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Dithiocarboxylic acids – an old theme revisited and augmented by new preparative, spectroscopic and structural facts

Johanna Grote née Glatthor, Felix Friedrich, Katarína Berthold, Loreen Hericks, Beate Neumann, Hans-Georg Stammler, and Norbert W. Mitzel*

In memoriam Professor Dr. Bernd Wrackmeyer

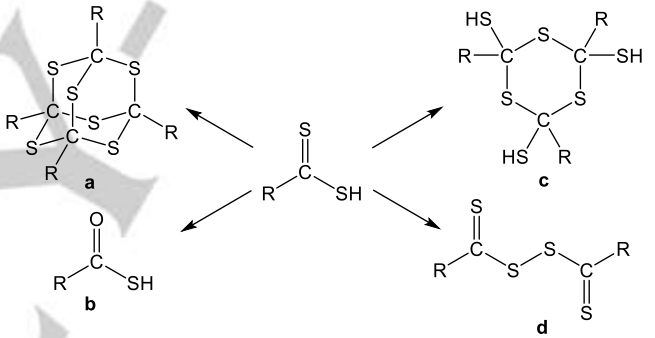
Abstract: The unstable dithiocarboxylic acids dithioacetic acid, 2-methyl-dithiopropionic acid, 2,2-dimethyl-dithiopropionic acid and dithiobenzoic acid were synthesized and characterized by NMR spectroscopy and GC/MS. The stable dithiocarboxylic acids 2,4,6-trimethyl benzoic acid, 2,4,6-tri-*iso*-propylbenzoic acid and 2,6-dimesityl benzoic acid were synthesized, isolated and characterized by spectroscopic methods and in parts by mass spectrometry and X-ray crystallography. The new data were used to reevaluate literature data on the synthesis, spectroscopy and structural data of dithiocarboxylic acids as a fundamental class or organic compounds in general.

Introduction

The number of carboxylic acids in organic chemistry is virtually unlimited. They show ample occurrence in nature; to name but a few: formic acid, lactic and citric acid. Various strategies for their syntheses are basic textbook knowledge in organic chemistry. Due to their stability, carboxylic acids are relevant in biological and biochemical processes, for chemical industry and generally in organic syntheses.[1,2] Dithiocarboxylic acids, in contrast, are much less present in literature. Their 873 entries in chemical literature (*Scifinder*, number of search results) are lower by a factor of about 1300.

Whereas the dithiocarboxylate functional group (–C(=S)S–) is known since as early as 1824, Fleischer reported the synthesis of thiophenol only in 1866 and in this context obtained dithiobenzoic acid as a byproduct and as the first dithiocarboxylic acid.[7–9] More than 50 years later Houben and Pohl brought the class of dithiocarboxylic acids into better focus.[9] They reported the syntheses of a variety of dithiocarboxylic acids and their characterization, partially by elemental analyses and by derivatization in the form of heavy metal salts.[9–11] However, reliable analytical data concerning isolated, pure dithiocarboxylic acids are still extremely scarce.[2,3,6] Houben and Pohl found dithiocarboxylic acids to be strong acids, to be soluble in organic solvents, to be of limited stability and to be generally of yellow, red or violet color, due to the C=S group chromophore. Another important characteristic is their strong and disgusting odor, which together with difficulties in handling due to instability make dithiocarboxylic acids a still grossly underexplored class of compounds.[2–6] Hence, instead of the free acids, their salts and esters were more frequently used.[5,14]

Unlike carboxylic acids, the dithio-analogues do not form thioanhydrates, but have a tendency to form disulfides (thioacyldisulfides) by oxidation with atmospheric oxygen (Scheme 1, **d**).[9,10] Thuillier published thiol acids (**b**) as decomposition products as well as the formation of hexathiaadamantanes (**a**) or different trithianes (**c**) as aggregation products.[12,13]



Scheme 1. Aggregation and decomposition of dithiocarboxylic acids (a: R = Me,[13,26] *i*-Pr, [26] b: R = Me, Et, Pr, Bu, *cyclo*-pentyl,[12] c: R = H,[17] Me[13,14])

Dithiocarboxylic acids and their derivatives are a group of highly reactive compounds, which generally react under much milder conditions than their dioxy-analogues.[2] Hartke found, that dithiocarboxylic acids form oligomers (dimers or trimers) after a short time even at −30 °C in the neat state or in solution.[14] Due to the lower electronegativity of σ-monovalent sulfur and its less efficient orbital overlap with the adjacent carbon atom, the π-system of a thiocarbonyl group is less stabilized than its carbonyl analogue. Based on the smaller orbital overlap, weak and relatively unstable C=S bonds tend to rearrange to more stable C–S single bonds. This is why thiocarbonyl compounds show a series of characteristic reactions which are mostly unknown or at least unusual for carbonyl compounds (Scheme 1).[5]

Dithiocarboxylic acids are accessible by thiolation of appropriate organic compounds with hydrogen sulfide or its salts, with elemental sulfur or other thiolation agents. The most widely used route is the reaction of carbon disulfide with strong nucleophiles.[2,3,5,6]

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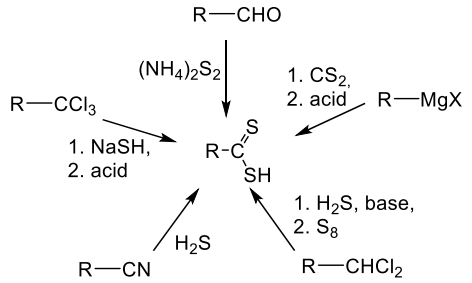
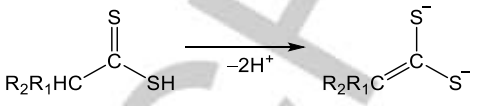


Scheme 2. Different synthetic pathways to free dithiocarboxylic acids. [2,3,5]

For the aromatic series of dithiocarboxylic acids sulfhydrolysis of geminal di- or trihalides by using hydrogen sulfides and elementary sulfur or alkali (hydrogen) sulfides is a common method.[3,5] Aromatic dithiocarboxylic acids were also synthesized by reactions of aromatic aldehydes with hydrogen sulfide. To obtain dithiocarboxylic acids the corresponding nitriles can be reacted with hydrogen sulfide.[5]

The most popular method to synthesize dithiocarboxylic acids is to react various alkyl or aryl Grignard reagents with carbon disulfide at low temperature.[2–5,9–12] Since Houben first synthesized them in this way in 1907, the procedure has continuously been refined and optimized[14] – mostly by replacing diethyl ether by tetrahydrofuran and by slow addition of the Grignard reagent. Under these conditions the magnesium salt (R–C(=S)SMgX) is prevented from further fast alkylation to the corresponding ester.[5,14] Note also, that dithiocarboxylic acids with an α-hydrogen atom are prone to double deprotonation and formation of a dianion (Scheme 3), leading to even more byproducts.[2,5,14]



Scheme 3. Twofold deprotonation of dithiocarboxylic acid with an α-hydrogen atom

Due to the described instability, dithiocarboxylic acids have been commonly transformed into their alkali metal cation, ammonium, phosphonium and arsonium salts or dithiocarboxylic esters for isolation, storage and further reactions.[2]

Table 1 contains an overview of available analytical data of selected alkyl or aryl dithiocarboxylic acids. We have chosen dithiocarboxylic acids with heteroatom-free, short saturated alkyl substituents (H-, Me-, Et-, *n*-Pr-, *i*-Pr-, *n*-Bu-, *t*-Bu-, *i*-Pen-, *cy*-Pr-, *cy*-Pen-, *cy*-Hex-) and heteroatom-free aryl substituents (Ph-, Tip- (2,4,6-tri*iso*propylphenyl)), Mes-, Mes*- (2,4,6-tri*tert*butylphenyl), Dmp- (2,6-dimesitylphenyl)) without any further functional groups to provide an meaningful overview. It is interesting to point out that all synthetic protocols refer to the work of Houben or Thuillier – and the latter refined Houben's instructions from 1907. Although all reports in Table 1 claim that almost every dithiocarboxylic acid has been isolated, from a todays view, for most cases there is no adequate evidence for their unequivocal identity as free, isolated compounds and their monomeric structure. Due to the fact that free dithiocarboxylic acids have the same mass proportions as their aggregates, elemental analyses are no sufficient proof for their identity as free acids.

Despite the availability of NMR data for different dithiocarboxylic acids, crucial characteristics like the ^{13}C NMR chemical shift of the dithiocarboxylic carbon atom were not accessible for most cases. Solely the assignment of resonances of the alkyl or aryl substituents linked to the C(=S)SH group is insufficient proof of identity of the complete molecule. The assignments of ^{1}H NMR chemical shifts to SH group

Table 1. Analytical data concerning the most common isolated dithiocarboxylic acids reported in literature

R	isol.	*bp* / *p*[a]	*mp*[b]	yield[c]	NMR	MS	IR	UV-vis	EA	lit.
H	●		55-60		●	●	●	●		17
Me	●	37/15		18					●	10
Me	●	35–37/15								14
Me	●			55						13
Me	●	31–32/15		48	●					12
Me	●	38–40/17					●			15
Me	●			56						16
Et	●	41–42/13		53	●					12
Et	●	48/17		12					●	11
Et	●			53						14
n-Pr	●			73						14
n-Pr	●	59/13		5					●	11
n-Pr	●	59–60/13		40	●					12
i-Pr	●	45–46/13		56	●					12
n-Bu	●	76–77/13		40	●					12
i-Bu	●	84/33		4					●	11
i-Pen		84/10		4					●	11
cy-Pr	●	71–72/17		42	●					12
cy-Pen	●	55–56/0.3		38	●					12
cy-Hex	●	67–69/0.3		25	●					12
Ph	●			100	●					18
Ph	●			70						19
Ph	●				●					20
Ph	●			67	●					21
Ph	●			40	●					22
Tip	●			76	●	●				23
Dmp	●			51	●		●		●	24

[a]boiling point *bp* in °C / pressure *p* in Torr; [b]melting point *mp* in °C; [c]yield in %.

resonances are often insufficient and generally hampered due to their strong concentration-dependence.[12] Only 2,6-dimesityl-dithiobenzoic acid (Dmp-C(=S)SH) has been fully characterized by NMR spectroscopy including the downfield shifted ^{13}C NMR signal of the dithiocarboxylic carbon at 229.2 ppm.[24]

There are hardly any mass spectrometric data of dithiocarboxylic acids in literature. However, it was mass spectrometry that revealed the oligomeric nature of dithioformic acid.[17] Tri-*iso*-propyl-dithiobenzoic acid (Tip-C(=S)SH) has been successfully characterized by high resolution mass spectrometry (HRMS).[24]

In infrared spectroscopy the S–H stretching vibrations of thiols or sulfides are in general weak and found in the range between 2540 and 2600 cm^{-1}. In the case of dithiocarboxylic acids the S–H stretching vibration at about 2550 cm^{-1} gives strong bands, while the C=S bands appear close to 1215 cm^{-1} (by comparison; 1080–1210 cm^{-1} for thioesters). On the basis of IR spectroscopy it is possible to distinguish between intact C(=S)SH acid functions and aggregated forms. For example the IR spectrum of the oligomeric dithioformic acid ($[HC(S)SH]_x$[17]) shows no strong band at about 2550 cm^{-1} and no C=S band near to 1215 cm^{-1}, but one below at 1163 cm^{-1}.[17] In contrast, the IR spectrum of Dmp-C(=S)SH shows a characteristic S–H stretching band at 2501 cm^{-1}.[24] Despite the fact, that dithiocarboxylic acids are strongly colored substances, there are virtually no available UV-vis spectroscopy reference data.

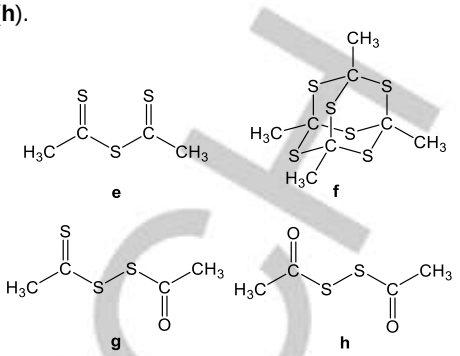
The reason, why we explored the chemistry of dithiocarboxylic acids was our intention to synthesize volatile (binuclear) heavy metal complexes with dithiocarboxylate ligands. One possible pathway to such substance involves the use of free dithiocarboxylic acids. In the course of this work we realized the distinct paucity of available information on this class of substances. This report is intended to serve as a short overview and to provide some examples of fully characterized and otherwise heteroatom-free examples of the fundamental class of dithiocarboxylic acids.

Results and Discussion

Syntheses and analytical data

We investigated in particular the syntheses, isolation and characterization of different free dithiocarboxylic acids with the following substituents at the C(=S)SH unit: Me-, *i*-Pr-, *t*-Bu-, Ph-, Mes-, Tip-, Mes*-, Dmp.

According to Thuillier's protocol we synthesized Me-C(=S)SH, *i*-Pr-C(=S)SH, *t*-Bu-C(=S)SH, Ph-C(=S)SH, Mes-C(=S)SH and Tip-C(=S)SH.[12] Any attempt to isolate pure Me-, *i*-Pr-, *t*-Bu- and Ph-C(=S)SH by evaporation, (vacuum) distillation, condensation or crystallization failed. In contrast to earlier literature reports, we were not able to isolate these as free acids and observed decomposition and aggregation instead. Dithioacetic acid was found to be the main product (GC/MS; 95.6 %, dithioacetic methyl ester 4.4 %) before attempts of purification, whereas after distillation or condensation the free acid could no longer be detected in the residue. Instead of dithioacetic acid the GC/MS measurements indicate the formation of aggregates and/or oxidation products like trithioacetic anhydride (**e**), tetramethyl hexathiaadamantane (**f**), thiodiacetyl disulfide (**g**) and diacetyl disulfide (**h**).



Scheme 5. Trithioacetic anhydride (**e**), hexamethyl hexathiaadamantane (**f**), thiodiacetyl disulfide (**g**), diacetyl disulfide (**h**) as aggregation and oxidation products of dithioacetic acid

Similarly, for to 2-methyl dithiopropionic acid (*i*-Pr-C(=S)SH), 2,2-dimethyl dithiopropionic acid (*t*-Bu-C(=S)SH) and dithiobenzoic acid (Ph-C(=S)SH) the corresponding alkyl or aryl esters were found as byproducts. The attempt to remove the solvent completely led to aggregation and oxidative decomposition products; they were verified by GC/MS analyses. In the case of the dithiobenzoic acid biphenyl was found to be a preferred decomposition product. We were not able to identify all of the large number of decomposition products (up to 45 different GC/MS signals). After considerable time of doing GC/MS measurements we also observed a blocking of the noble metal syringe of the GC/MS equipment. Although diluted solutions were used, the stamp and the inner of the syringe were found to be coated with a dark, ill smelling residue.

However, we obtained dithioacetic acid as a THF solution by the standard procedure via a Grignard reaction in 33% yield (calculated from NMR data). Also *i*-Pr-C(=S)SH was obtained in 38% yield in solution. In the case of *t*-Bu-C(=S)SH and Ph-C(=S)SH we were able to determine NMR chemical shifts. However, the determination of the concentrations was not possible, due to the high dilution.

Only Mes-C(=S)SH and Tip-C(=S)SH could be isolated in pure form in 80% and 33% yield, respectively. Both were purified by conversion into their sodium salts and reconversion into their free acid. Mes*-C(=S)SH and Dmp-C(=S)SH were synthesized by reacting the corresponding organolithium compound with carbon disulfide and subsequent hydrolysis. The purification was carried out in the same was as described above. We obtained Mes*- and Dmp-C(=S)SH with 27% and 45% yield, respectively.

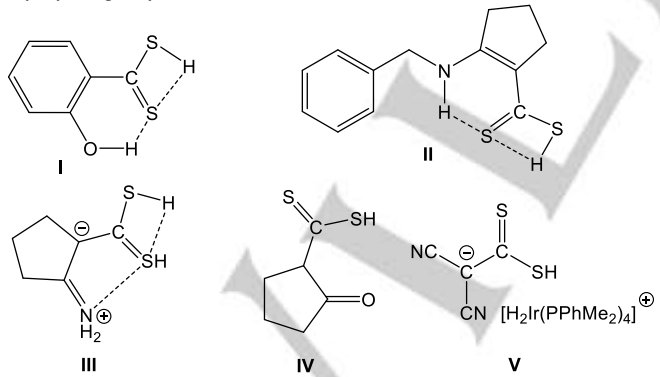
The ^{1}H and ^{13}C NMR spectra of the isolated dithiocarboxylic acids (Mes-, Tip-, Mes*-, Dmp-C(=S)SH) showed the expected signals concerning the Mes, Tip, Mes* and Dmp groups. Furthermore the ^{13}C NMR spectra show the characteristic $^{13}C(=S)SH$ signal (Table 2). The hydrogen atom of the C(=S)SH group could be observed in the ^{1}H NMR spectra as a broad singlet, explaining why this led to difficulties in the past.

Due to the variations in concentration and the reactivity to diverse types of cell materials, IR spectroscopy of the free, instable dithiocarboxylic acids (Me-, *i*-Pr-, *t*-Bu-, Ph-C(=S)SH) in solution was not practical. Their disgusting smell also made such analyses not attractive. IR spectra of the stable dithiocarboxylic acids (Mes-, Tip-, Mes*-, Dmp-C(=S)SH) show C–H stretching vibrations in the rage between 2970 and 2850 cm^{-1}. Furthermore all spectra show the characteristic S–H stretching vibrations in the small interval between 2500 and 2530 cm^{-1} and C=S stretching vibrations in the region between 1010 and 1150 cm^{-1}.

On the basis of NMR- and IR-spectroscopy it is possible to demonstrate that the C(=S)SH-group is intact and not aggregated. Elemental analyses gave additional information on the purity of the free dithiocarboxylic acid (see experimental section).

Single crystal X-ray diffraction

Up to now there is no structure determination by X-ray diffraction (XRD) of single crystals for free and simply substituted dithiocarboxylic acids (CCSD data base, February 2017).[36] Compounds with C(=S)SH groups that have been examined by XRD are only in combination with other functional groups. In three of these cases the solid state structures show intramolecular hydrogen bonds to these additional functional groups and may therefore distort the structural characteristics compared to pure dithiocarboxylic acid (Scheme 4, **I**, **II**, **III**).[30,31,33] Salt **V** is a dimer (with two linear hydrogen bonds) of the dithiocarboxylic acid unit.[32] The inter- and intramolecular association patterns of the C(=S)SH groups in **IV** are unclear.[34]



Scheme 4. 2-Hydroxy-dithiobenzoic acid (**I**),[30] 2-amino-1-cyclo-pentene-1-carbodithioic acid (**II**),[31] 2-imino-cyclo-pentanedithioic acid (**III**),[33] 2-oxo-cyclo-pentane dithiocarboxylic acid (**IV**),[34] dicyano(dithiocarboxy)-methanide salt (**V**).[32]

All bulkily substituted dithiocarboxylic acids (Tip-, Mes*-, Dmp-C(=S)SH) are deep red to pink colored, crystalline solids, from which we have now obtained single crystals. These allowed the determination of their molecular structure by X-ray diffraction. All sulfur bonded hydrogen atoms could be located in the difference Fourier maps and their positional and displacement parameters were refined, also if the uncertainty of these values are naturally large. We use these positions in the following discussion, but the fact, that X-ray diffraction is locating electron density rather than nuclear position must be kept in mind, when interpreting parameters involving hydrogen positions.

Table 2. ^{13}C-NMR and ^{1}H NMR chemical shifts δ of the C(=S)SH group of the isolated dithiocarboxylic acids (75 MHz / 300 MHz, $CDCl_3$)

Substituent *R*	$\delta(^{13}C)$ / ppm	$\delta(^{1}H)$ / ppm
Mes	236.0	6.65
Tip	236.6	6.75
Mes*	241.5	6.91
Dmp	229.0	6.18

Figure 1 shows the molecular structure of the Tip-substituted dithiocarboxylic acid. Its C–S distances and S–C–S angles have a conformable magnitude for C(=S)SH groups (in comparison to the data for other compounds containing C(=S)SH groups, **I**-**V**, Scheme 4).[30–34] The atoms of its C(=S)SH unit are coplanar and within the margin of error this plane is almost orthogonal to the ring plane of the Tip-substituent, the angle of the mean planes is 88.7(1)°. The S(1)···H(2) measures 3.01(7) Å, which is the same as the sum of the van der Waals radii of H and S (3.05 Å).[39] It can thus only be speculated if the orientation of the SH hydrogen atom indicates a form of weak intramolecular hydrogen bonding.

Besides this possible intramolecular hydrogen bond, there is a more pronounced intermolecular hydrogen bond, S(1)···H(2'), of 2.87(7) Å in length. It involves an S···H–S angle of 120(3)°. Both values are indicative of weak hydrogen bonds.[29] Though weak, it leads to a chain pattern running along the a axis as shown in Figure 1, in contrast the solid state structure and crystal packing pattern of the dioxy analog acid Tip-C(=O)OH exhibit a dimer structure via two intermolecular hydrogen bonds.[35]

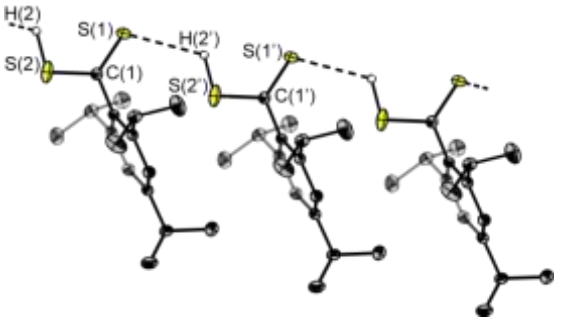


Figure 1. Molecular structure and crystal packing of the Tip-substituted dithiocarboxylic acid.

Table 3. Characteristic intra- and intermolecular structural parameters of Tip-C(=S)SH

C(1)–S(1)	1.6379(15) Å	C(1)–S(2)–H(2)	107(3)°
C(1)–S(2)	1.7197(15) Å	S(1)···H(2')	2.87(7) Å
S(2)–H(2)	1.42(6) Å	S(1)···H(2')–S(2')	120(3)°
S(1)···H(2)	3.01(7) Å	plane (C(=S)SH)	±0.006 Å

Symmetry code for H(2'): *–x*, *y*, *z*

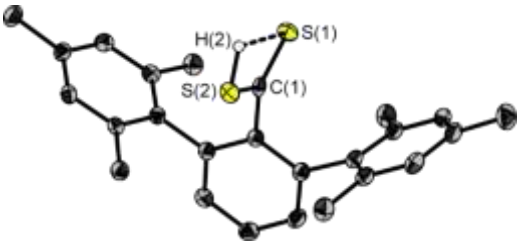


Figure 2. Molecular structure of the Dmp-substituted dithiocarboxylic acid

Table 4. Characteristic intramolecular structural parameters of Dmp-C(=S)SH

C(1)–S(1)	1.6307(15) Å	S(1)–C(1)–S(2)	124.81(9)°
C(1)–S(2)	1.7278(15) Å	C(1)–S(2)–H(2)	97.3(10)°
S(2)–H(2)	1.22(2) Å	C(1)–S(1)···H(2)	52.6(4)°
S(1)···H(2)	2.82(2) Å	plane (C(=S)SH)	± 0.001 Å

Figure 2 shows the molecular structure of the Dmp substituted dithiocarboxylic acid. Its C(=S)SH plane is again coplanar within the limits of error. The hydrogen atom is bent inward at a much smaller angle C(1)–S(2)–H(2) of 97(1)°. This and the absence of an intermolecular hydrogen bond leads to a much smaller distance between H(2) and S(1) of 2.82(2) Å in this case; this can be interpreted on one hand as an intramolecular H(2)···S(1) hydrogen bond, on the other hand as a result of a SH···π interaction, which reveals a distance of 2.46(2) Å from a centroid of one aromatic ring to the H–S hydrogen atom forming a dimer as shown in Figure 3. The centroid–S(2) distance is 3.58(1) Å.

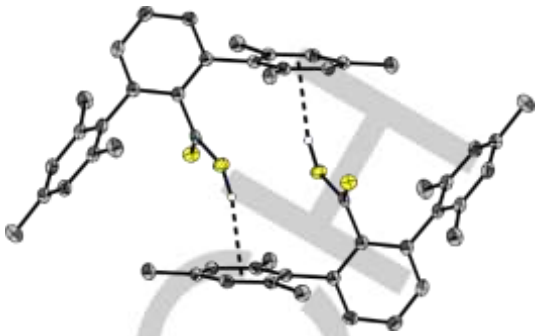


Figure 3. Crystal packing of Dmp-C(=S)SH by SH···π interaction (*d*(SH···centroid) = 2.46(2) Å). Carbon bonded hydrogens were omitted for clarity.

The intramolecular C–S distances and S–C–S angle adopt values comparable to those of other C(=S)SH groups (in comparison to **I-V**, Scheme 4).[30–34] The dihedral angle between the C(=S)SH unit and the ring mean plane of the Dmp substituent is 78.7(1)°.

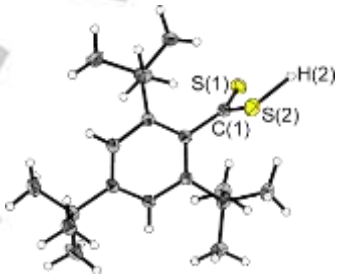


Figure 4. Molecular structure of the Mes*-substituted dithiocarboxylic acid

Table 5. Characteristic intra- and intermolecular structural parameters of Mes*-C(=S)SH.

C(1)–S(2)	1.7362(19) Å	S(2)–C(1)–S(1)	122.98(11)°
C(1)–S(1)	1.633(2) Å	C(1)–S(2)–H(2)	104.3(13)°
S(2)–H(2)	1.63(4) Å	H(2)···centroid	2.06(4) Å
S(1)···H(2)	3.03(4) Å	H(2)···C_{ring}	2.27(4)–2.71(4) Å
plane(C(=S)SH)	± 0.011 Å	S(2)···centroid	3.5148(9) Å

Figure 4 shows the molecular structure of Mes*-C(=S)SH in the solid state. The hydrogen atom of the planar C(=S)SH group is bent inward comparable to Tip-C(=S)SH. Here the distance S(1)···H(2) measures 3.03(4) Å, which is the same as the sum of the van der Waals radii of H and S (3.05 Å).[39] Again the distance and angles of the C(=S)SH group have a conformable magnitude for C(=S)SH groups (in comparison to the data for other compounds containing C(=S)SH groups, I-V, Scheme 4).[30–34] The dihedral angle between the C(=S)SH unit and the ring mean plane of the Mes* substituent is 99.73(10)°. Conspicuous is the long S(2)–H(2) distance of 1.63(4) Å and is accompanied by a notably short distance of 2.06(4) Å of this hydrogen atom to the centroid of the neighbouring π-system. Also if the uncertainty of the hydrogen atom position is taken into account, the centroid–S(2) distance of 3.51 Å reveals an SH···π interaction, which forms a chain pattern as shown in Figure 5.

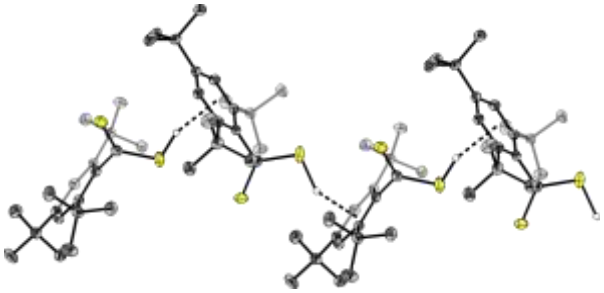


Figure 5. Crystal packing of Mes*-C(=S)SH. Carbon bonded hydrogens were omitted for clarity.

Although SH···π interactions are known to be relatively strong in comparison to OH···π, NH···π, CH···π interactions from theoretical studies,[46] there are no corresponding molecular structures or crystal packing motifs in the CCSD data base, which show a similarly short distance between an SH group and a π-system. There are only few crystal structures, which show SH···π distances shorter than the sum of C and H van der Waal radii. The crystal packing of 1,1'-biphenyl 2,2'-dithiole shows an intermolecular SH···π interaction, which measures 2.50 Å (the shortest intermolecular SH-centroid distance, *d*(SH···centroid) = 3.605 Å; CCSD database, August 2017).[47] Here we found a shorter SH···π distance of 2.46(2) for Dmp-C(=S)SH and 2.06(4) Å length for Mes*-C(=S)SH (*d*(SH···π) = 3.58(1) resp. 3.51(1) Å) demonstrating strong SH···π interactions.

Conclusions

Herein we reported the syntheses and characterization of unstable dithiocarboxylic acids with Me, *i*-Pr, *t*-Bu, and Ph groups bonded to the C(=S)SH unit as solutions. They did not allow isolation of the pure compounds and aggregate or decompose upon attempts of separation from the solvent. Isolation is possible for dithiocarboxylic acids with larger organic groups including Mes, Tip, Mes* and Dmp. For the latter compounds it is possible to obtain a full set of analytical data including ^{1}H and ^{13}C NMR spectra, IR spectra, UV-vis spectra and elemental analyses. The structures of Dmp-C(=S)SH and Tip-C(=S)SH show a preference of dithiocarboxylic acids for weak S···H–S hydrogen bonding. The Tip-C(=S)SH molecules aggregate in the form of chains through links to neighbor molecules, whereas Dmp-C(=S)SH shows a unique intramolecular S···H–S hydrogen bonding motif within one C(=S)SH group, leading to a four-membered HSCS ring and additionally SH···π interactions. This makes dithiocarboxylic acids completely different from typical carboxylic acids in their hydrogen-bonded dimers.[41–45] Conversely, the Mes*-C(=S)SH molecules show no structure determining intermolecular hydrogen bonds, but as well as Dmp-C(=S)SH SH···π-type interactions in the solid state. With the background of a critical reevaluation of the experimental and analytical data concerning dithiocarboxylic acids collected in literature over the last 150 years, our new data provide unequivocal proof for the presence of simple examples of free dithiocarboxylic acids, but also demonstrate the limitations of stability in dependence of the size of the stabilizing organic group carrying the C(=S)SH unit.

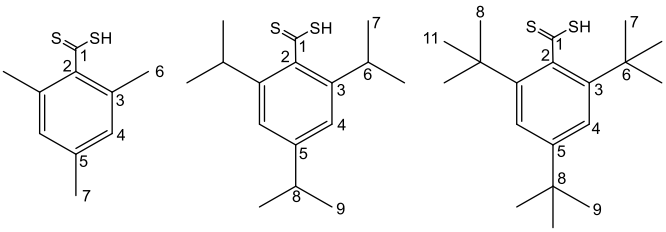
All structural data have been obtained from dithiocarboxylic acids with aromatic substituents, and in all cases the dithiocarboxylic acid groups are oriented about orthogonal to the aromatic ring thus resulting in a minimum for possible conjugation. The present data do not allow concluding, whether this is an inherent structural feature for all dithiocarboxylic acids or due to the more or less big groups in the two *ortho*-positions in all three cases investigated in this work.

Dithiocarboxylic acids are precursors for dithiocarboxylates (R–C(=S)S^{-}), which are excellent ligands containing two equivalent soft sulfur atoms for coordination and a delocalized negative charge. We have used them to prepare complexes of 1:1 stoichiometry with monovalent coinage metal(I) ions. They show various binding motifs and shapes of aggregation. These results will be communicated in forthcoming reports.

Experimental Section

NMR spectra were recorded on a BRUKER AVANCE II 300, a BRUKER DRX 500 and a BRUKER AVANCE III 500 instrument. The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm; C_6D_6: ^{1}H NMR δ = 7.16 ppm, ^{13}C NMR δ = 128.06 ppm. Elemental analyses were performed with CHNS elemental analyzer HEKATECH EURO EA. For all GC/MS measurements a SHIMADZU GC-2010/GC/MS-QP 2010 S (column: RTX-200 CROSSBOND, trifluoropropylmethyl polysiloxane) instrument was used. IR spectroscopic measurements were performed with a BRUKER ALPHA spectrometer. The vibrations (υ) were measured in cm^{-1} and the intensity is labelled with strong (s), medium (m), weak (w) and broad (br).

Moisture- and air-sensitive reactions were carried out by using freshly distilled and dry solvents from solvent stills. 2,4,6-Tri-*iso*-propylphenyl bromide, 2,4,6-tri-*tert*-butylphenyl bromide, 2,6-Dimesityl-1-iodo-benzene and the corresponding lithium salt were prepared according to literature protocols.[37,38,40] 2,4,6-Trimethylphenyl bromide (FLUKA), iodine (VWR), carbon disulfide (J. T. BAKER, FISHER SCIENTIFIC), *n*-butyl lithium and 1,3-dichlorobenzene (ACROS), magnesium, methyl iodide and 2-bromopropane and phenyl bromide (MERCK) were purchased.



Scheme 8. Atom numbering used for NMR assignment

Unstable dithiocarboxylic acids (Me-C(=S)SH, *i*-Pr-C(=S)SH, *t*-Bu-C(=S)SH, Ph-C(=S)SH)

General procedure: A freshly prepared Grignard reagent in diethyl ether (or commercially available solution for *t*-Bu, ACROS) was diluted with THF. Then carbon disulfide was added dropwise at −5 °C. The reaction mixture was stirred for 20 h at room temperature and then hydrolyzed with hydrochloric acid (half conc.) at 0 °C. The aqueous phase was extracted with diethyl ether until it was colorless. The combined organic phases

were concentrated and analyzed. Isolation was not possible due to the instability of the compounds.

Dithioacetic acid, Me-C(=S)SH. Mg 3.89 g, 160 mmol; MeI 22.8 g, 160 mmol; Et_2O 60 mL; THF 320 mL; CS_2 13.2 g, 170 mmol; half conc. HCl 150 mL; yield 33% (calcd. from NMR); GC/MS *m/z* [fragment] 92.0 $[M]^+$, 76.9 $[M-CH_3]^+$, 59.1 $[M-SH]^+$, 45.0; ^{1}H NMR [300 MHz, C_6D_6, *δ*/ppm] 3.20 (s, 3H, CH_3), 5.60 (s, 1H, SH); ^{1}H NMR [300 MHz, $CDCl_3$, *δ*/ppm] 2.85 (s, 3H, CH_3), 6.85 (s, 1H, SH); ^{13}C NMR [75.5 MHz, C_6D_6, *δ*/ppm] 43.46 (CH_3), 237.15 (C(=S)SH).

Table 5. Crystal and refinement data for the structure determinations

	Tip-C(=S)SH[a]	Mes*-C(=S)SH[b]	Dmp-C(=S)SH
Formula	$C_{16}H_{24}S_2$	$C_{19}H_{30}S_2$	$C_{25}H_{26}S_2$
M_r	280.47	322.55	390.58
Cryst.size/mm	0.19×0.07×0.03	0.3×0.1×0.1	0.26×0.15×0.03
Cryst. system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
F(000)	608	704	416
a /Å	5.84478(9)	17.0215(5)	8.3561(2)
b /Å	13.3984(2)	9.6592(2)	9.10008(19)
c /Å	20.4410(4)	11.4153(3)	14.7252(3)
α /°	90	90.0	101.8810(18)
β /°	93.4511(17)	95.801(2)	98.2156(19)
γ /°	90	90.0	101.1035(19)
V /Å^3	1597.84(5)	1867.22(8)	1055.62(4)
Z	4	4	2
ρ_{calc} /mg·mm^{-3}	1.166	1.147	1.229
μ /mm^{-1}	2.852	2.499	2.312
2θ-range /°	7.9–145.4	5.218–151.32	6.2–144.7
Reflns collected	41231	9391	17976
Unique reflns	4122	4347	4190
R_{int}	0.0166	0.0249	0.0340
Refl $I>2\sigma(I)$	3933	3982	3795
Parameters	260	311	254
R_1/wR_2 [$I>2\sigma(I)$]	0.0330/0.0962	0.0422/0.1233	0.0358/0.0958
R_1/wR_2 [all data]	0.0342/0.0972	0.0452/0.1265	0.0397/0.0995
GoF	1.054	1.081	1.031
$\Delta\rho_{max/min}$ /e·Å^{-3}	0.36/−0.33	0.57/−0.54	0.34/−0.25
CCDC number	1572721	1572722	1572723

[a]Refined as a non-merohedral twin. The second domain is rotated by −179.96° around 001, ratio 67:33. [b]Refined as a non-merohedral twin. The second domain is rotated by -180° around 001, ratio 74:26

2-Methyl-dithiopropionic acid, *i*-Pr-C(=S)SH. Mg 0.50 g, 21 mmol; *i*-PrBr 2.63 g, 21 mmol; Et_2O 15 mL; THF 30 mL; CS_2 1.89 g, 25 mmol; half conc. HCl 100 mL; yield 38% (calcd. from NMR); GC/MS *m/z* [fragment] 120.0 $[M]^+$, 87.0 $[M-SH]^+$, 76.9 $[M-{}^iPr]^+$; ^{1}H NMR [300 MHz, $CDCl_3$, *δ*/ppm] 1.31 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, $CH(C\underline{H}_3)_2$), 3.36 (hept, $^3J_{H,H}$ = 6.7 Hz, 1H, $C\underline{H}(CH_3)_2$), 5.70 (s, 1H, S<u>H</u>); ^{13}C NMR [75.5 MHz, $CDCl_3$, *δ*/ppm] 24.0 ($CH(\underline{C}H_3)_2$), 50.87 ($\underline{C}H(CH_3)_2$), 246.0 (<u>C</u>(=S)SH).

2,2-Dimethyl-dithiopropionic acid, *t*-Bu-C(=S)SH. *t*-BuMgBr 1.7 M in Et_2O, 30 mL, 51 mmol; THF 250 mL; CS_2 3.9 g, 52 mmol; half conc. HCl 150 mL; n. d.; GC/MS *m/z* [fragment] 134 $[M]^+$, 101 $[M-SH]^+$, 57 $[M-C(=S)SH]^+$.

Dithiobenzoic acid, Ph-C(=S)SH. Mg 2.40 g, 100 mmol; PhBr 15.8 g, 100 mmol; Et_2O 40 mL; THF 60 mL; CS_2 8.5 g, 110 mmol; half conc. HCl 40 mL; yield n. d.; GC/MS *m/z* [fragment] 154.0 $[M]^+$, 121.0 $[M-SH]^+$, 77.1 $[M-C(=S)SH]^+$; ^{1}H NMR [300 MHz, C_6D_6, *δ*/ppm] 4.7 (s, 1H, SH), 7.2 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, *meta*-H), 7.4 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, *para*-H), 7.9 (d, $^3J_{H,H}$ = 7.4 Hz, 2H, *ortho*-H); ^{1}H NMR [300 MHz, $CDCl_3$, *δ*/ppm] 6.3 (s, 1H, SH), 7.4 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, *meta*-H), 7.6 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, *para*-H), 8.1 (d, $^3J_{H,H}$ = 7.3 Hz, 2H, *ortho*-H).

Stable dithiocarboxylic acids (Mes-C(=S)SH, Tip-C(=S)SH, Mes*-C(=S)SH, Dmp-C(=S)SH)

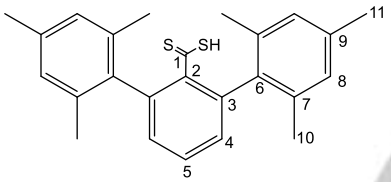
2,4,6-Trimethyldithiobenzoic acid, Mes-C(=S)SH. To a freshly prepared Grignard reagent based on mesityl bromide (6.0 mL, 40 mmol) in THF (20 mL) more THF (20 mL) and carbon disulfide (1.2 mL, 20 mmol) were added dropwise at –5 °C. The mixture was stirred for 3 h at room temperature. The reaction mixture was hydrolyzed with hydrochloric acid (75 mL, half conc. HCl). The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried with magnesium sulfate and the solvent was removed in vacuum. For purification the free acid was converted into its sodium salt by reaction with sodium hydride (1 eq.) in pentane (ca. 50 mL). Water (ca. 100 mL) was added and phases were separated. Finally the sodium salt in aqueous solution was acidified with hydrochloric acid and extracted with diethyl ether for several times, until the aqueous solution was colorless. 2,4,6-Trimethyl-dithiobenzoic acid (3.1 g, 16 mmol) was isolated as cherry-red oil with a yield of 80%. ^{1}H NMR [300 MHz, $CDCl_3$, *δ*/ppm] 2.30 (s, 3H, *para*-CH_3) 2.39 (s, 6H, *ortho*-CH_3), 6.65 (s, 1H, C(=S)SH), 6.88 (s, 2H, Ar-H); ^{13}C NMR [75 MHz, $CDCl_3$, *δ*/ppm] 19.2 (C6) 21.1 (C7), 128.7 (C4), 131.3 (C5), 138.2 (C3), 146.3 (C2), 236.0 (C1). EA [for $C_{10}H_{12}S_2$ / %] calcd. C 61.18, H 6.16, S 32.66; found C 61.75, H 6.29, S 32.19.

2,4,6-Tri-*iso*-propyl-dithiobenzoic acid, Tip-C(=S)SH. To a freshly prepared Grignard reagent based on 1-bromo-2,4,6-tri-*iso*-propyl benzene (2.5 mL, 10 mmol) in THF (30 mL) carbon disulfide (0.7 mL, 11 mmol) was added dropwise at –5 °C. The mixture was stirred for 11 h at room temperature. Afterwards the reaction mixture was hydrolyzed with hydrochloric acid (40 mL, half conc. HCl). The precipitate was filtered off and washed with water and ethanol (20 mL each). For purification the free acid was converted into its sodium salt by reaction with sodium hydride (analogous to Mes-C(=S)SH). 2,4,6-Tri-*iso*-propyl-dithiobenzoic acid (920 mg, 3.3 mmol, 33%) was isolated in form of an grapefruit-pink solid. ^{1}H NMR [500 MHz, $CDCl_3$, *δ*/ppm] 1.25 (m, 18H, CH_3) 2.87 (hept, $^3J_{H,H}$ = 6.9 Hz, 1H, *para*-C<u>H</u>$(CH_3)_2$), 3.27 (hept, $^3J_{H,H}$ = 6.8 Hz 2H, *ortho*-C<u>H</u>$(CH_3)_2$), 7.00 (s, 2H, Ar-H); ^{13}C NMR [75 MHz, $CDCl_3$, *δ*/ppm] 23.9 (C7, C9), 24.6 (C7, C9), 30.4 (C6), 34.3 (C8), 121.4 (C4), 142.2 (C5), 149.4 (C3),236.6 (C1); IR [*υ*/cm^{-1}] 1602, 1456, 1436, 1423, 1381, 1362, 1126, 1096, 1061, 1049, 942, 915, 876, 804, 755, 643, 606; EA [for $C_{16}H_{24}S_2$ / %] calcd. C 68.51, H 8.62, S 22.86; found C 68.04, H 8.58, S 21.77.

2,4,6-Tri-*tert*-butyl-dithiobenzoic acid, Mes*-C(=S)SH. To a solution of supermesityl bromide (2.1 g, 6.4 mmol) in diethyl ether (12 mL) *n*-butyl lithium (1.6 M in hexane, 3.9 mL, 6.2 mmol) was added at 0 °C. The reaction mixture was allowed to achieve room temperature overnight. Carbon disulfide (0.40 mL, 6.7 mmol) were added at −70 °C. The reaction mixture was allowed to reach room temperature and was stirred for 5 h. Then the reaction mixture was hydrolyzed with hydrochloric acid (half conc. HCl). The aqueous phase was extracted with diethyl ether (3 × 70 mL). The combined organic phases were dried with magnesium sulfate and the solvent was removed in vacuum. For purification 2,4,6-tri-

tert-butyl-dithiobenzoic acid was converted into its sodium salt by reaction with sodium hydride (0.15 g, 7 mmol) in hexane (23 mL). Water was added and the phases separated. Then hydrochloric acid was added to the aqueous phase and afterwards extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried with magnesium sulfate and the solvent was removed in vacuum. 2,4,6-Tri-*tert*-butyl-dithiobenzoic acid (0.55 g, 1.7 mmol, 27%) was isolated as a red solid. ^{1}H NMR [300 MHz, $CDCl_3$, *δ*/ppm] 1.31 (s, 9H, *para*-C(C$\underline{H}_3$)$_3$), 1.59 (s, 18H, *ortho*-C(C$\underline{H}_3$)$_3$), 6.91 (br s, 1H, C(=S)SH), 7.45 (s, 2H, CH); ^{13}C NMR [75 MHz, $CDCl_3$, *δ*/ppm] 31.2 (C9), 33.7 (C7), 35.3 (C8), 39.2 (C6), 124.2 (C4), 144.3 (C3), 150.1 (C5), 241.5 (C1); IR [*υ*/cm^{-1}] 2961, 2907, 2866 (*υ*(C–H)), 2518 (st, *υ*(S–H)), 1598, 1548, 1534, 1461, 1394, 1360, 1259, 1148, 1093, 1057, 881, 797, 741; EA [for $C_{19}H_{30}S_2$ / %] calcd. C 70.75, H 9.37, S 19.88; found C 67.95, H 9.29, S 17.29.

2,6-Dimesityldithiobenzoic acid, Dmp-C(=S)SH. Lithium 2,6-dimesityldithiobenzoate (0.5 g, 1.2 mmol) was acidified with hydrochloric and extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried with magnesium sulfide and the solvent was removed in vacuum. The free 2,6-dimesityl-dithiobenzoic acid (0.283 g, 0.7 mmol) was isolated in a pink, crystalline form with a yield of 61%. GC/MS *m/z* [fragment] 388 [M]$^+$, 373 [M−CH$_3$]$^+$; ^{1}H NMR [500 MHz, $CDCl_3$, *δ*/ppm] 2.09 (s, 12H, H10), 2.30 (s, 6H, H11), 6.17 (s, 1H, C(=S)SH), 6.87 (s, 4H, H8), 7.12 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, H4), 7.44 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, H5); ^{13}C NMR [125 MHz, $CDCl_3$, *δ*/ppm] 21.3 (C11) 21.3 (C10), 128.1 (C8), 129.2 (C5), 129.5 (C4), 136.6 (C7, C9), 136.7 (C7, C9), 137.3 (C6), 137.6 (C2), 145.2 (C3), 229.0 (C1); IR [*υ* / cm^{-1}] 2962, 2909, 2851 (*υ*(C–H)), 2500(*υ*(S–H)), 1611, 1447, 1373, 1259, 1088, 1054, 1014, 934, 850, 796, 751, 739, 687; EA [for $C_{25}H_{26}S_2$ / %] calcd. C 76.87, H 6.71, S 16.42; found C 76.57, H 6.73, S 16.27.



Scheme 9. Numbering used for NMR assignment.

X-Ray diffraction experiments

Suitable crystals of the compound Tip-, Mes*- and Dmp-C(=S)SH were obtained by slow evaporation of a saturated solution of *n*-pentane (Tip, Mes*) and diethyl ether (Dmp). They were selected, coated with *paratone-N* oil, mounted on a glass fiber and transferred onto a goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a *SuperNova* diffractometer using Cu-Kα radiation (*λ* = 1.54184 Å) at 100.0(1) K. Using Olex2,[48] the structures were solved and refined with the ShelX program package.[48] Crystal and refinement details, as well as CCDC numbers are provided in Table 5. The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: dithiocarboxylic acid • sulfur • crystal structure • NMR spectroscopy • hydrogen bonding • SH···π interaction

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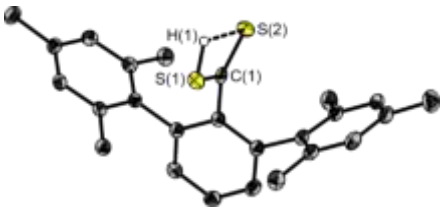
FULL PAPER

Although described since more than 150 years, dithiocarboxylic acids remained a scarcely characterized class of compounds; here we describe synthesis and isolation of true free acids and critically review earlier data.



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Dithiocarboxylic acids – an old theme revisited and augmented by new preparative, spectroscopic and structural facts