids drawn at 50% probability. Potassium cations were omitted in the packing representation for clarity. (CCDC # 1557060)

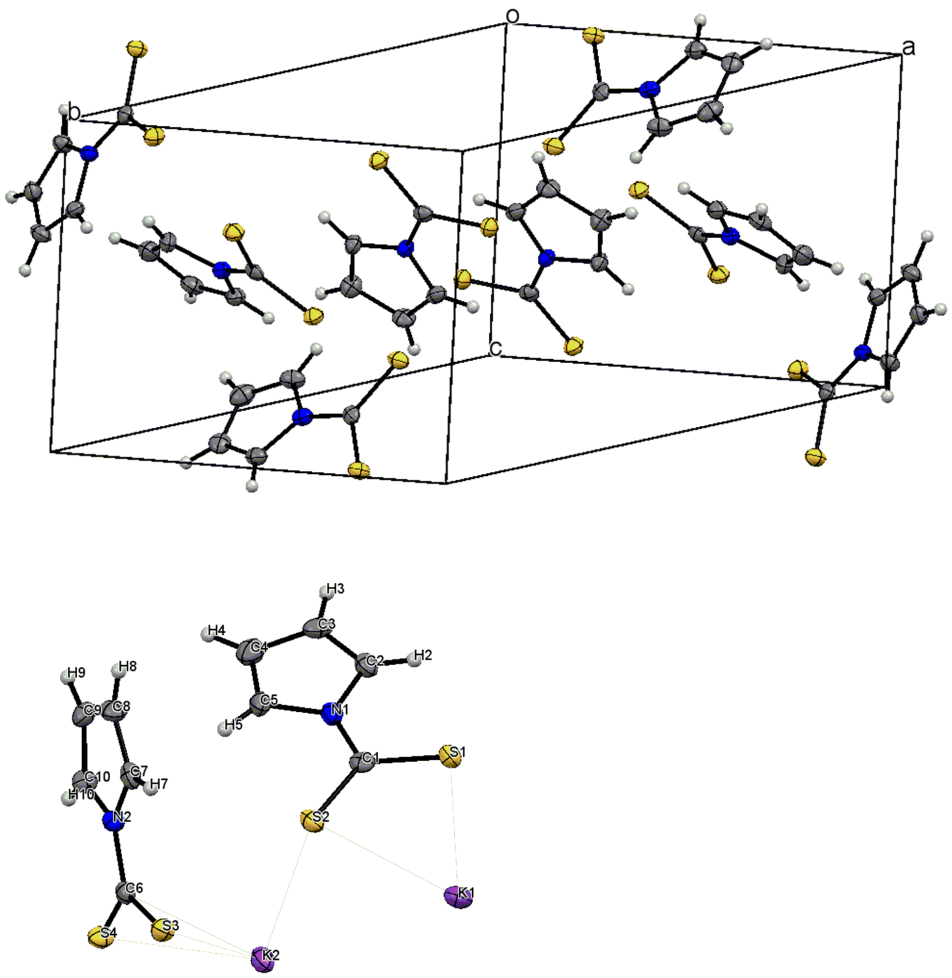


Figure S3. X-ray structure packing diagram (upper) and asymmetric unit (bottom) of potassium pyrroledithiocarbamate K[PyrDTC] (with 50% thermal ellipsoids). Potassium cations were omitted in the packing representation for clarity. (CCDC# 1557061)

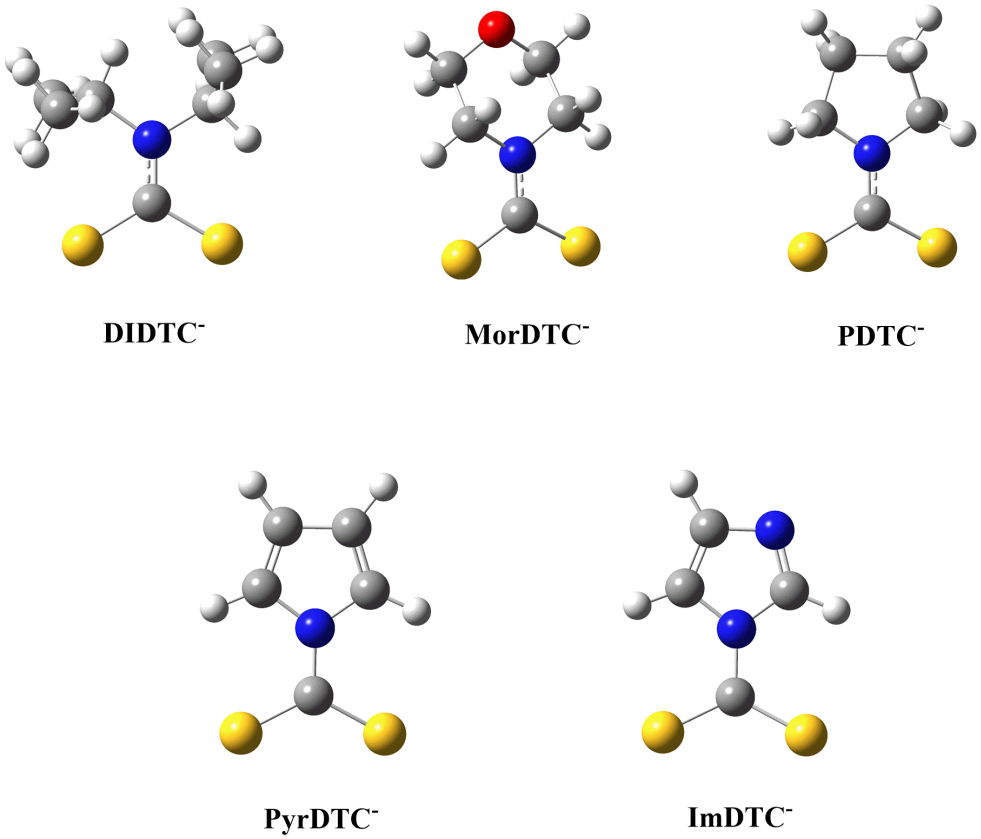


Figure S4. Optimized geometries of various DTCs in a PCM (solvent=water)/B3LYP/6-31+G(d,p) theory level. Abbreviations: $DIDTC^-$ = diisopropyldithiocarbamate anion, $MorDTC^-$ = morpholine-dithiocarbamate, $PDTC^-$ = pyrrolidinedithiocarbamate anion, $PyrDTC^-$ = pyrroledithiocarbamate anion, $ImDTC^-$ = imidazoledithiocarbamate anion.

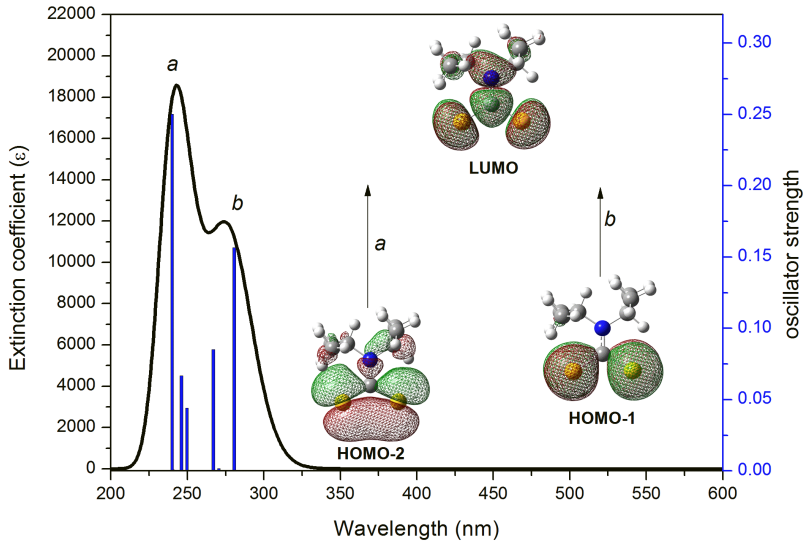


Figure S5. DIDTC⁻ TD-DFT-calculated spectrum in an PCM model solvent (water) and M062X/6-31+G(d,p) level of theory for the optimized DIDTC⁻ geometry. The theoretical spectrum was generated from GaussSum 3.0 software with half-widths of 4100 cm^{-1} (the electronic transitions are identified by their relative oscillator strengths: blue bars). Insert: Calculated MOs involved in electronic transitions.

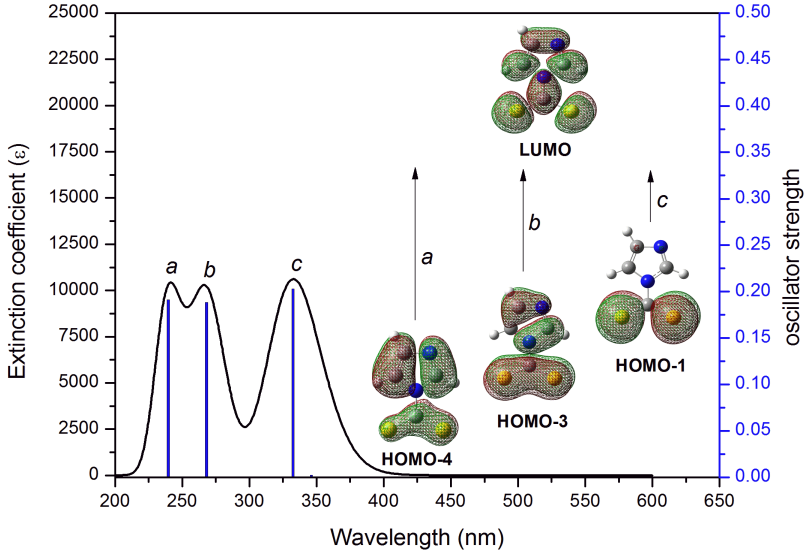


Figure S6. TD-DFT-calculated spectrum in an PCM model solvent (water) and M062X/6-31+G(d,p) level of theory for the ImDTC⁻ geometry. The theoretical spectrum was generated from GaussSum 3.0 software with half-widths of 4300 cm^{-1} (the electronic transitions are identified by their relative oscillator strengths: blue bars). Insert: Calculated MOs involved in electronic transitions.

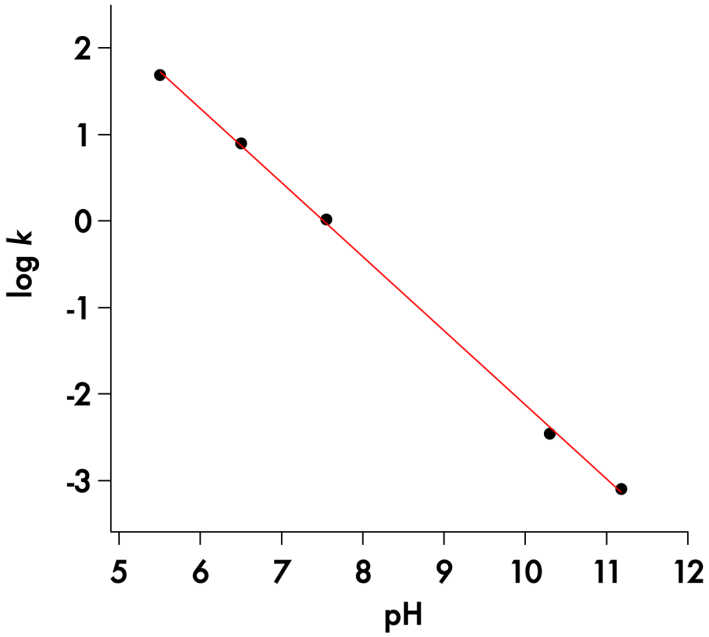


Figure S7. Linear fit of the plot of the log(k_{obs}) *versus* pH for the decay of the ImDTC$^-$ anion. R^2 = 0.999; Slope = -0.86.

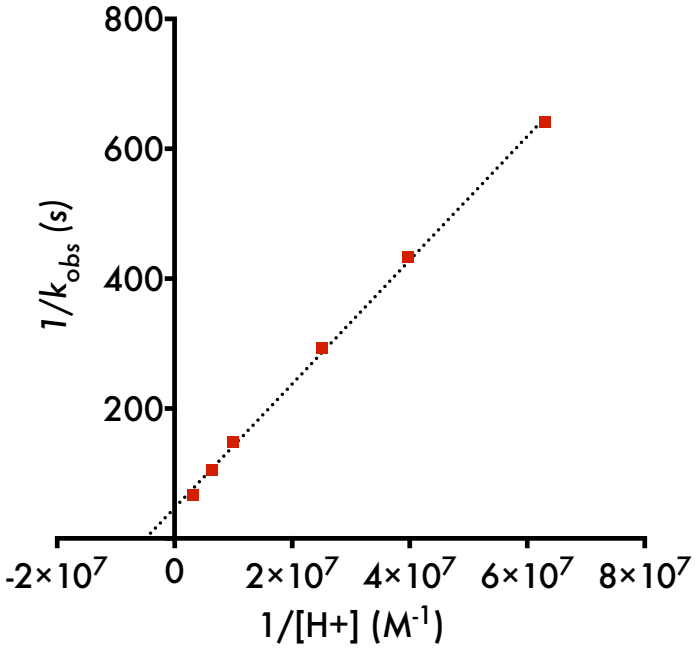


Figure S8. Double reciprocal plot of k_{obs}^{-1} vs $[H^+]^{-1}$ for the decay of DIDTC$^-$ in phosphate buffer (50 mM) with ionic strength adjusted to 154 mM with NaCl. pH 6.5-7.8 at 37 °C. According to eq. 2, $k_{obs}^{-1} = K_a/k_1[H+] + 1/k_1$ *so* k_1 = 1/intercept and K_a = slope over internet, from which the values k_1 = 0.021 ± 0.002 s^{-1} and K_a = 2.02 x 10^{-7} (pK_a =6.69) were derived.

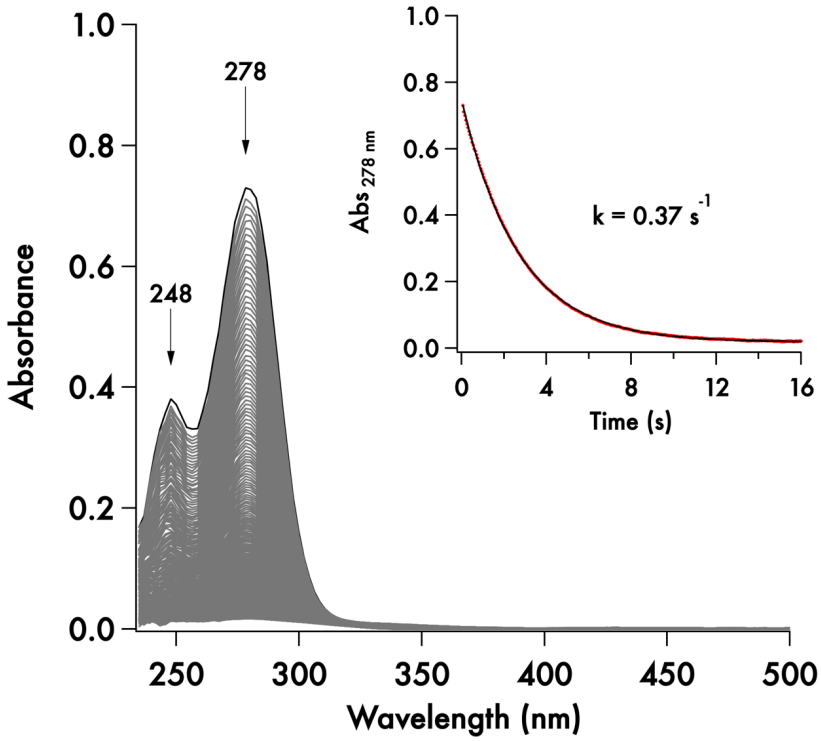


Figure S9. Temporal spectra of the $DIDTC^-$ anion in acidic media. [DIDTC] = 0.1 mM; pH 2.0; μ = 0.154 M (NaCl); T = 37.1 °C.

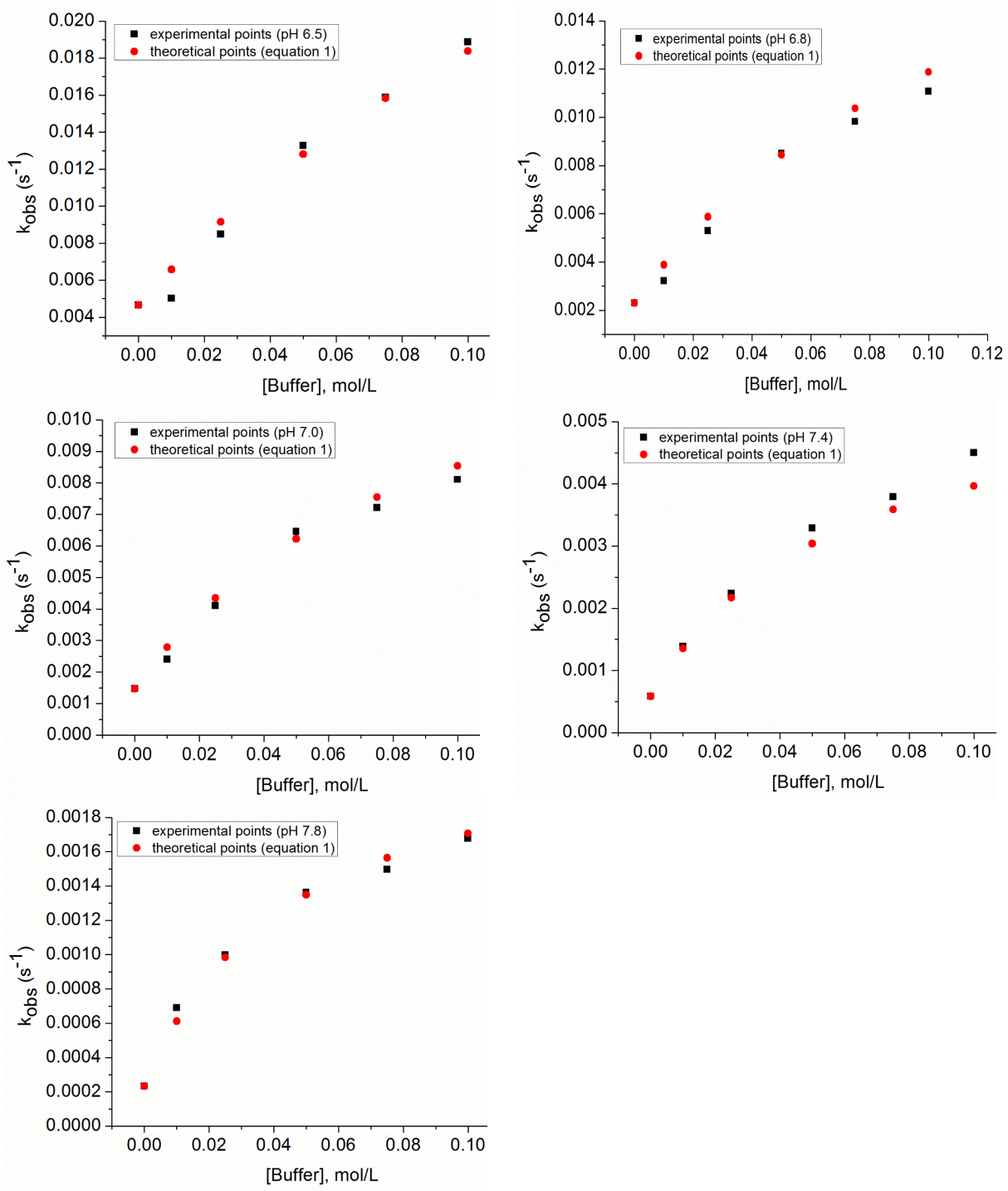


Figure S10. Fits of k_{obs} values observed at 37 °C for the decay of $DIDTC^-$ as a function of the total buffer concentration $[B]_{tot}$ as fit to eq. D for pH's 6.5 and 6.8 (top row), 7.0 and 7.4 (middle) and 7.8 (bottom). Black squares are experimental points; Red dots are theoretical values calculated using k_1 = 0.37 s^{-1}, K_a = 2.5 x 10^{-5} M, K_a^B = 6.84 x10^{-8}, k_{ga} = 0.27 $M^{-1}s^{-1}$, K_c = 26 M^{-1}.

$$k_{obs} = (k_1 K_a^{-1}[H^+] + \frac{k_{ga}[H^+][B]_{tot}}{K_a^B + [H^+]})(\frac{K_a^B + [H^+]}{K_a^B + [H^+] + K_a^B K_C[B]_{tot}}) \quad \text{(eq. D)}$$

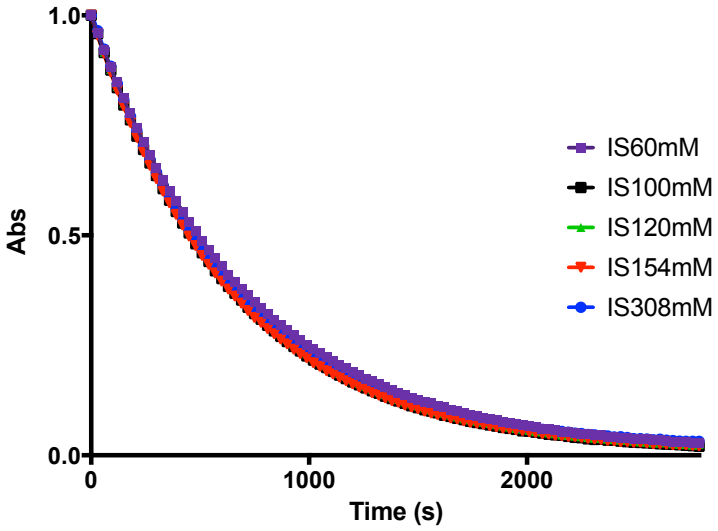


Figure S11. Ionic strength effects on $DIDTC^-$ decay. Conditions: pH 7.4 phosphate buffer (10 mM). m varied from 60 mM to 308 mM.

m (mM)	k_{obs} (s^{-1})
60	0.00143
100	0.00152
120	0.00150
154	0.00149
308	0.00153

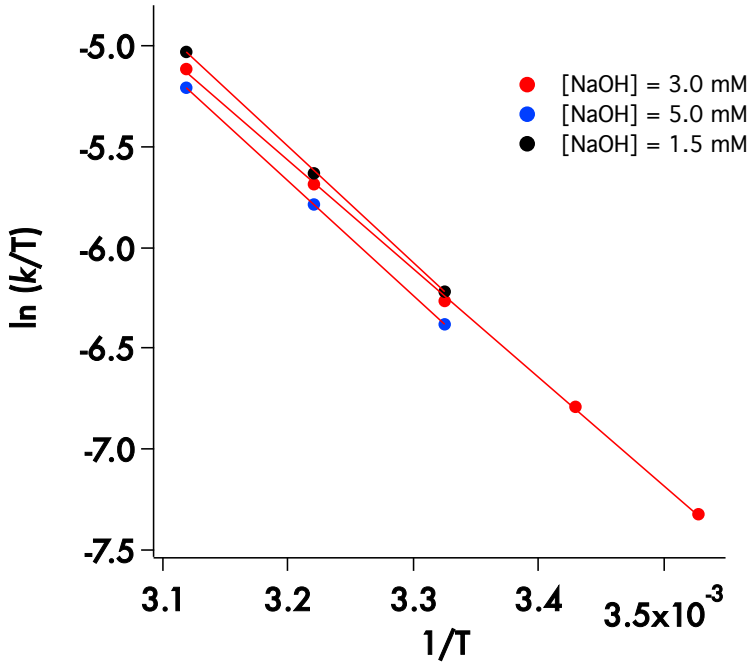


Figure S12. Eyring plots of k_{obs} values measured at over the temperature range 283.5-320.6 K for the decay of ImDTC⁻. The kinetics experiments were performed by mixing equal volumes of phosphate buffer (pH 7.45, 0.15 M) and K[ImDTC] (0.2 mM) in aq. NaOH (1.5 mM, 3.0 mM and 5.0 mM) in the stopped-flow spectrophotometer. The final pH values for the three solutions were 7.53, 7.55 and 7.59, respectively.

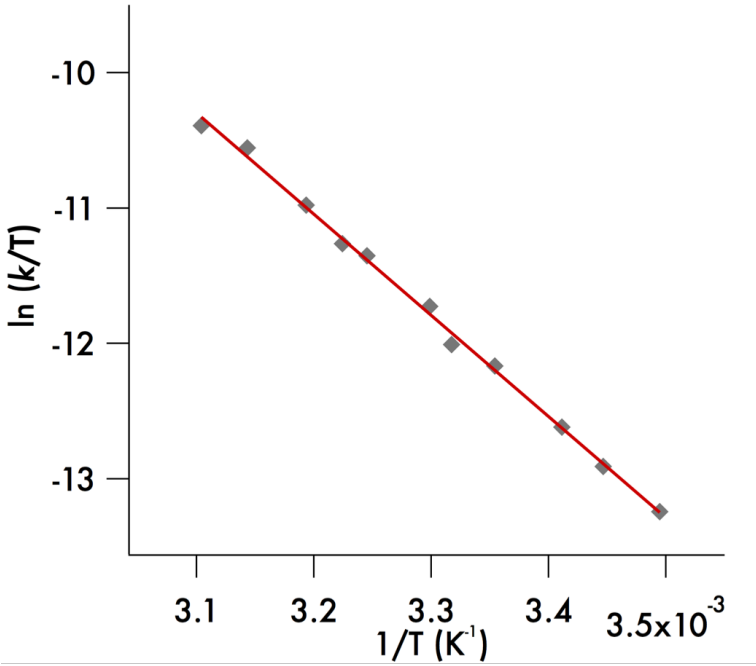


Figure S13. Eyring plot of k_{obs} values measured over the temperature range 286.1 to 322.1 K for the decay of DIDTC in phosphate buffer (pH 7.40, 50 mM, m = 154 mM).

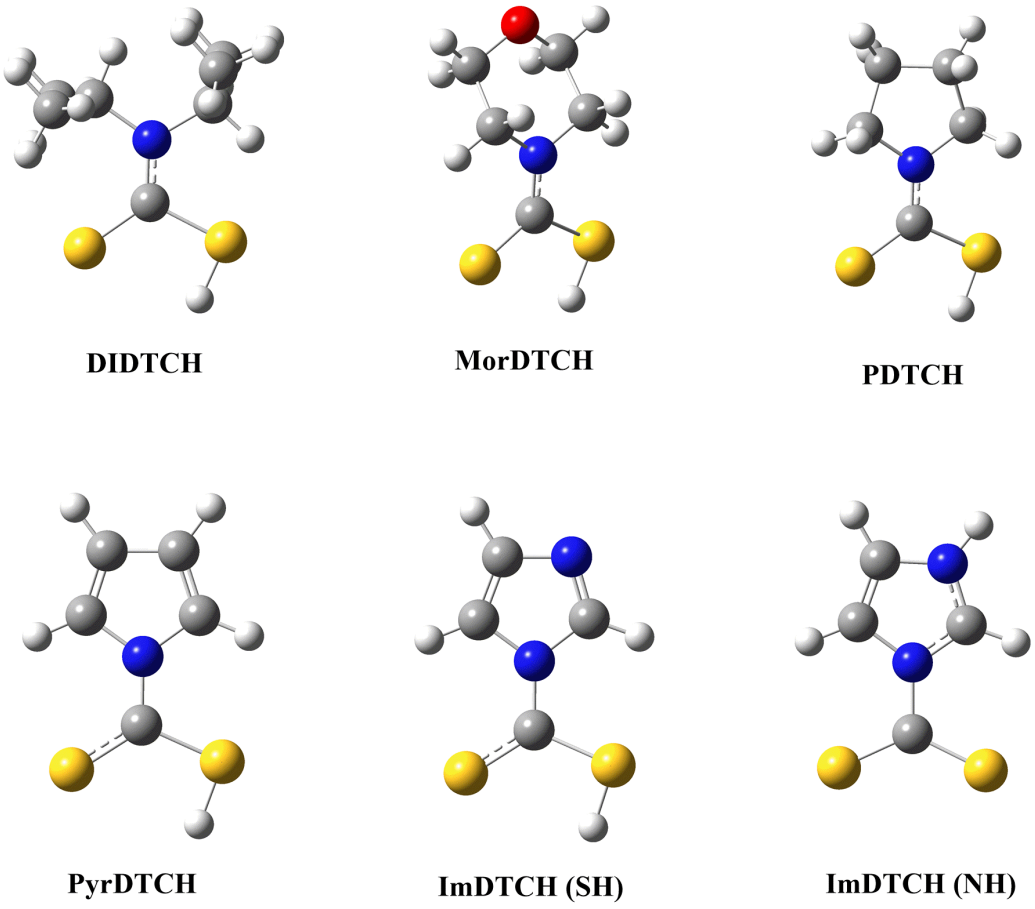


Figure S14. Optimized geometries of the protonated DTCs in a PCM(solvent=water)/B3LYP/6-31+G(d,p) theory level. Abbreviations: DIDTCH = diisopropyldithiocarbamic acid, MorDTCH = N-(morpholine-N-dithiocarbamic acid, PDTCH = pyrrolidinedithiocarbamic acid, PyrDTCH = pyrroledithiocarbamic acid, ImDTCH(SH) = imidazoledithiocarbamic acid, ImDTCH(NH) = N protonated zwiterionic form.

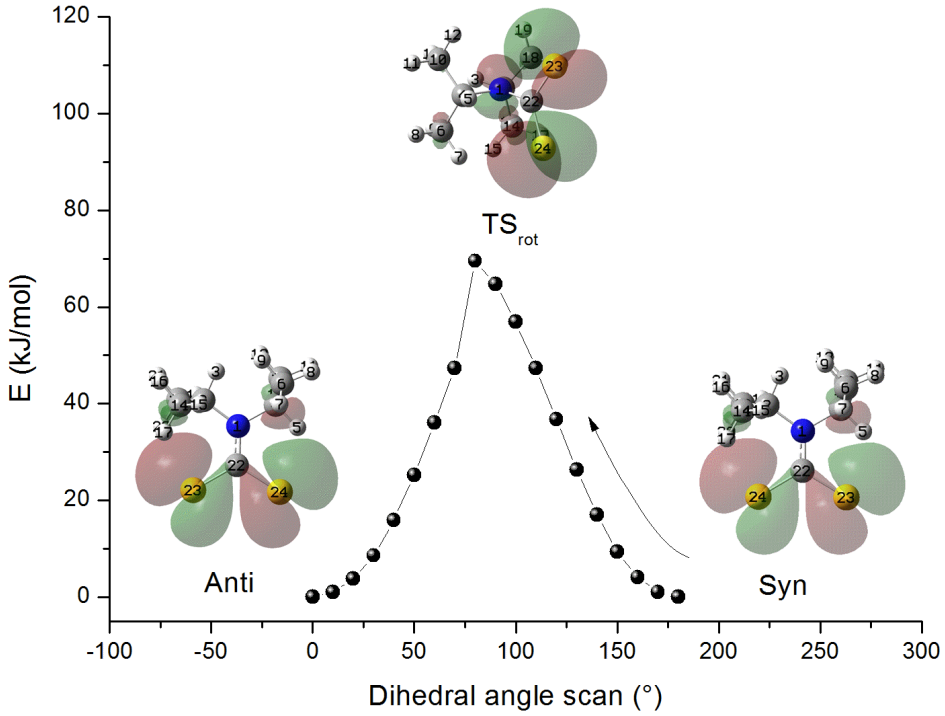


Figure S15. Potential Energy Surface (PES) generated from the CS_2 rotation along the N-C bond on the $DIDTC^-$ anion. The transition state (TS_{rot}) correspond to a pyramidal $DIDTC^-$ geometry. Calculated at the PCM(water)/B3LYP/6-31+G(d,p) theory level.

Tables:

Table S1. X-ray structural data for potassium diisopropyldithiocarbamate (K[DIDTC).

Formula	$C_7H_{18}KNO_2S_2$
MW (g/mol)	251.44
Temperature	100 K
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P 21/m
Unit cell dimensions	a = 5.7640(9) Å; α =90°
	b = 28.756(5) Å; β = 110.631(10
	c = 7.9313(14) Å; γ =90°
Z	4
Calculated density (Mg/cm^3)	1.357
Absorption coefficient (mm^{-1})	0.745
Crystal size (mm)	0.200 x 0.100 x 0.100
F(0 0 0)	536.0
Theta range for data collection	1.416 to 26.363
Reflections collected	5442
Independent reflections	2558
Completeness to θ = 26.363°	100%
Absorption correction	multi-scan
Max. And min. Transmission	0.745 and 0.639
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2558/18/153
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R1=0.0521, wR=0.0992
R indices (all data)	R1=0.0886, wR=0.1115

Table S2. X-ray structural data for potassium imidazoledithiocarbamate (K[ImDTC]).

Formula	$C_4H_3KN_2S_2$
MW (g/mol)	182.30
Temperature	100 K
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 7.425(6) Å; α = 78.314 (12)°
	b = 8.392(7) Å; β = 80.939 (15) °
	c = 11.614 (9) Å; γ = 89.287 (17)°
Z	4
Calculated density (Mg/cm^3)	1.731
Absorption coefficient (mm^{-1})	1.258
Crystal size (mm)	0.250 x 0.200 x 0.100
F(0 0 0)	368.0
Theta range for data collection	1.813 to 24.711
Reflections collected	5549
Independent reflections	2311
Completeness to θ = 24.711°	96.9%
Absorption correction	multi-scan
Max. And min. Transmission	0.745 and 0.497
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2311/0/151
Goodness-of-fit on F^2	0.877
Final R indices [I>2σ(I)]	R1=0.0521, wR2=0.1103
R indices (all data)	R1=0.0973, wR2=0.1182

Table S3. X-ray structural data for potassium pyrroledithiocarbamate (K[PyrDTC])

Formula	$C_5H_4KNS_2$
MW (g/mol)	181.31
Temperature	100 K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 13.41(2) Å; α = 90°
	b = 14.04(2) Å; β = 100.64 °
	c = 8.042 (13) Å; γ = 90°
Z	8
Calculated density (Mg/cm^3)	1.619
Absorption coefficient (mm^{-1})	1.179
Crystal size (mm)	0.250 x 0.100 x 0.050
F(0 0 0)	736.0
Theta range for data collection	2.119 to 26.296
Reflections collected	5708
Independent reflections	2936
Completeness to θ = 26.296°	97.6%
Absorption correction	multi-scan
Max. And min. Transmission	0.745 and 0.542
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2936/0/163
Goodness-of-fit on F^2	0.969
Final R indices [I>2σ(I)]	R1=0.0497, wR2=0.0926
R indices (all data)	R1=0.0983, wR2=0.1100

Table S4. Bond lengths and angles for potassium diisopropyldithiocarbamate (K[DIDTC)

Atom1	Atom2	Length (Å)
C1	N1	1.344(5)
C1	S1	1.725(3)
C1	S2	1.731(3)
C2	H2	0.999
C2	C3	1.515(5)
C2	C4	1.533(6)
C2	N1	1.486(5)
C3	H3A	0.979
C3	H3B	0.980
C3	H3C	0.979
C4	H4A	0.980
C4	H4B	0.979
C4	H4C	0.980
C5	H5	1.000
C5	C6	1.524(6)
C5	C7	1.525(4)
C5	N1	1.492(4)
C6	H6A	0.980
C6	H6B	0.981
C6	H6C	0.981
C7	H7A	0.980
C7	H7B	0.980
C7	H7C	0.980
H11	O1	0.81
H12	O1	0.81
H21	O2	0.82(5)
H22	O2	0.82(4)
H31	O3	0.82
H31	O3	0.82
H32	O3	0.81(4)
K1	O1	3.331
K1	O2	2.793
K1	S2	3.421
K1	O2	2.793
K1	S2	3.421
K1	O3	2.841
K1	O3	2.841
K1	S2	3.427
K1	S2	3.427
K2	O1	2.798
K2	O2	2.706
K2	O3	3.129

K2	O3	3.129
K2	O2	2.706
K2	O3	2.888
K2	O3	2.888
K2	S2	3.266
K2	S2	3.266
O1	H11	0.81
O3	O3	1.135(8)
O3	K1	2.841
O3	K2	2.888
S2	K1	3.427
S2	K2	3.266
H32	O3	0.81(4)
O3	K1	2.841
O3	K2	2.888
C1	N1	1.344(5)
C1	S1	1.725(3)
C1	S2	1.731(3)
C2	H2	0.999
C2	C3	1.515(5)
C2	C4	1.533(6)
C2	N1	1.486(5)
C3	H3A	0.979
C3	H3B	0.980
C3	H3C	0.979
C4	H4A	0.980
C4	H4B	0.979
C4	H4C	0.980
C5	H5	1.000
C5	C6	1.524(6)
C5	C7	1.525(4)
C5	N1	1.492(4)
C6	H6A	0.980
C6	H6B	0.981
C6	H6C	0.981
C7	H7A	0.980
C7	H7B	0.980
C7	H7C	0.980
H21	O2	0.82(5)
H22	O2	0.82(4)
S2	K1	3.427
S2	K2	3.266
K1	S2	3.427
K1	S2	3.427

K2	O3	2.888
K2	O3	2.888
O3	O3	1.135(8)
O3	O3	1.135(8)

Atom1	Atom2	Atom3	Angle (º)
N1	C1	S1	121.1(3)
N1	C1	S2	121.5(3)
S1	C1	S2	117.3(2)
H2	C2	C3	107.3
H2	C2	C4	107.4
H2	C2	N1	107.4
C3	C2	C4	112.1(3)
C3	C2	N1	111.8(3)
C4	C2	N1	110.6(3)
C2	C3	H3A	109.5
C2	C3	H3B	109.4
C2	C3	H3C	109.5
H3A	C3	H3B	109.5
H3A	C3	H3C	109.4
H3B	C3	H3C	109.5
C2	C4	H4A	109.5
C2	C4	H4B	109.4
C2	C4	H4C	109.5
H4A	C4	H4B	109.4
H4A	C4	H4C	109.5
H4B	C4	H4C	109.5
H5	C5	C6	105.1
H5	C5	C7	105.1
H5	C5	N1	105.1
C6	C5	C7	113.2(3)
C6	C5	N1	113.3(3)
C7	C5	N1	114.0(3)
C5	C6	H6A	109.5
C5	C6	H6B	109.5
C5	C6	H6C	109.4
H6A	C6	H6B	109.4
H6A	C6	H6C	109.5
H6B	C6	H6C	109.5
C5	C7	H7A	109.5
C5	C7	H7B	109.4
C5	C7	H7C	109.5
H7A	C7	H7B	109.5
H7A	C7	H7C	109.5

H7B	C7	H7C	109.5
O3	H31	O3	87
O1	K1	O2	63.07
O1	K1	S2	59.56
O1	K1	O2	63.07
O1	K1	S2	59.56
O1	K1	O3	122.0
O1	K1	O3	122.0
O1	K1	S2	139.22
O1	K1	S2	139.22
O2	K1	S2	81.98
O2	K1	O2	81.93
O2	K1	S2	121.60
O2	K1	O3	127.4
O2	K1	O3	150.3
O2	K1	S2	76.21
O2	K1	S2	115.10
S2	K1	O2	121.60
S2	K1	S2	60.79
S2	K1	O3	66.0
S2	K1	O3	78.2
S2	K1	S2	114.64
S2	K1	S2	158.16
O2	K1	S2	81.98
O2	K1	O3	150.3
O2	K1	O3	127.4
O2	K1	S2	115.10
O2	K1	S2	76.21
S2	K1	O3	78.2
S2	K1	O3	66.0
S2	K1	S2	158.16
S2	K1	S2	114.64
O3	K1	O3	23.1
O3	K1	S2	80.7
O3	K1	S2	92.3
O3	K1	S2	92.3
O3	K1	S2	80.7
S2	K1	S2	60.69
O1	K2	O2	72.0
O1	K2	O3	53.5
O1	K2	O3	53.5
O1	K2	O2	72.0
O1	K2	O3	150.6
O1	K2	O3	150.6

O1	K2	S2	128.05
O1	K2	S2	128.05
O2	K2	O3	102.5
O2	K2	O3	117.5
O2	K2	O2	85.17
O2	K2	O3	80.6
O2	K2	O3	95.8
O2	K2	S2	102.77
O2	K2	S2	159.80
O3	K2	O3	20.9
O3	K2	O2	117.5
O3	K2	O3	146.6
O3	K2	O3	155.0
O3	K2	S2	79.3
O3	K2	S2	90.4
O3	K2	O2	102.5
O3	K2	O3	155.0
O3	K2	O3	146.6
O3	K2	S2	90.4
O3	K2	S2	79.3
O2	K2	O3	95.8
O2	K2	O3	80.6
O2	K2	S2	159.80
O2	K2	S2	102.77
O3	K2	O3	22.7
O3	K2	S2	67.7
O3	K2	S2	80.2
O3	K2	S2	80.2
O3	K2	S2	67.7
S2	K2	S2	64.02
C1	N1	C2	121.0(3)
C1	N1	C5	124.9(3)
C2	N1	C5	114.1(3)
H11	O1	H12	114
H11	O1	K1	120
H11	O1	K2	86
H11	O1	H11	118
H12	O1	K1	52
H12	O1	K2	134
H12	O1	H11	114
K1	O1	K2	81.9
K1	O1	H11	120
K2	O1	H11	86
H21	O2	H22	114(4)

H21	O2	K1	104
H21	O2	K2	107
H22	O2	K1	111
H22	O2	K2	124
K1	O2	K2	94.48
H31	O3	H32	115
H31	O3	K2	95
H31	O3	O3	46
H31	O3	K1	121
H31	O3	K2	51
H32	O3	K2	118
H32	O3	O3	158(4)
H32	O3	K1	113
H32	O3	K2	79
K2	O3	O3	79.5
K2	O3	K1	91.4
K2	O3	K2	146.6
O3	O3	K1	78.5
O3	O3	K2	78.7
K1	O3	K2	108.5
C1	S2	K1	119.7
C1	S2	K1	103.1
C1	S2	K2	145.8
K1	S2	K1	114.64
K1	S2	K2	88.09
K1	S2	K2	79.43
H31	O3	K2	95
H31	O3	O3	46
H31	O3	H32	115
H31	O3	K1	121
H31	O3	K2	51
K2	O3	O3	79.5
K2	O3	H32	118
K2	O3	K1	91.4
K2	O3	K2	146.6
O3	O3	H32	158(4)
O3	O3	K1	78.5
O3	O3	K2	78.7
H32	O3	K1	113
H32	O3	K2	79
K1	O3	K2	108.5
N1	C1	S1	121.1(3)
N1	C1	S2	121.5(3)
S1	C1	S2	117.3(2)

H2	C2	C3	107.3
H2	C2	C4	107.4
H2	C2	N1	107.4
C3	C2	C4	112.1(3)
C3	C2	N1	111.8(3)
C4	C2	N1	110.6(3)
C2	C3	H3A	109.5
C2	C3	H3B	109.4
C2	C3	H3C	109.5
H3A	C3	H3B	109.5
H3A	C3	H3C	109.4
H3B	C3	H3C	109.5
C2	C4	H4A	109.5
C2	C4	H4B	109.4
C2	C4	H4C	109.5
H4A	C4	H4B	109.4
H4A	C4	H4C	109.5
H4B	C4	H4C	109.5
H5	C5	C6	105.1
H5	C5	C7	105.1
H5	C5	N1	105.1
C6	C5	C7	113.2(3)
C6	C5	N1	113.3(3)
C7	C5	N1	114.0(3)
C5	C6	H6A	109.5
C5	C6	H6B	109.5
C5	C6	H6C	109.4
H6A	C6	H6B	109.4
H6A	C6	H6C	109.5
H6B	C6	H6C	109.5
C5	C7	H7A	109.5
C5	C7	H7B	109.4
C5	C7	H7C	109.5
H7A	C7	H7B	109.5
H7A	C7	H7C	109.5
H7B	C7	H7C	109.5
C1	N1	C2	121.0(3)
C1	N1	C5	124.9(3)
C2	N1	C5	114.1(3)
K1	O2	K2	94.48
K1	O2	H21	104
K1	O2	H22	111
K2	O2	H21	107
K2	O2	H22	124

H21	O2	H22	114(4)
K1	S2	C1	119.7
K1	S2	K1	114.64
K1	S2	K2	88.09
C1	S2	K1	103.1
C1	S2	K2	145.8
K1	S2	K2	79.43
O3	K1	O3	23.1
O3	K1	S2	80.7
O3	K1	S2	92.3
O3	K1	S2	92.3
O3	K1	S2	80.7
S2	K1	S2	60.69
S2	K1	S2	60.69
O3	K2	O3	22.7
S2	K2	S2	64.02
S2	K2	O3	67.7
S2	K2	O3	80.2
S2	K2	O3	80.2
S2	K2	O3	67.7
O3	K2	O3	22.7
K2	O3	O3	78.7
K1	O3	K2	108.5
K1	O3	O3	78.5
K2	O3	O3	78.7
K2	O3	O3	78.7
K1	O3	K2	108.5
K1	O3	O3	78.5
K2	O3	O3	78.7
K2	S2	K1	79.43
K2	S2	K1	79.43

Table S5. Bond lengths and angles for potassium imidazoledithiocarbamate (K[ImDTC]).

Atom1	Atom2	Length
C1	N1	1.419(8)
C1	S1	1.663(5)
C1	S2	1.706(5)
C2	H2	0.950
C2	N1	1.354(6)
C2	N2	1.292(8)
C3	H3	0.949
C3	C4	1.353(8)
C3	N2	1.396(7)
C4	H4	0.950
C4	N1	1.399(6)
C5	N4	1.418(7)
C5	S3	1.703(5)
C5	S4	1.661(6)
C6	H6	0.951
C6	N3	1.302(7)
C6	N4	1.358(8)
C7	H7	0.950
C7	C8	1.327(9)
C7	N3	1.403(8)
C8	H8	0.950
C8	N4	1.391(6)
K1	N2	2.831(5)
K1	N3	2.814(6)
K1	S1	3.306(3)
K1	S2	3.298(3)
K1	S2	3.594(2)
K1	S3	3.267(3)
K1	S3	3.620(3)
K1	S4	3.343(3)
K2	N3	2.863(5)
K2	N2	2.886(5)
K2	S1	3.316(3)
K2	S2	3.296(3)
K2	S2	3.509(3)
K2	S3	3.247(3)
K2	S3	3.546(3)
K2	S4	3.366(2)

N2	K2	2.886(5)
S1	K1	3.306(3)
S1	K2	3.316(3)
S2	K1	3.298(3)
S2	K1	3.594(2)
S2	K2	3.296(3)
S2	K2	3.509(3)
S3	K1	3.267(3)
S3	K1	3.620(3)
S3	K2	3.247(3)
S3	K2	3.546(3)
S4	K1	3.343(3)
S4	K2	3.366(2)
K1	S2	3.594(2)
K1	S2	3.298(3)
K1	S3	3.620(3)
K1	S3	3.267(3)
K2	S1	3.316(3)
K2	S2	3.296(3)
K2	S3	3.546(3)
K2	S2	3.509(3)
K2	S2	3.296(3)
K2	S3	3.247(3)

Atom1	Atom2	Atom3	Angle
N1	C1	S1	118.8(4)
N1	C1	S2	116.2(4)
S1	C1	S2	125.0(3)
H2	C2	N1	123.1
H2	C2	N2	123.1
N1	C2	N2	113.8(5)
H3	C3	C4	124.7
H3	C3	N2	124.6
C4	C3	N2	110.7(5)
C3	C4	H4	127.3
C3	C4	N1	105.4(5)
H4	C4	N1	127.3
N4	C5	S3	116.7(4)
N4	C5	S4	118.1(4)
S3	C5	S4	125.2(3)
H6	C6	N3	123.2

H6	C6	N4	123.3
N3	C6	N4	113.4(5)
H7	C7	C8	124.8
H7	C7	N3	124.7
C8	C7	N3	110.4(5)
C7	C8	H8	126.5
C7	C8	N4	107.0(5)
H8	C8	N4	126.5
N2	K1	N3	136.8(1)
N2	K1	S1	75.9(1)
N2	K1	S2	104.8(1)
N2	K1	S2	155.7(1)
N2	K1	S3	86.4(1)
N2	K1	S3	68.8(1)
N2	K1	S4	76.3(1)
N3	K1	S1	77.2(1)
N3	K1	S2	85.2(1)
N3	K1	S2	67.3(1)
N3	K1	S3	103.9(1)
N3	K1	S3	154.2(1)
N3	K1	S4	76.9(1)
S1	K1	S2	53.80(4)
S1	K1	S2	120.74(5)
S1	K1	S3	153.04(6)
S1	K1	S3	113.35(5)
S1	K1	S4	101.68(5)
S2	K1	S2	76.76(4)
S2	K1	S3	152.60(6)
S2	K1	S3	83.25(4)
S2	K1	S4	152.77(6)
S2	K1	S3	82.98(5)
S2	K1	S3	87.59(4)
S2	K1	S4	113.64(5)
S3	K1	S3	77.61(4)
S3	K1	S4	53.70(4)
S3	K1	S4	121.00(5)
N3	K2	N2	136.3(1)
N3	K2	S1	77.7(1)
N3	K2	S2	86.4(1)
N3	K2	S2	68.1(1)
N3	K2	S3	103.3(1)

N3	K2	S3	154.2(1)
N3	K2	S4	75.9(1)
N2	K2	S1	75.1(1)
N2	K2	S2	103.6(1)
N2	K2	S2	155.5(1)
N2	K2	S3	86.4(1)
N2	K2	S3	69.4(1)
N2	K2	S4	76.5(1)
S1	K2	S2	53.73(4)
S1	K2	S2	120.40(5)
S1	K2	S3	151.94(6)
S1	K2	S3	115.04(5)
S1	K2	S4	100.80(5)
S2	K2	S2	76.24(4)
S2	K2	S3	153.61(6)
S2	K2	S3	84.44(4)
S2	K2	S4	152.12(6)
S2	K2	S3	84.61(5)
S2	K2	S3	86.30(4)
S2	K2	S4	115.27(5)
S3	K2	S3	76.25(4)
S3	K2	S4	53.65(4)
S3	K2	S4	120.26(5)
C1	N1	C2	127.5(5)
C1	N1	C4	126.8(4)
C2	N1	C4	105.7(4)
C2	N2	C3	104.4(5)
C2	N2	K1	113.6(4)
C2	N2	K2	112.6(4)
C3	N2	K1	125.1(4)
C3	N2	K2	119.2(4)
K1	N2	K2	81.0(1)
C6	N3	C7	104.0(5)
C6	N3	K1	116.7(4)
C6	N3	K2	113.3(4)
C7	N3	K1	122.6(4)
C7	N3	K2	118.0(4)
K1	N3	K2	81.7(1)
C5	N4	C6	126.2(5)
C5	N4	C8	128.7(5)
C6	N4	C8	105.1(4)

C1	S1	K1	85.4(2)
C1	S1	K2	85.4(2)
K1	S1	K2	68.20(4)
C1	S2	K1	85.1(2)
C1	S2	K1	128.6(2)
C1	S2	K2	85.4(2)
C1	S2	K2	128.9(2)
K1	S2	K1	103.24(5)
K1	S2	K2	68.54(4)
K1	S2	K2	145.35(6)
K1	S2	K2	145.18(5)
K1	S2	K2	63.00(4)
K2	S2	K2	103.76(5)
C5	S3	K1	85.7(2)
C5	S3	K1	127.2(2)
C5	S3	K2	87.6(2)
C5	S3	K2	129.1(2)
K1	S3	K1	102.39(5)
K1	S3	K2	69.50(4)
K1	S3	K2	145.03(6)
K1	S3	K2	144.47(5)
K1	S3	K2	62.41(4)
K2	S3	K2	103.75(5)
C5	S4	K1	83.8(2)
C5	S4	K2	84.3(2)
K1	S4	K2	67.19(4)
S3	K1	S4	53.70(4)
S1	K1	S2	53.80(4)
S3	K1	S2	87.59(4)
S3	K1	S2	83.25(4)
S2	K1	S2	76.76(4)
S2	K1	S3	87.59(4)
S2	K1	S3	82.98(5)
S3	K1	S3	77.61(4)
S3	K2	S4	53.65(4)
N2	K2	S1	75.1(1)
N2	K2	S2	103.6(1)
N2	K2	S3	69.4(1)
S1	K2	S2	53.73(4)
S1	K2	S3	115.04(5)
S2	K2	S3	84.44(4)

S1	K2	S2	53.73(4)
S3	K2	S2	86.30(4)
S3	K2	S2	84.44(4)
S2	K2	S2	76.24(4)
S2	K2	S3	84.61(5)
K1	S1	K2	68.20(4)
K2	S2	K2	103.76(5)
K1	S2	K1	103.24(5)
K1	S2	K2	68.54(4)
K1	S2	K2	145.18(5)
K1	S2	K2	63.00(4)
K1	S2	K1	103.24(5)
K1	S2	K2	145.18(5)
K2	S2	K1	145.35(6)
K2	S2	K2	103.76(5)
K1	S2	K2	68.54(4)
K1	S3	K2	69.50(4)
K1	S3	K1	102.39(5)
K2	S3	K1	144.47(5)
K1	S3	K1	102.39(5)
K1	S3	K2	62.41(4)
K1	S3	K2	144.47(5)
K1	S3	K2	145.03(6)
K1	S3	K2	69.50(4)
K2	S3	K2	103.75(5)
K1	S4	K2	67.19(4)

Table S6. Bond lengths and angles for potassium pyrroledithiocarbamate (K[PyrDTC]).

Atom1	Atom2	Length (Å)
C1	N1	1.408(6)
C1	S1	1.712(4)
C1	S2	1.685(5)
C2	H2	0.931
C2	C3	1.347(6)
C2	N1	1.413(6)
C3	H3	0.930
C3	C4	1.432(8)
C4	H4	0.930
C4	C5	1.359(7)
C5	H5	0.930
C5	N1	1.415(6)
C6	K2	3.307(6)
C6	N2	1.404(7)
C6	S3	1.712(5)
C6	S4	1.693(5)
C7	H7	0.930
C7	C8	1.354(7)
C7	N2	1.403(6)
C8	H8	0.930
C8	C9	1.424(6)
C9	H9	0.930
C9	C10	1.354(7)
C10	H10	0.930
C10	N2	1.394(6)
K1	S1	3.161(4)
K1	S2	3.350(5)
K1	S2	3.213(4)
K1	S3	3.403(5)
K1	S3	3.240(5)
K1	S4	3.264(4)
K2	S2	3.153(5)
K2	S3	3.499(5)
K2	S4	3.156(3)
K2	S1	3.170(4)
K2	S1	3.220(4)
K2	S3	3.336(5)
S1	K2	3.170(4)
S1	K2	3.220(4)
S2	K1	3.213(4)
S3	K1	3.403(5)
S3	K1	3.240(5)

S3	K2	3.336(5)
S4	K1	3.264(4)
K1	S2	3.350(5)
K2	S3	3.499(5)
K2	S4	3.156(3)
K2	S1	3.170(4)
K2	S3	3.336(5)

Atom1	Atom2	Atom3	Angle (°)
N1	C1	S1	116.8(3)
N1	C1	S2	119.8(3)
S1	C1	S2	123.4(3)
H2	C2	C3	126.1
H2	C2	N1	126.1
C3	C2	N1	107.8(4)
C2	C3	H3	125.4
C2	C3	C4	109.2(4)
H3	C3	C4	125.4
C3	C4	H4	126.3
C3	C4	C5	107.3(5)
H4	C4	C5	126.3
C4	C5	H5	125.9
C4	C5	N1	108.3(4)
H5	C5	N1	125.8
K2	C6	N2	121.8(3)
K2	C6	S3	81.8(2)
K2	C6	S4	69.9(1)
N2	C6	S3	117.8(3)
N2	C6	S4	118.4(3)
S3	C6	S4	123.7(3)
H7	C7	C8	125.9
H7	C7	N2	125.9
C8	C7	N2	108.1(4)
C7	C8	H8	126.0
C7	C8	C9	108.0(4)
H8	C8	C9	126.0
C8	C9	H9	126.1
C8	C9	C10	107.8(4)
H9	C9	C10	126.0
C9	C10	H10	125.8
C9	C10	N2	108.5(4)
H10	C10	N2	125.8
S1	K1	S2	54.60(4)
S1	K1	S2	81.92(4)
S1	K1	S3	66.27(4)

S1	K1	S3	126.38(5)
S1	K1	S4	174.36(5)
S2	K1	S2	81.11(4)
S2	K1	S3	109.18(4)
S2	K1	S3	88.24(4)
S2	K1	S4	121.45(4)
S2	K1	S3	126.83(5)
S2	K1	S3	133.96(5)
S2	K1	S4	93.62(4)
S3	K1	S3	99.02(4)
S3	K1	S4	119.34(4)
S3	K1	S4	54.99(3)
C6	K2	S2	73.43(8)
C6	K2	S3	28.97(8)
C6	K2	S4	30.25(8)
C6	K2	S1	120.97(9)
C6	K2	S1	151.23(9)
C6	K2	S3	126.50(9)
S2	K2	S3	71.10(4)
S2	K2	S4	99.57(4)
S2	K2	S1	162.04(5)
S2	K2	S1	81.68(4)
S2	K2	S3	89.95(4)
S3	K2	S4	53.33(3)
S3	K2	S1	115.58(4)
S3	K2	S1	148.65(5)
S3	K2	S3	97.58(4)
S4	K2	S1	97.42(4)
S4	K2	S1	150.37(5)
S4	K2	S3	142.71(5)
S1	K2	S1	86.46(4)
S1	K2	S3	72.90(4)
S1	K2	S3	66.46(4)
C1	N1	C2	127.3(4)
C1	N1	C5	125.2(4)
C2	N1	C5	107.4(4)
C6	N2	C7	126.4(4)
C6	N2	C10	126.0(4)
C7	N2	C10	107.6(4)
C1	S1	K1	93.5(2)
C1	S1	K2	96.9(2)
C1	S1	K2	92.4(2)
K1	S1	K2	129.21(5)
K1	S1	K2	103.60(5)

K2	S1	K2	125.33(5)
C1	S2	K1	87.6(2)
C1	S2	K2	123.5(2)
C1	S2	K1	92.0(2)
K1	S2	K2	90.71(4)
K1	S2	K1	98.89(4)
K2	S2	K1	143.69(5)
C6	S3	K2	69.3(2)
C6	S3	K1	111.4(2)
C6	S3	K1	88.7(2)
C6	S3	K2	151.5(2)
K2	S3	K1	171.34(5)
K2	S3	K1	80.78(4)
K2	S3	K2	82.42(4)
K1	S3	K1	107.80(4)
K1	S3	K2	96.18(4)
K1	S3	K2	89.48(4)
C6	S4	K2	79.8(2)
C6	S4	K1	88.3(2)
K2	S4	K1	85.81(4)
S3	K1	S4	54.99(3)
S2	K1	S2	81.11(4)
S3	K2	S3	97.58(4)
S3	K2	S4	142.71(5)
S3	K2	S4	53.33(3)
S1	K2	S1	86.46(4)
S1	K2	S3	66.46(4)
S1	K2	S3	72.90(4)
K2	S1	K2	125.33(5)
K1	S2	K1	98.89(4)
K1	S3	K2	96.18(4)
K1	S3	K2	89.48(4)
K1	S3	K2	80.78(4)
K2	S3	K2	82.42(4)
K1	S4	K2	85.81(4)

Table S7. Experimental (black) and calculated (blue) important bond and angles of the DTC^- anions. The second value in the parentheses (red) is the calculated value for the conjugate acids DTCH.

DTC anion	N-CS_2 (Å)	$C_{(R1)}$-N-$C_{(R2)}$ (°)	S-C_1-S (°)
$ImDTC^-$	1.418 (1.435; 1.398)	105.4 (105.8; 105.8)	125.1 (125.6; 124.3)
$PyrDTC^-$	1.406 (1.421; 1.384)	107.5 (107.8; 107.9)	123.6 (124.2; 123.0)
$PDTC^-$	1.326 (1.349; 1.331)	111.0 (111.9; 111.4)	122.1 (122.3; 121.7)
$MorDTC^-$	1.341 (1.364; 1.341)	112.1 (111.4; 112.1)	119.8 (120.7; 119.9)
$DIDTC^-$	1.345 (1.362; 1.339)	113.4 (113.5; 114.3)	118.1 (118.1; 117.5)
$MeDTC^-$	- (1.358; 1.339)	- (117.4; 118.5)	- (121.9; 121.3)
$DMDTC^-$	- (1.359; 1.338)	- (113.9; 114.9)	- (120.5; 119.9)

Table S8. Selected chemical and spectroscopic data relevant to the dithiocarbamato anions.

DTC	pK_a (CA) [a]	pK_a (NH)*	λ_1, nm (ε, $M^{-1}cm^{-1}$)	λ_2, nm (ε, $M^{-1}cm^{-1}$)	λ_3, nm (ε, $M^{-1}cm^{-1}$)
$DIDTC^-$	11.07 [b]	36 [c]	261 (1.15 x 10^4)	286 (1.1 x 10^4)	-
$MorDTC^-$	8.5 [e]	-	263 (1.50 x 10^4)	286 (1.40 x 10^4)	-
$PDTC^-$	11.27 [b]	44 [f]	253 (1.40 x 10^4)	277 (1.30 x 10^4)	-
$PyrDTC^-$	-2	23 [f] (17.5)	-	297 (1.29 x 10^4)	343 (6.30 x 10^3)
$ImDTC^-$	7.0 [g]	18.6 [f] (14.5) [g]	255 (6.36 x 10^3)	280 (9.38 x 10^3)	353 (1.24 x 10^4)

[a]Conjugate acid of the amine; water, [b]ref.12; [c]ref.13; [d] value for diethylamine *; [e]ref.9; [f]ref.14; [g]ref 15; *Values measured in DMSO and water in parentheses.* IDTC *crystalline structure was solved as a potassium complex formed by two asymmetric unity of the dithiocarbamate.*

Table S9. Calculated E_{rot} for rotation around DTC C-N bonds and HOMO orbital composition of several deprotonated (DTC^-) and protonated (DTCH) aliphatic DTCs at the ground state (GS) and rotation transition state (TS_{rot}). DFT calculations at a PCM(water)/B3LYP/6-31+G(d,p) level of theory.

DTC	*N** [a]	N-C (Å) (GS)	N-C (Å) (TS)	HOMO (%)(GS)	HOMO (%) (TS)	E_{rot} (kJ/mol)
$DIDTC^-$	14.68	1.363	1.431	CS_2 (95) N (0)	CS_2 (87) N (10)	70.6
DIDTCH		1.339	1.408	CS_2 (98) N (0)	CS_2 (50) N (38)	75.6
$MorDTC^-$	15.62	1.364	1.453	CS_2 (96) N (0)	CS_2 (94) N (4)	60.2
MorDTCH		1.341	1.454	CS_2 (100) N (0)	CS_2 (82) N (15)	67.8
$PDTC^-$	17.21	1.349	1.444	CS_2(95) N (0)	CS_2 (95) N (3)	83.4
PDTCH		1.331	1.421	CS_2(99) N (0)	CS_2 (83) N (15)	92.4

*Mayr nucleophilicity parameter for the secondary amine (*ref.50*); [a]value for diethylamine.

Table S10. Calculated E_{rot} for rotation around DTC C-N bonds and HOMO orbital composition of several deprotonated (DTC^-) and protonated (DTCH) aromatic DTCs at the ground state (GS) and rotation transition state (TS_{rot}). DFT calculations at a PCM(water)/B3LYP/6-31+G(d,p) level of theory.

DTC	N-C (Å) (GS)	N-C (Å) (TS_{rot})	HOMO (%) (GS)	HOMO (%) (TS_{rot})	E_{rot} (kJ/mol)
$PyrDTC^-$	1.421	1.455	CS_2 (94); N (0)	CS_2 (96); N (1)	29.48
PyrDTCH	1.384	1.426	CS_2 (95); N (0)	CS_2 (2); N (0)	37.9
$ImDTC^-$	1.435	1.462	CS_2 (96); N (1)	CS_2 (97); N (1)	22.3
ImDTCH (SH)[a]	1.398	1.434	CS_2 (94); N (0)	CS_2 (8); N (4)	25.6
ImDTCH (NH)[b]	1.483	1.492	CS_2 (94); N (2)	CS_2 (98); N (1)	15.4

[a] S protonated. [b] N protonated

Table S11. DFT calculated Cartesian coordinates (x, y, z) of anions DTC^-, their conjugate acids DTCH and rotational transition states (TS_{rot}). (PCM-model, water) - B3LYP/6-31+G(d,p). The transition state geometries were optimized with the QST3 keyword using three geometries: 1) the DTCs and DTCHs initial geometries (syn), 2) the higher energy geometry (TS guess) taken from the potential energy surface (PES) generated by scanner the dihedral angle (see Figure S14), 3) a lower energy geometry (no imaginary frequency) from the potential energy surface (PES).

Table 11a. DTC^- (Syn geometry); E(B3LYP) = -1126.49471861 a.u.

N	0.28121800	-0.01644900	-0.00005200
C	0.72681000	1.41485900	0.00018300
H	1.81490400	1.33702900	0.00007800
C	1.41214200	-0.99264500	-0.00017600
H	0.93095700	-1.96895700	-0.00039200
C	2.25607800	-0.89546700	1.27862900
H	1.62766100	-1.00322500	2.16844700
H	2.99269500	-1.70610200	1.28373600
H	2.80743800	0.04772800	1.35792800
C	2.25622100	-0.89497300	-1.27884700
H	2.99284300	-1.70560200	-1.28417800
H	1.62790400	-1.00239800	-2.16877700
H	2.80758600	0.04825500	-1.35772700
C	0.37127500	2.18000000	1.28412200
H	0.67236300	1.61172000	2.16995300
H	0.91932200	3.12933600	1.28999600
H	-0.69651700	2.38926200	1.34819200
C	0.37104900	2.18048600	-1.28340400
H	0.67197600	1.61254200	-2.16950400
H	-0.69675400	2.38977600	-1.34720400
H	0.91909800	3.12982300	-1.28901800
C	-1.01408500	-0.44039400	-0.00012500
S	-1.38745100	-2.15628900	-0.00024600
S	-2.33985800	0.68721200	0.00003000

Table 11b. DTC^- (Anti geometry); E(B3LYP) = -1126.49471876 a.u.

N	-0.28129900	-0.01630400	-0.00007200
C	-0.72597900	1.41538000	0.00011600
H	-1.81411000	1.33794400	0.00023600
C	-1.41242800	-0.99227100	-0.00004400
H	-0.93131200	-1.96863700	-0.00038100
C	-2.25658900	-0.89423300	-1.27857400
H	-1.62833100	-1.00187200	-2.16850700
H	-2.99344100	-1.70466500	-1.28378300
H	-2.80761200	0.04920600	-1.35734500
C	-2.25620000	-0.89499700	1.27882100
H	-2.99273600	-1.70570800	1.28400200
H	-1.62759800	-1.00274100	2.16850100
H	-2.80758600	0.04816300	1.35817600
C	-0.37061800	2.18083700	-1.28367400
H	-0.67200400	1.61280800	-2.16955900
H	-0.91857400	3.13023100	-1.28916700
H	0.69718400	2.38989900	-1.34795700
C	-0.37010200	2.18053700	1.28394400
H	-0.67160400	1.61254500	2.16980500
H	0.69781000	2.38912700	1.34798200
H	-0.91757900	3.13020600	1.28965600
C	1.01382400	-0.44075800	-0.00039400
S	2.34016700	0.68622300	0.00004800
S	1.38640400	-2.15680700	-0.00019400

Table 11c. DTC^- (TS_{rot} geometry); E(B3LYP) = -1126.46782243 a.u.

N	0.31355500	-0.06182500	-0.28008600
C	0.85729700	1.30918700	-0.35555500
H	1.91121900	1.16563700	-0.61699600
C	1.23349100	-1.18600500	0.01092400
H	0.58070100	-2.05657100	0.14054700
C	2.06275300	-1.03905900	1.30155000
H	1.41525500	-0.84779400	2.16098200
H	2.62590300	-1.96088100	1.48916100
H	2.78765100	-0.22112100	1.22110800
C	2.14322000	-1.48265100	-1.19465000
H	2.75579200	-2.36996200	-0.99713600
H	1.54704200	-1.66547800	-2.09354100
H	2.82762000	-0.65174700	-1.40039000
C	0.82927800	2.15315700	0.93772000
H	1.26479700	1.61726800	1.78355000
H	1.40717300	3.07164600	0.77694900
H	-0.19150400	2.43694900	1.20873900
C	0.21537900	2.09916900	-1.50884000
H	0.32327000	1.56510000	-2.45750700
H	-0.85298400	2.26162400	-1.33015000
H	0.69269900	3.08110700	-1.60440400
C	-1.05661400	-0.28426200	0.07209400
S	-2.11566900	-0.74661700	-1.19658000

Table 11d. DIDTCH (Syn geometry); E(B3LYP) = -1126.94931321 a.u.

N	0.30455200	-0.00610600	-0.00009700
C	0.88385400	1.38378900	0.00019500
H	1.95847700	1.20240500	0.00016300
C	1.32887800	-1.10200700	-0.00029900
H	0.77882700	-2.04247000	-0.00057800
C	2.17273400	-1.08569300	1.28114000
H	1.53616000	-1.12542200	2.16960000
H	2.82222300	-1.96630200	1.28591700
H	2.81471600	-0.20263900	1.34971100
C	2.17292800	-1.08512800	-1.28160300
H	2.82234900	-1.96578500	-1.28668700
H	1.53649200	-1.12440100	-2.17018300
H	2.81499900	-0.20210100	-1.34966400
C	0.58093900	2.16509300	1.28571400
H	0.82814300	1.57172400	2.17092700
H	1.20495400	3.06502000	1.29704700
H	-0.46487300	2.46688600	1.34556300
C	0.58088900	2.16556600	-1.28501800
H	0.82848300	1.57269800	-2.17045500
H	-0.46503700	2.46696600	-1.34489200
H	1.20452600	3.06576000	-1.29583500
C	-1.01088400	-0.25908100	-0.00002900
S	-1.47319200	-2.01278600	-0.00020800

S	-1.57172800	-0.15402200	1.70284400

S	-2.26551800	0.88166500	0.00018000
H	-2.78898700	-1.73689400	-0.00011300

Table 11e. DIDTCH (Anti geometry); E(B3LYP) = -1126.94915774 a.u.

N	0.32591500	-0.02162600	0.00002600
C	0.69341100	1.43816700	0.00023800
H	1.78215700	1.41496300	0.00061300
C	1.50088000	-0.95600400	0.00018600
H	1.06098600	-1.95129900	-0.00009500
C	2.33116700	-0.81154700	1.28131800
H	1.70635100	-0.94304800	2.16976900
H	3.10040800	-1.59017500	1.28939600
H	2.84208700	0.15395600	1.35355800
C	2.33189300	-0.81116700	-1.28043100
H	3.10110900	-1.58982200	-1.28829900
H	1.70758600	-0.94238900	-2.16928000
H	2.84290100	0.15433300	-1.35209700
C	0.28953000	2.17391200	1.28760000
H	0.59450400	1.60794800	2.17203900
H	0.80657400	3.13856500	1.30632500
H	-0.78181300	2.36987500	1.35384000
C	0.29033700	2.17393900	-1.28735200
H	0.59640800	1.60827700	-2.17160400
H	-0.78105700	2.36930900	-1.35451400
H	0.80687500	3.13887600	-1.30546200
C	-0.91715700	-0.52548800	-0.00021900
S	-2.28042600	0.64879200	-0.00025000
S	-1.31785000	-2.18391800	-0.00049000
H	-3.21443000	-0.31683600	-0.00057200

Table 11f. DIDTCH (TS_{rot} geometry); E(B3LYP) = -1126.92052942 a.u.

N	0.33112900	-0.03135300	-0.27222000
C	0.87220900	1.35632100	-0.21342200
H	1.92459100	1.23610200	-0.48609500
C	1.26525100	-1.18606200	-0.10376400
H	0.61559200	-2.06711400	-0.06250300
C	2.09221900	-1.15703700	1.19156800
H	1.44858800	-1.05992600	2.06975700
H	2.65887400	-2.09013300	1.28310100
H	2.81245100	-0.33197300	1.19071300
C	2.15740000	-1.33719100	-1.34434300
H	2.77320800	-2.23809000	-1.24984100
H	1.55026600	-1.42502800	-2.24993100
H	2.83632700	-0.48621200	-1.46454100
C	0.82409900	2.04653500	1.16192200
H	1.26754800	1.43039800	1.94657600
H	1.38596800	2.98577900	1.10576600
H	-0.20152900	2.28779600	1.45593000
C	0.21962400	2.24134800	-1.28538500
H	0.31202900	1.78880800	-2.27693300
H	-0.84389000	2.40209600	-1.07767900
H	0.70561600	3.22255600	-1.30408500
C	-0.99235600	-0.27796200	0.13769700
S	-2.00003600	-0.55644100	-1.29010600
S	-1.56365500	-0.36500400	1.69213300
H	-3.17514900	-0.80817500	-0.67276400

Table 11g. MorDTC$^-$ (Syn geometry); E(B3LYP) = -1121.87417563 a.u.

N	-0.11044100	-0.00000300	0.26479500
C	-0.90767400	1.21466900	0.48976400
C	-2.18702800	1.17491200	-0.34242600
O	-2.95740200	-0.00003500	-0.07819300
C	-2.18695600	-1.17489700	-0.34264400
C	-0.90763500	-1.21474800	0.48959200
H	-1.16186700	-1.27548500	1.55772500
H	-0.30956300	-2.08460500	0.22403400
H	-0.30964200	2.08459900	0.22427700
H	-1.16182400	1.27527900	1.55790700
H	-2.82197700	2.02836200	-0.09146200
H	-1.93863800	1.21944200	-1.41406100
H	-1.93852900	-1.21918100	-1.41428000
H	-2.82187900	-2.02845900	-0.09189300
C	1.23391300	0.00004100	0.03137800
S	2.08211600	1.51284200	-0.11677200
S	2.08216500	-1.51281100	-0.11661900

Table 11h. MorDTC$^-$ (Anti geometry); E(B3LYP) = -1121.87417600 a.u.

N	-0.11033700	-0.00015000	0.26764100
C	-0.90816800	1.21433200	0.49213200
C	-2.18567800	1.17506100	-0.34282700
O	-2.95658600	0.00002300	-0.08052700
C	-2.18575300	-1.17485100	-0.34388700
C	-0.90801200	-1.21498500	0.49080400
H	-1.16448800	-1.27552900	1.55839400
H	-0.30958400	-2.08501200	0.22658900
H	-0.30974300	2.08472300	0.22917900
H	-1.16491800	1.27344900	1.55974500
H	-2.82109900	2.02856400	-0.09325600
H	-1.93510200	1.21965500	-1.41392400
H	-1.93549500	-1.21871800	-1.41508200
H	-2.82121300	-2.02844600	-0.09473500
C	1.23356500	0.00005000	0.03200600
S	2.08179500	-1.51274700	-0.11693000
S	2.08139100	1.51303100	-0.11779200

Table 11i. MorDTC$^-$ (TS_{rot} geometry); E(B3LYP) = -1121.85123666 a.u.

N	-0.13509600	-0.28800900	0.00034500
C	-0.82302000	0.19727700	-1.20748500
C	-2.27153900	-0.28056700	-1.18025200
O	-2.94645500	0.16869200	-0.00027200
C	-2.27170700	-0.27834900	1.18061200
C	-0.82312900	0.19945100	1.20720000
H	-0.79571500	1.30029500	1.27196800
H	-0.32123400	-0.20809200	2.09119400
H	-0.32091100	-0.21169400	-2.09069300

Table 11j. MorDTCH (Syn geometry); E(B3LYP) = -1122.32363538 a.u.

N	0.14314700	0.03424300	0.28162400
C	0.91244700	-1.20781500	0.49147900
C	2.18696400	-1.18671900	-0.35416400
O	2.97490900	-0.03158200	-0.07858300
C	2.23769000	1.16080800	-0.35236700
C	0.96751900	1.24025800	0.49118200
H	1.22349800	1.29458300	1.55671400
H	0.38227600	2.11812700	0.22365000
H	0.31960700	-2.08096500	0.22147600

H	-0.79576500	1.29801200	-1.27410900
H	-2.82586300	0.12950500	-2.02862100
H	-2.30741500	-1.37968000	-1.22778600
H	-2.30762100	-1.37736700	1.23024700
H	-2.82608800	0.13339500	2.02813300
C	1.29734600	-0.04143500	0.00010400
S	2.28024800	-1.43003300	0.00086900
S	1.86789100	1.56777600	-0.00097100

Table 11k. MorDTCH (Anti geometry); E(B3LYP) = -1122.32363548 a.u.

N	0.14312300	0.03432600	0.28076900
C	0.91247900	-1.20756900	0.49143200
C	2.18756000	-1.18678300	-0.35330800
O	2.97520000	-0.03146300	-0.07767500
C	2.23801400	1.16068000	-0.35257500
C	0.96727300	1.24054800	0.49009900
H	1.22246800	1.29570400	1.55576600
H	0.38218100	2.11821000	0.22151600
H	0.31989800	-2.08090000	0.22145900
H	1.16540500	-1.27697400	1.55637600
H	2.80107400	-2.05685400	-0.10953200
H	1.93000300	-1.21941400	-1.42220000
H	1.98574600	1.20338600	-1.42231100
H	2.89254300	2.00045800	-0.10935400
C	-1.17561200	0.09533400	0.04343400
S	-1.99625500	-1.49986100	-0.09424400
S	-2.07129800	1.52290600	-0.11926200
H	-3.20023000	-0.95418000	-0.33411100

Table 11m. MorDTCH (TS_{rot} geometry, boat conformation); E(B3LYP) = -1122.29059003 a.u.

N	-0.01488700	-0.76852000	0.00079400
C	-0.84235200	-0.79240800	1.22965500
C	-2.01041600	0.19295400	1.18282400
O	-2.79529000	-0.00735200	-0.00033200
C	-2.00989800	0.19093400	-1.18359200
C	-0.84185200	-0.79442400	-1.22835400
H	-1.23591100	-1.81397500	-1.32290900
H	-0.20439100	-0.59866900	-2.09468300
H	-0.20525200	-0.59534700	2.09593400
H	-1.23655400	-1.81177600	1.32559800
H	-2.67951300	0.02282800	2.03096400
H	-1.65009900	1.23002900	1.21593200
H	-1.64971500	1.22799100	-1.21821500
H	-2.67869900	0.01928000	-2.03165600
C	1.09837100	0.11149600	0.00025300
S	2.55295500	-0.87906100	0.00033300
S	1.08272200	1.76635300	-0.00086600
H	3.47270500	0.11010700	-0.00005500

Table 11o. PDTC$^-$ (Anti geometry); E(B3LYP) = -1046.66557228 a.u.

C	-2.60956900	-0.70307100	0.30892100
C	-2.60980500	0.70268600	-0.30817600
C	-1.19890700	1.21922500	-0.00323800
C	-1.19895300	-1.21965600	0.00264600
H	-2.75917300	-0.64029100	1.39318300
H	-3.38333700	-1.35798800	-0.10077400

H	1.16604100	-1.27758600	1.55621900
H	2.80062100	-2.05694600	-0.11129900
H	1.92859500	-1.21879300	-1.42287600
H	1.98482300	1.20419500	-1.42193200
H	2.89243700	2.00037300	-0.10898800
C	-1.17552500	0.09537900	0.04414200
S	-1.99613200	-1.49975200	-0.09429000
S	-2.07097000	1.52303600	-0.11967300
H	-3.20013800	-0.95403600	-0.33390300

Table 11l. MorDTCH (TS_{rot} geometry, chair conformation); E(B3LYP) = -1122.29780872 a.u.

N	-0.15515500	0.23559100	-0.00024100
C	-0.85494000	-0.23238700	1.21804300
C	-2.29402300	0.27065300	1.17921400
O	-2.96915100	-0.17487700	-0.00001300
C	-2.29379100	0.26936000	-1.17958900
C	-0.85505600	-0.23458800	-1.21759400
H	-0.84168700	-1.33378600	-1.27787600
H	-0.34549500	0.16930500	-2.09737400
H	-0.34570900	0.17391000	2.09691600
H	-0.84074300	-1.33143200	1.28087400
H	-2.85397800	-0.12730600	2.02892100
H	-2.31083700	1.36978700	1.22285600
H	-2.30984400	1.36847700	-1.22392400
H	-2.85394000	-0.12878900	-2.02907800
C	1.24234000	-0.05337800	0.00002500
S	2.11409600	1.46779600	-0.00072100
S	1.91750600	-1.56131300	0.00072900
H	3.36870000	0.96802300	-0.00023800

Table 11n. PDTC$^-$ (Syn geometry); E(B3LYP) = -1046.66557228 a.u.

C	-2.60982400	0.70285600	0.30864200
C	-2.60988100	-0.70288800	-0.30851800
C	-1.19911400	-1.21952300	-0.00304100
C	-1.19909400	1.21945700	0.00294700
H	-3.38349500	1.35784200	-0.10126700
H	-2.75980100	0.64002700	1.39286900
H	-2.76002100	-0.64005400	-1.39272200
H	-3.38350400	-1.35785800	0.10150600
H	-1.14713100	-1.70495000	0.98005900
H	-0.82281900	-1.93032700	-0.74098300
H	-0.82267800	1.93028000	0.74081100
H	-1.14724300	1.70484500	-0.98018000
N	-0.36150900	-0.00003800	-0.00008200
C	0.98819600	-0.00001400	-0.00012900
S	1.82931800	-1.52451900	0.07530900
S	1.82915500	1.52459000	-0.07524300

Table 11p. PDTC$^-$ (TS_{rot} geometry); E(B3LYP) = -1046.63382496 a.u.

C	-2.60981800	-0.20213300	-0.77851600
C	-2.60982000	-0.20135900	0.77866000
C	-1.15382100	0.11576900	1.16759700
C	-1.15382900	0.11453600	-1.16778100
H	-2.90801900	-1.18226600	-1.16232300
H	-3.29791200	0.53827500	-1.19730900

H	-3.38319000	1.35767600	0.10212100
H	-2.76038800	0.63979200	-1.39230100
H	-0.82318100	1.93005500	-0.74147400
H	-1.14637300	1.70467200	0.97984000
H	-1.14749900	-1.70503400	-0.98052300
H	-0.82238200	-1.93044500	0.74044200
N	-0.36141500	-0.00018100	-0.00075800
C	0.98811200	0.00002500	-0.00023900
S	1.82959800	-1.52421000	-0.07509000
S	1.82853700	1.52468300	0.07542200

Table 11q. PDTCH (Syn geometry); E(B3LYP) = -1047.11719676 a.u.

C	2.62250400	-0.72720000	0.30054900
C	2.65532300	0.68877200	-0.29497900
C	1.25813600	1.23975200	0.00940300
C	1.20215300	-1.21031300	-0.01506100
H	3.37854600	-1.39220200	-0.12314000
H	2.77059800	-0.68862200	1.38507600
H	2.81237000	0.64182600	-1.37811800
H	3.43993800	1.31584700	0.13475700
H	1.20336700	1.71048500	0.99801500
H	0.89309900	1.95748800	-0.72751400
H	0.81787100	-1.92040100	0.72183500
H	1.13970900	-1.66767700	-1.00991500
N	0.39455400	0.03540000	0.00245600
C	-0.93510800	0.09368800	0.00535200
S	-1.73657800	-1.51333100	-0.06661700
S	-1.82938100	1.53157600	0.06564500
H	-2.98007400	-1.00466900	-0.03421400

Table 9s. PDTCH (TS geometry); E(B3LYP) = -1047.08200641 a.u.

C	-2.63347200	-0.18905900	-0.77838200
C	-2.63331100	-0.19057500	0.77828600
C	-1.18706700	0.15216400	1.17662800
C	-1.18714500	0.15391900	-1.17641700
H	-2.91344100	-1.17354200	-1.16296000
H	-3.33260900	0.54043600	-1.19613500
H	-2.91271400	-1.17595500	1.16101100
H	-3.33270700	0.53775400	1.19762400
H	-1.06331700	1.23586600	1.32454800
H	-0.84368000	-0.36390000	2.07706600
H	-1.06320200	1.23779600	-1.32281200
H	-0.84389500	-0.36095700	-2.07758400
N	-0.40520700	-0.30331300	-0.00026600
C	0.97038800	0.05202500	-0.00003900
S	1.91877000	-1.42498500	-0.00054900
S	1.58237200	1.58993300	0.00059800
H	3.14738000	-0.86431900	-0.00014600

Table 11u. PyrDTC$^-$ (Anti geometry); E(B3LYP) = -1044.22918841 a.u.

C	-1.33571700	1.12880100	0.05434500
C	-2.64247900	0.71793800	0.03627500
C	-1.33573800	-1.12849600	-0.05466000
N	-0.51254800	0.00015300	-0.00049900
H	-0.89936000	2.11173600	0.10531200
H	-3.50707400	1.36725300	0.07173100
H	-0.89941500	-2.11142500	-0.10626800
C	0.90932500	-0.00001600	-0.00103500
S	1.70850800	-1.51016600	0.03487000

H	-2.90796800	-1.18112600	1.16345800
H	-3.29793800	0.53943000	1.19672900
H	-1.01698800	1.19976400	1.31641600
H	-0.82103100	-0.39922100	2.07433700
H	-1.01690200	1.19835500	-1.31774200
H	-0.82100800	-0.40145400	-2.07393600
N	-0.38469600	-0.35953500	0.00018700
C	1.02681100	-0.04132400	0.00000100
S	1.52639200	1.59479700	-0.00038400
S	2.08507700	-1.37654400	0.00033900

Table 11r. PDTCH (Anti geometry); E(B3LYP) = -1047.11719675 a.u.

C	-2.65540300	0.68871200	-0.29475800
C	-2.62240700	-0.72727800	0.30074400
C	-1.20217700	-1.21035200	-0.01536700
C	-1.25811600	1.23969500	0.00921800
H	-2.81283200	0.64185800	-1.37784200
H	-3.43986400	1.31574500	0.13531300
H	-3.37858600	-1.39228300	-0.12268700
H	-2.77016200	-0.68868200	1.38532700
H	-0.81774400	-1.92074800	0.72114300
H	-1.14005900	-1.66736700	-1.01041700
H	-1.20309800	1.71066900	0.99769200
H	-0.89323300	1.95727000	-0.72794600
N	-0.39456400	0.03531600	0.00233100
C	0.93510600	0.09367600	0.00540200
S	1.73673300	-1.51326300	-0.06657600
S	1.82922400	1.53164600	0.06565400
H	2.98018500	-1.00452600	-0.03358000

Table 9t. PyrDTC$^-$ (Syn geometry); E(B3LYP) = -1044.22918859 a.u.

C	1.33574700	-1.12860000	0.05514000
C	2.64248700	-0.71779200	0.03631300
C	1.33573800	1.12859100	-0.05509300
N	0.51256100	-0.00001200	-0.00001100
H	0.89948000	-2.11149300	0.10715400
H	3.50710500	-1.36704100	0.07194700
H	0.89945200	2.11148500	-0.10704200
C	-0.90933500	-0.00000400	-0.00001100
S	-1.70891200	-1.50994000	-0.03535800
S	-1.70882500	1.50997200	0.03535600
C	2.64248600	0.71774600	-0.03634200
H	3.50710400	1.36697000	-0.07198900

Table 11v. PyrDTC$^-$ (TSr_{ot} geometry); E(B3LYP) = -1044.21795875 a.u.

C	1.30959300	0.00016100	-1.12394000
C	2.63109400	0.00011500	-0.71320900
C	1.30939900	-0.00011400	1.12387700
N	0.51152100	0.00002500	-0.00011200
H	0.86995300	0.00028600	-2.11052300
H	3.49381000	0.00023500	-1.36596600
H	0.86956600	-0.00022000	2.11037100
C	-0.94437200	0.00000000	-0.00006900
S	-1.68529000	1.52199400	0.00009800

S	1.70920500	1.50985300	-0.03443800
C	-2.64249600	-0.71766400	-0.03552100
H	-3.50709900	-1.36698700	-0.07061700

S	-1.68519200	-1.52203900	-0.00008000
C	2.63097700	-0.00009700	0.71339300
H	3.49358000	-0.00013400	1.36630100

Table 11x. PyrDTCH (Syn geometry); E(B3LYP) = -1044.66900285 a.u.

C	1.33665300	-1.12502400	0.05350800
C	2.64559200	-0.74448300	0.03103800
C	1.39691500	1.14772400	-0.04800300
N	0.53965200	0.03501500	0.00490100
H	0.89739400	-2.10791700	0.11168000
H	3.49442100	-1.41325700	0.06148300
H	0.98688800	2.14241400	-0.09559000
C	-0.84343000	0.09854700	0.00426100
S	-1.62368200	-1.49887400	-0.03620200
S	-1.69923400	1.52266400	0.03030400
C	2.68310000	0.69569100	-0.03475600
H	3.56735200	1.31659300	-0.06969300
H	-2.86992700	-0.99831800	0.01589300

Table 11z. PyrDTCH (Anti geometry); E(B3LYP) = -1044.66900297 a.u.

C	1.39676800	1.14764700	-0.05025300
C	2.68291000	0.69562900	-0.03618600
C	1.33665900	-1.12506100	0.05569700
N	0.53964200	0.03490100	0.00537600
H	0.98651900	2.14215300	-0.10017200
H	3.56716900	1.31642100	-0.07259100
H	0.89736900	-2.10778700	0.11660300
C	-0.84339900	0.09848400	0.00462700
S	-1.62374700	-1.49877500	-0.03780500
S	-1.69898700	1.52270400	0.03159400
C	2.64552600	-0.74445400	0.03234900
H	3.49444600	-1.41305800	0.06401700
H	-2.87004500	-0.99837500	0.01648600

Table 11aa. PyrDTCH (TS_{rot} geometry); E(B3LYP) = -1044.65456892 a.u.

C	1.34145200	0.02560300	1.13224200
C	2.65421300	0.00386200	0.71442600
C	1.34143300	0.02480600	-1.13224500
N	0.53891100	0.03667800	-0.00000800
H	0.90116400	0.03766100	2.11801500
H	3.51818700	-0.01063400	1.36454900
H	0.90112800	0.03620100	-2.11801900
C	-0.88855000	0.09707600	0.00004200
S	-1.56286800	-1.52153900	0.00021000
S	-1.71000900	1.51673500	-0.00024600
C	2.65420300	0.00338600	-0.71443200
H	3.51816400	-0.01140700	-1.36456400
H	-2.86151000	-1.16011300	0.00047100

Table 11bb. ImDTC$^-$ (Syn geometry); E(B3LYP) = -1060.27988825 a.u.

C	1.36603000	1.11404900	0.08205700
C	2.63884000	0.62114600	0.04608900
C	1.35197500	-1.09658900	-0.07965200
N	0.52095600	0.00700400	0.00319500
H	0.97375200	2.11326700	0.15848100
H	3.56669400	1.17428700	0.08973600
H	0.95156500	-2.09445200	-0.15706500
N	2.62235400	-0.76546600	-0.05881000
C	-0.91478900	0.00730700	0.00080300
S	-1.69520300	-1.50474500	0.04820000
S	-1.68901700	1.51978500	-0.04805200

Table 11cc. ImDTC$^-$ (Anti geometry); E(B3LYP) = -1060.27988826 a.u.

C	-1.36611100	1.11412600	0.08033500
C	-2.63893600	0.62112100	0.04497500
C	-1.35192300	-1.09674900	-0.07777300
N	-0.52098700	0.00699500	0.00319900
H	-0.97387800	2.11350700	0.15524400
H	-3.56686700	1.17424200	0.08748000
H	-0.95168400	-2.09484100	-0.15342400
N	-2.62235200	-0.76563700	-0.05758600
C	0.91489800	0.00730000	0.00081500
S	1.68890100	1.51987400	-0.04702200
S	1.69536300	-1.50469900	0.04710200

Table 11dd. ImDTC$^-$ (TS geometry); E(B3LYP) = -1060.27139834 a.u.

C	1.34202100	-0.00032400	1.11344200
C	2.62673700	-0.00019100	0.62086300
C	1.33057000	0.00034600	-1.09400100
N	0.51893000	0.00001000	0.00412700
H	0.94370700	-0.00070500	2.11630200
H	3.55171500	-0.00034900	1.18072100
H	0.93258500	0.00066800	-2.09883300
N	2.61176200	0.00022300	-0.75932800
C	-0.94326300	-0.00001000	0.00661200
S	-1.67123300	1.52462600	0.00665800
S	-1.67122000	-1.52463700	0.00626200

Table 11ee. ImDTCH (NH) (Syn geometry); E(B3LYP) = -1060.73176784 a.u.

C	-1.30734800	-1.14324200	0.11760100
C	-2.59692700	-0.71343400	0.07326800
C	-1.27809600	1.06406400	-0.11032900
N	-0.48987700	-0.02008400	0.00364000
H	-0.88897700	-2.12897400	0.22122200
H	-3.52817500	-1.25225300	0.13255100
H	-0.92844800	2.07692400	-0.21682600
N	-2.54619400	0.66235500	-0.07095100
C	0.99331500	-0.00074100	0.00095600

Table 11ff. ImDTCH (NH) (Anti geometry); E(B3LYP) = -1060.73176756 a.u.

C	-1.36611100	1.11412600	0.08033500
C	-2.63893600	0.62112100	0.04497500
C	-1.35192300	-1.09674900	-0.07777300
N	-0.52098700	0.00699500	0.00319900
H	-0.97387800	2.11350700	0.15524400
H	-3.56686700	1.17424200	0.08748000
H	-0.95168400	-2.09484100	-0.15342400
N	-2.62235200	-0.76563700	-0.05758600
C	0.91489800	0.00730000	0.00081500

S	1.70537200	1.52534300	0.07022600
S	1.73688900	-1.50752800	-0.07094900
H	-3.34375000	1.28348500	-0.14318200

Table 11gg. ImDTCH (NH) (TS geometry); E(B3LYP) = -1060.72592113 a.u.

C	1.28104600	-0.00033000	1.13962300
C	2.57747500	-0.00024900	0.71342600
C	1.26038300	0.00070000	-1.07553300
N	0.48080500	0.00032600	0.00778500
H	0.86002700	-0.00059700	2.13146000
H	3.50507600	-0.00027100	1.26157700
H	0.92215800	0.00116900	-2.09913700
N	2.53493200	0.00045500	-0.66588300
C	-1.01209400	-0.00003100	-0.00335800
S	-1.69958800	1.53105900	-0.00117400
S	-1.69882400	-1.53145500	-0.00174700
H	3.33630900	0.00002800	-1.28541400

Table 11ii. ImDTCH (SH) (Anti geometry); E(B3LYP) = -1060.71497685 a.u.

C	1.36775300	1.10682100	0.13866200
C	2.64637100	0.64556500	0.07128800
C	1.41303600	-1.10884200	-0.12611900
N	0.54713100	-0.02474600	0.01504000
H	0.97340600	2.09916900	0.28407300
H	3.56059100	1.21718300	0.13841400
H	1.03715000	-2.11182500	-0.25338600
N	2.66297600	-0.73783900	-0.09909900
C	-0.84938400	-0.09164100	0.01065100
S	-1.60659100	1.50483400	-0.08435100
S	-1.68383800	-1.51783500	0.07473200
H	-2.86168200	1.03016500	0.00631600

S	1.68890100	1.51987400	-0.04702200
S	1.69536300	-1.50469900	0.04710200

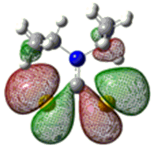
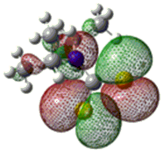
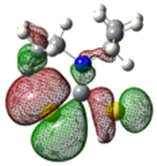
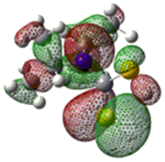
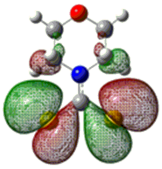
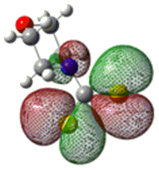
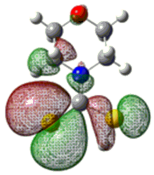
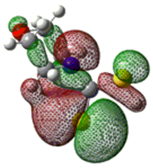
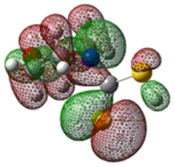
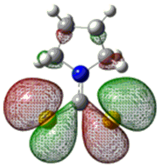
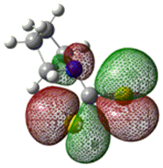
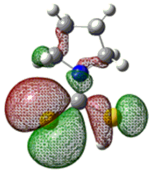
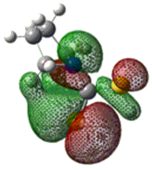
Table 11hh. ImDTCH (SH) (Syn geometry); E(B3LYP) = -1060.71477842 a.u.

C	1.42522200	1.12158000	0.14698100
C	2.67793500	0.59352700	0.08582100
C	1.35743300	-1.08876600	-0.15134500
N	0.54853300	0.03987200	-0.00078100
H	1.06031400	2.12450600	0.28855200
H	3.62104800	1.11371600	0.16872900
H	0.94868800	-2.07540300	-0.31194800
N	2.62509200	-0.78669000	-0.10623500
C	-0.84848000	0.10497700	-0.00778600
S	-1.61441400	-1.48914400	0.09723900
S	-1.67657100	1.53221400	-0.08366100
H	-2.86231500	-1.01213500	-0.05550100

Table 11jj. ImDTCH (SH) (TS_{rot} geometry); E(B3LYP) = -1060.70500598 a.u.

C	-1.37453100	0.03247900	-1.12062200
C	-2.65203000	0.00663400	-0.62227900
C	-1.36480100	0.01075500	1.10288600
N	-0.54723200	0.03341700	-0.00449300
H	-0.97614100	0.05242400	-2.12300200
H	-3.57758000	-0.00298200	-1.18005500
H	-0.96474000	0.01149300	2.10675200
N	-2.63516600	-0.00662900	0.75970400
C	0.88581000	0.09648900	-0.00705800
S	1.55739200	-1.52092900	-0.01189600
S	1.69102200	1.52257800	-0.00031800
H	2.85393600	-1.15298200	-0.01231100

Table S12. Graphical representation of the HOMOs calculated for ground and transition states of various DTC and DTCH. The transition state was generated in each case by rotating the CS_2 group around the N-C bond. The surface contours were generated using Gaussview 5.0 and the composition analysis were performed using the GaussSum software.[16]

Ground State (GS) HOMO	Transition State (TS) HOMO
DIDTC$^-$  N = 0% and CS_2 = 95%	DIDTC$^-$  N = 10% and CS_2 = 87%
DIDTCH  N = 0% and CS_2 = 98%	DIDTCH  N = 38% and CS_2 = 50%
MorDTC$^-$  N = 0% and CS_2 = 96%	MorDTC$^-$  N = 4% and CS_2 = 94%
MorDTCH  N = 0% and CS_2 = 99%	MorDTCH  N = 10% and CS_2 = 87% (Chair conformation)  N = 10% and CS_2 = 87% (Boat conformation)
PDTC$^-$  N = 0% and CS_2 = 95%	PDTC$^-$  N = 3% and CS_2 = 95%
PDTCH  N = 0% and CS_2 = 99%	PDTCH  N = 15% and CS_2 = 83%

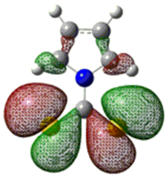
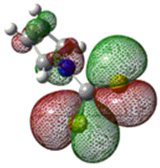
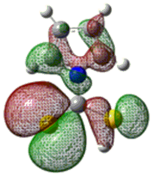
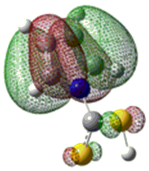
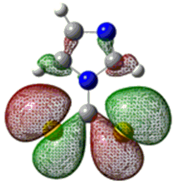
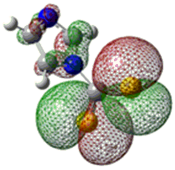
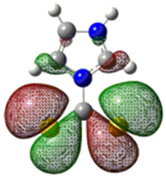
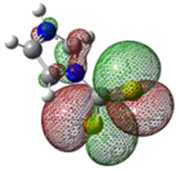
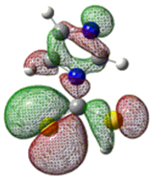
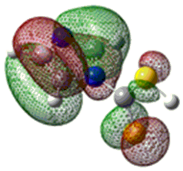
Ground State (GS) HOMO	Transition State (TS) HOMO
PyrDTC$^-$  N = 0% and CS_2 = 94%	PyrDTC$^-$  N = 1% and CS_2 = 96%
PyrDTCH  N = 0% and CS_2 = 95%	PyrDTCH  N = 0% and CS_2 = 2%
ImDTC$^-$  N = 0% and CS_2 = 96%	ImDTC$^-$  N = 1% and CS_2 = 97%
ImDTCH (NH)  N = 0% and CS_2 = 94%	ImDTCH (NH)  N = 1% and CS_2 = 98%
ImDTCH (SH)  N = 0% and CS_2 = 94%	ImDTCH (SH)  N = 4% and CS_2 = 8%

Table 4. Calculated activation energies for rotation E_{rot} around the DTC C-N bond, the bond lengths and the HOMO orbital compositions of several deprotonated DTCs (DTC^-) and protonated DTCs (DTCH) at the ground state (GS) and rotation transition state (TS_{rot}). Calculated in a PCM/B3LYP/6-31+G(d,p) level of theory.

DTC	N-C (Å) (GS)	N-C (Å) (TS_{rot})	HOMO (%) (GS)	HOMO (%) (TS_{rot})	E_{rot} (kJ/mol)
$PyrDTC^-$	1.421	1.455	CS_2 (94); N (0)	CS_2 (96); N (1)	29.48
PyrDTCH	1.384	1.426	CS_2 (95); N (0)	CS_2 (2); N (0)	37.9
$ImDTC^-$	1.435	1.462	CS_2 (96); N (1)	CS_2 (97); N (1)	22.3
ImDTCH (SH)[a]	1.398	1.434	CS_2 (94); N (0)	CS_2 (8); N (4)	25.6
ImDTCH (NH)[b]	1.483	1.492	CS_2 (94); N (2)	CS_2 (98); N (1)	15.4

[a] S protonated. [b] N protonated

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