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Thion (RCSOH), Selenon (RCSeOH), and Telluron (RCTeOH) Acids as Predominant Species

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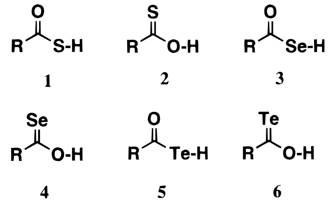
Abstract: Thiocarboxylic acids, such as selenocarboxylic acids, exist predominantly in the thioxo form (RCSOH, thion acid) in polar solvents such as tetrahydrofuran (THF) at temperatures below −50 °C. Tellurocarboxylic acids (**5**) were observed for the first time by acidolysis of the corresponding cesium tellurocarboxylates with hydrogen chloride. The telluroic acids (**6**) exist predominantly in the telluroxo form (RCTeOH, telluron acid) in THF at temperatures below −70 °C. Telluron acids were reddish to blue violet for the aliphatics (R = alkyl) and dark green for the aromatics (R = aryl) and reacted with aryl isocyanates at −70 °C to give crystalline acyl carbamoyl tellurides in good yields.

Introduction

There are generally considered to be six kinds of monochalcogenocarboxylic acids in which one of the two oxygen atoms of the carboxylic acid is replaced by S, Se, or Te (Scheme 1). However, with exception of thiocarboxylic acid (**1**), which is an important class of compounds biologically with a great variety of uses in chemistry,[1] there has been little known about these compounds. Historically, the first synthesis of a thiocarboxylic acid was reported in 1854 by Kekulé, who prepared thioacetic acid.[2] Since then, thiocarboxylic acid has been considered to exist in the thiol form **1** (thiol acid). In contrast, the thioxo form **2** (hereafter called thion acid), the tautomer of **1**, has remained elusive, even spectroscopically.[3] We report here that thion acid **2** is the predominat species in polar solvents at low temperature. In relation to thio- (**1**) and selenocarboxylic acids (**3**),[4] we attempted to prepare tellurocarboxylic acids (**5**). In this article, we report for the first time tellurocarboxylic acids which exist predominantly as the telluroxo form **6** (hereafter called telluron acid) in polar solvents at low temperature.

Scheme 1



Results and Discussion

By analogy with carboxylic acids, the structures of thiocarboxylic acids have been investigated in great detail using various techniques, including cryoscopic,[5] spectroscopic,[5,6] chemical,[7] and theoretical methods.[6r,s,8] These investigations have strengthened the belief that the thiol form **1** best describes the properties of these acids. The thion acid **2** (thioxo form) has probably evaded clear experimental identification because of the small energy difference between the two forms.[8a] Very recently, we have isolated a series of selenocarboxylic acids and found that their structures in a polar solvent are the selenoxo form (**4**) (RCSeOH, selenon acid) at low temperature.[4] This prompted us to reexamine thiocarboxylic acids.

When 4-methoxybenzenecarbothioic acid (**1d**) (R = $4\text{-}CH_3\text{-}OC_6H_4$) was dissolved in a polar solvent such as THF, the color of the solution changed from a light yellow to a deep yellow, with an absorption maximum at 413 nm,[9] whereas hexane or

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

[1] (a) Bauer, W.; Khüren, K. In *Methoden der Organischen Chemie,* 5th ed.; Falbe, J., Ed.; Georg Thieme Publishers: Stuttgart, Germany, 1985; pp 832−890. (b) Abeles, R. H.; Frey, P. A.; Jencks, W. P. *Biochemistry*; Jones and Bartlett: Boston, MA, 1992. (c) Ishii, Y.; Nakayama, J. In *Organic Functional Group Transformations*; Rees, C. W., Ed.; Pergamon Press: New York, 1995; Vol. 5, Chapter 5.12.

[2] Kekulé, A. *Ann. Chem. Pharm.* **1854**, *90*, 309.

[3] The possibility of the presence of a tautomer **2** of **1** was described by Hantzsch and Scharf in 1913: Hantzsch, A.; Scharf, E. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 3570. Reports that favor a detectable amount of the thion acid from spectral data (infrared[6b,c,g] and UV/visible spectra[6q]) are not based on unambiguously assigned bands.

[4] Kageyama, H.; Murai, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1994**, *116*, 2195.

[5] Murthy, A. S. N.; Rao, C. N. R.; Rao, B. D. N.; Venkateswarhu, P. *Trans. Faraday Soc.* **1962**, *58*, 855.

[6] For infrared, see: (a) Kohlrausch, K. W. F.; Pongratz, A. *Z. Phyz. Chem. B* **1934**, *27*, 176. (b) Sheppard, N. *Trans. Faraday Soc.* **1949**, *45*, 693. (c) Crouch, W. W. *J. Am. Chem. Soc.* **1952**, *74*, 2926. (d) Mecke, R.; Spiesecke, H. *Chem. Ber.* **1956**, *89*, 1110. (e) Sjöberg, B. *Acta Chem. Scand.* **1957**, *11*, 945. (f) Nyquest, R. A.; J. Potts, W. *Spectrochim. Acta* **1959**, *15*, 514. (g) Ginzburg, I. M.; Loginova, L. A. *Opt. Spectrom.* **1966**, *20*, 130. (h) Engler, V. R.; Gattow, G. *Z. Anorg. Allg. Chem.* **1972**, *388*, 78. (i) Beumer, A. E.; Harkema, S. *Acta Crystallogr.* **1973**, *B29*, 682. (j) Bicca de Alencastro, R.; Sandorfy, C. *Can. J. Chem.* **1973**, *51*, 1443. (k) Crowder, G. A. *Appl. Spectrosc.* **1973**, *27*, 440. (l) Randhawa, H. S.; Rao, C. N. R. *J. Mol. Struct.* **1974**, *21*, 123. (m) Crowder, G. A.; Robertson, E.; Potter, K. *Can. J. Spectrosc.* **1975**, *20*, 49. (n) Crowder, G. *J. Mol. Struct.* **1976**, *32*, 207. (o) Randhawa, H. S.; Meese, C. O.; Walter, W. *J. Mol. Struct.* **1977**, *36*, 25. (p) Randhawa, H. S.; Walter, W. *J. Mol. Struct.* **1977**, *38*, 89. For UV/vis, see: (q) Sheinker, Yu N.; Ioffe, S. T.; Kabachnik, M. *Izv. Akad. Nauk. SSSR., Otd. Khim. Nauk.* **1960**, 1571 (English Transl. p 1463). (r) Nagata, S.; Yamabe, T.; Fukui, K. *J. Phys. Chem.* **1975**, *79*, 2335. (s) Yamabe, T.; Akagi, K.; Nagata, S.; Kato, H.; Fukui, K. *J. Phys. Chem.* **1976**, *80*, 611. For NMR, see refs 6a,b.

[7] (a) Holmberg, B. *Ark. Kemi, Mineral. Geol.* **1938**, *12B*, No. 47. (b) Holmberg, B.; Schjinberg, C. *Ark. Kemi, Mineral. Geol.* **1940**, *14A*, No. 2.

[8] (a) Naito, T.; Ohashi, O.; Yamaguchi, I. *J. Mol. Spectrosc.* **1977**, *68*, 32. (b) Fausto, R.; Batista de Carbalho, L. A. E.; Teixeira-Dias, J. J. C. *J. Mol. Struct. (THEOCHEM)* **1987**, *150*, 38. For thioformic acid, see: (c) George, P.; Bock, C. W.; Schmiedekamp, A. S. *J. Mol. Struct. (THEOCHEM)* **1981**, *76*, 363. (d) Fausto, R.; Batista de Carbalho, L. A. E.; Teixeira-Dias, J. J. C.; Ramos, V. *J. Chem. Soc., Faraday Trans.* **1989**, *2*, 1945. (e) Fausto, R.; Batista de Carbalho, L. A. E.; Teixeira-Dias, J. J. C. *J. Mol. Struct.* **1990**, *207*, 67.

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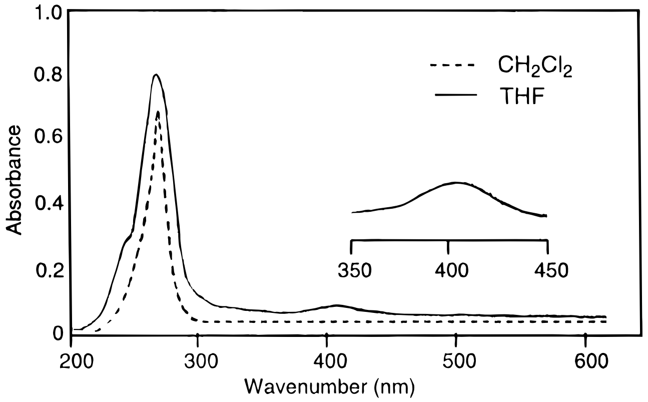


Figure 1. Electron spectra in CH_2Cl_2 solution and in THF solution for 4-methoxybenzenecarbothioic acid at 20 °C.

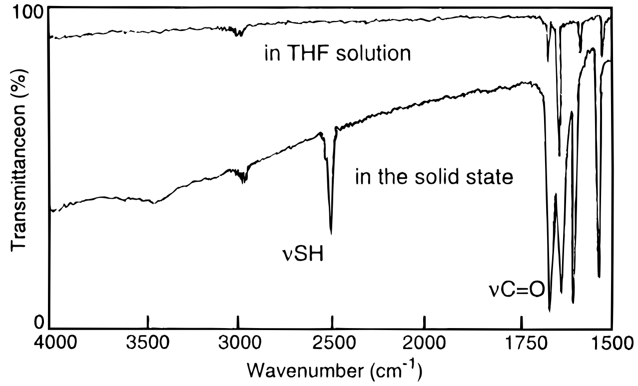
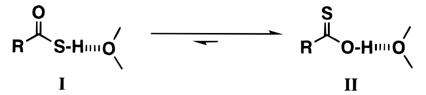


Figure 2. Comparison of IR spectra in THF solution and in the solid state for 4-methoxybenzenecarbothioic acid at 20 °C.

CH_2Cl_2 solutions of **1d** were light yellow and showed no absorption in the region 350−500 nm (Figure 1). The IR and NMR spectra of the deep yellow solution showed some critical differences from those in the solid state (light yellow) or in dichloromethane solution. As shown in Figure 2, neither of the strong ν(C=O) (1670 cm^{-1}) and ν(S−H) bands (2512 cm^{-1}) in the solid state can be observed in THF solution. In THF, the ^1H and ^{13}C NMR spectra do not show signals corresponding to S−*H* and *C*=O moieties. Upon measuring these spectra at a lower temperature of −70 °C, new broad signals near δ 14 and 212 appeared which were ascribed to the OH proton and the C=S carbon,[10] respectively. Upon further lowering of the temperature to −90 °C, these broad signals became markedly sharp at δ 14.52 and 212.3 (Figure 3A),[11−13] indicating clearly that tautomeric equilibrium exists between the thiol (**I**) and thioxo forms (**II**) in a polar solvent (eq 1) (Table 1). A close similarity of ^1H and ^{13}C NMR spectra has been observed in other polar solvents such as acetone and methanol (Table 2) and for other thiocarboxylic acids such as benzenecarbothioic and 4-chloro- and 4-methylbenzenecarbothioic acids in THF solution. In addition, for 2-methoxybenzenecarbothioic and thioacetic acids, ^1H and ^{13}C NMR signals indicating the existence of the two forms were observed at −90 °C, respectively[14] (Figure 3B,C). *These results apparently suggest that thiocarboxylic acids exist predominantly as the thioxo form* **II** (thion acid) *at low temperature in polar solvents such as THF.* To our knowledge, no explanation for the yellow chromophore



(1)

I **II**

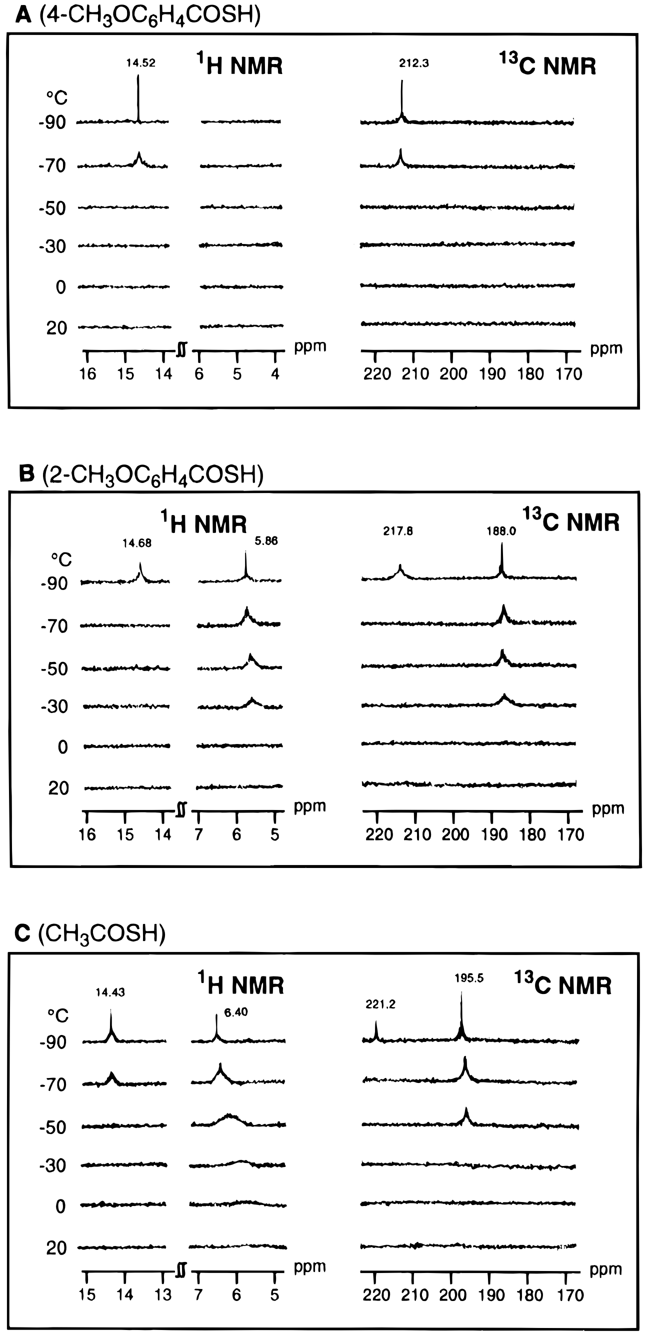


Figure 3. Variable-temperature NMR spectra in THF-d_8 solution for thiocarboxylic acids.

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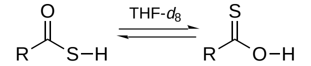
[9] UV/vis λ_{max} (log ϵ) (THF): 289 (4.40), 413 (2.13). $PhCSOCH_3$, UV/vis λ_{max} (log ϵ): 418 (2.20) (hexane) (Ohno, A.; Koizumi, T.; Ohishi, Y.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3556).

[10] The ^{13}C=S values of the known compounds having the C=S moiety are as follows. $4\text{-}CH_3OC_6H_4CSOCH_3$: δ 211.3 ($CDCl_3$), 212.8 (THF-d_8). $PhCSOCH_3$: 213.4 (THF-d_8): δ 212.2 ($CDCl_3$) (Pedersen, B. S.; Sheiby, S.; Klausen, K.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *42*, 3556). $4\text{-}CH_3OC_6H_4CSOSiMe_3$: δ 220.6 ($CDCl_3$), 221.3 (THF-d_8). No equilibrium between $RCOSSiMe_3$ and $RCSOSiMe_3$ is observed (Kato, S.; Mitani, T.; Mizuta, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 244. Mikoliajczyk, M.; Kielbasinski, O.; Schiebel, H. M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 564). An equilibrium between *t*-$BuCOTeSiMe_3$ and *t*-$BuCTeOSiMe_3$ has been reported (Severengiz, T.; du Mont, W. W. *J. Chem. Soc., Chem. Commun.* **1987**, 820). Cf. the ^{13}C=O values of $ArCOSCH_3$. $4\text{-}CH_3OC_6H_4\text{-}COSCH_3$: δ 184.2 ($CDCl_3$), 184.8 (THF-d_8). $PhCOSCH_3$: δ 185.0 (THF-d_8), 185.9 ($CDCl_3$).

[11] Proton ratio of OH/SH = 2.99:0.01 (−90 °C) (on the basis of a proton ratio of OH/CH_3 = 2.99:3.00).

[12] Two groups have reported the existence of thioacetic[6b,c] and trichlorothioacetic *O*-acids[6g] (thioxo form **II**) on the basis of the IR bands at 1220 and 1160 cm^{-1}, respectively.

Table 1. Thion and Thioxo Forms of RCOSH (R = 4-$CH_3OC_6H_4$) in THF-d_8[a]

		
temp (°C)	%[b]	%
23	50?	50?
0		
−30	40	60
−50	21	79
−70	13	87
−90	<1	>99

[a] On the basis of the proton ratio of OH and CH_3 groups. [b] The SH proton is not detected.

Table 2. IR and NMR Spectral Data of 4-Methoxybenzenecarbothioic Acid at 23 °C

	NMR (δ)		IR (cm^{-1})	
solvent	^1H (SH)	$^{13}C{=}O$	ν(C=O)	[solvent]
$CDCl_3$	4.48	188.5	1664 (s)[a]	[$CHCl_3$]
CD_2Cl_2	4.49	188.7	1682 (s)	[CH_2Cl_2]
C_6D_6	4.20	187.8	1679 (s)	[CCl_4]
THF-d_8			1670 (w)	[THF]
CD_3OD			1698 (w)	[Et_2O]
acetone-d_6				

[a] s = strong, w = weak.

of a thiocarboxylic acid has been described in the literature. Presumably, the absorption maximum at 413 nm observed for **1d** can be attributed to the n−π* transition of the thiocarbonyl group in the thion acid **2**. Thionoacetic acid is more stable than thiolacetic acid,[15] while the reverse is true for the monosulfur formic acid.[6l,s] However, thiocarboxylic acids exist only in the thioxo form (**2**) at low temperature despite the fact that they require double bonding between carbon and sulfur, which is more energetically unfavorable than that between carbon and oxygen.[16] In a polar solvent, hydrogen-bonding interactions with the solvent may enable the electrons on the thiocarboxyl group to delocalize more easily. In this system, the equilibrium in eq 1 is shifted to **II**. This can be explained by the notion that the proton on a thiocarboxyl group localizes on the more electronegative atom, i.e. oxygen rather than sulfur, which enables the involvement of the C=S bond in **II**.

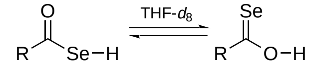
As reported previously,[4] selenocarboxylic acids also exist in selenoxo form (**4**) rather than the selenol form (**3**) in polar solvent at low temperature. Thus, both the strong ν(C=O) and ν(Se−H) bands, which are observed in the solid state or in nonpolar solvent such as dichloromethane, disappear or become very small in a polar solvent such as THF, acetone, or methanol. In the ^1H, ^{13}C, and ^{77}Se NMR spectra, signals of SeH, OH, C=O, and C=Se moieties are not detected (Table 3, see ref 4 (Figure 3)). Upon measuring these spectra at −70 °C, new broad signals near δ 15, 220, and 750 ppm appear, which can be ascribed to the OH proton, C=Se carbon, and C=Se selenium, respectively. These broad signals become markedly sharp, indicating clearly that tautomeric equilibrium exists between the selenol (**III**) and the selenoxo (**IV**) forms in a polar solvent (eq 2, Table 4).

Table 3. IR and NMR Spectral Data of 4-Methoxybenzenecarboselenoic Acid at 23 °C

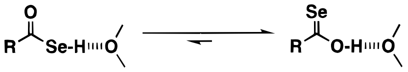
	NMR (δ)		IR (cm^{-1})	
solvent	^1H (SeH)	C=O	ν(C=O)	[solvent]
$CDCl_3$	2.59	189.6	1680 (s)[a]	[$CHCl_3$]
CD_2Cl_2	2.60	189.6	1682 (s)	[CH_2Cl_2]
C_6D_6	2.45	189.6	1697 (s)	[CCl_4]
THF-d_8			1693 (w)	[THF]
CD_3OD	4.99	212.4 (w)[a]	1698 (w)	[Et_2O]
acetone-d_6				

[a] s = strong, w = weak.

Table 4. Selenol and Selenoxo Forms of RCOSeH (R = 4-$CH_3OC_6H_4$) in THF-d_8

		
temp (°C)	%[b]	%
23	50?	50?
0		
−30	25	75
−70	9	91
−90	<1	>99

[a] On the basis of the proton ratio of OH and CH_3 groups. [b] Se-H proton is not detected.



III **IV** (2)

Tellurocarboxylic acids are of interest both for comparison with thio- and selenocarboxylic acids and for understanding the bonding between tellurium and hydrogen. However, the synthesis of such heavy chalcogenocarboxylic acids has not been possible because of their extreme instability and the difficulty of preparing alkali metal tellurocarboxylates, which are the most important starting compounds for the preparation of such labile chalcogenocarboxylic acids. Very recently, we succeeded in isolating rubidium and cesium tellurocarboxylates as crystals.[17] This encouraged us to prepare tellurocarboxylic acids.

When a solution of an excess of dry hydrogen chloride in ether was added to a solution of cesium 4-methoxybenzenecarbotelluroate (**7a**) in THF at −90 °C, the dark red solution of the salt immediately changed to dark green with the precipitation of CsCl. The ^1H and ^{13}C NMR spectra did not show any signals corresponding to the expected Te*H* and *C*O moieties, respectively (Figure 4). Instead, sharp signals were observed at δ 16.02 and 222.9, which are ascribed to the OH proton and the C=Te carbon, respectively.[18] Upon allowing the temperature to rise to −70 °C, the signals broadened substantially, indicating

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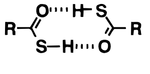
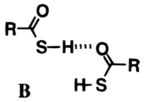
(13) It has been reported that the thioxo form can be observed more readily at a higher temperature than at a lower temperature. There are a few ill-defined in OH proton chemical shifts for thioacetic acid.[6p]

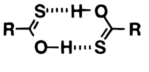
(14) Acetic acid is well-known to form cyclic dimers, both in the gas phase and in a dilute solution (Gordy, W. *J. Chem. Phys.* **1946**, *21*, 1217.). Vibrational spectra of thioacetic,[6d,j,m] thiopropionic,[6k] and thiobenzoic acids[5,6g,j] have been interpreted in terms of hydrogen-bonded dimers **A** and **B** (self-association) in the solid state and in a dilute solution. However, no evidence was obtained, indicating the presence of the cyclic dimer **C** of a thion acid in a polar solvent such as THF. Further comment on the self-association will be left for the discussion.



A



B



C

(15) The energy of the hydrogen bond of CH_3COSH does not exceed 25.1−33.4 kJ/mol.[6b]

(16) The synthesis and characterization of carbon−chalcogen multiple bond are of current research interest. For review, see: Okazaki, R. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 1149. (b) Usov, V. A.; Timokhina, L. V.; Voronkov, M. G. *Sulfur Rep.* **1992**, *12*, 95−158. (d) Guziec, F. S., Jr. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 2, pp 215−273. (e) Guziec, F. S., Jr. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley-Interscience: New York, 1987; p 77.

(17) (a) Kawahara, Y.; Kato, S.; Kanda, T.; Murai, T. *Chem. Lett.* **1995**, *87*. (b) Kawahara, Y.; Kato, S.; Kanda, T.; Murai, T.; Ebihara, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3507.

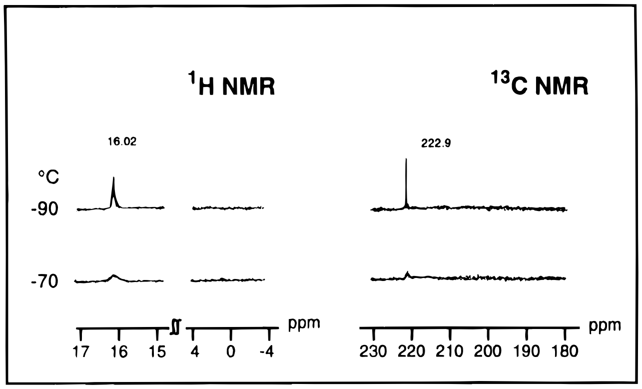


Figure 4. Variable-temperature NMR spectra in THF-d_8 solution for 4-methoxybenezenecarbotelluroic *O*-acid (**9a**).

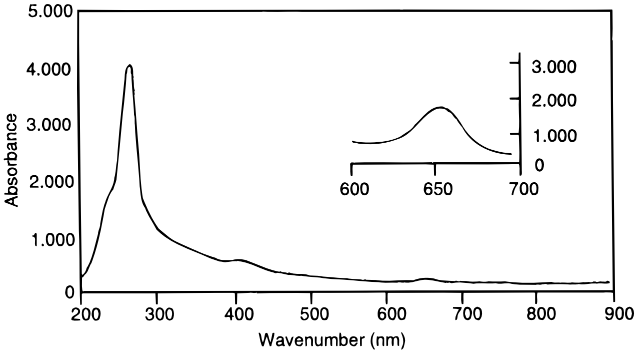
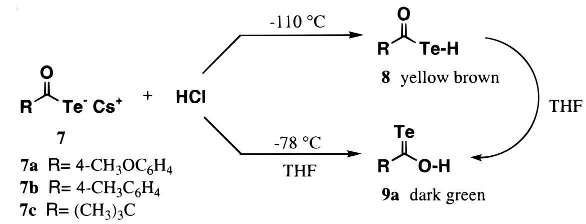


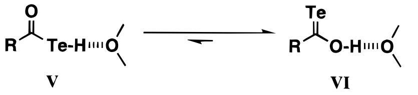
Figure 5. Electron spectra in THF solution for 4-methoxybenzenecarbotelluroic *O*-acid (**9a**) at −90 °C.

the existence of some dynamic NMR exchange process (probably involving making and breaking of the hydrogen bond (eq 3). The ^{125}Te NMR spectrum showed a characteristic signal at δ 952 due to the C=Te group.[19] Furthermore, the UV/visible spectrum at −73 °C showed an absorption maximum at 652 nm which was ascribed to the n−π* transitions of the C=Te group (Figure 5).[20] These results apparently suggest that *the tellurocarboxylic acid exists predominantly in the telluroxo form* (**VI**) (telluron acid) (4-methoxybenzenecarbotelluroic *O*-acid (**9a**)) *in THF at low temperature.* Under similar conditions, acidolysis of cesium 4-methylbenzenecarbotelluroate (**7b**) and 2,2-dimethylpropanetelluroate (**7c**) with HCl led to dark green (λ_{max} 672 nm) and blue violet solutions (λ_{max} 594 nm), respectively, indicating the formation of the corresponding tellurocarboxylic acids **9b** and **9c**.

Next, to confirm the existence of a tellurol acid **5**, acidolysis of the salt **7a** with hydrogen chloride was carried out without solvents. Thus, when an excess of pure liquid hydrogen chloride was added to **7a** at −195 °C and the temperature was raised to −90 °C, the dark brown salt quickly changed to a yellow solid near −110 °C. Addition of toluene to the yellow solid at −90 °C gave a yellow solution with a characteristic ^{125}Te NMR signal at δ 535, which changed instantly to a dark green with further addition of THF, indicating the formation of **9a** with an absorption maximum at 652 nm. However, the direct addition of THF to the yellow solid at −78 °C led to a dark green solution of **9a**. Although tellurol acid **8** is too labile to allow us to measure the TeH proton and carbonyl carbon chemical shifts, these results indicate that, at low temperature, tellurol acid **8a** exists as a yellow solid or a yellow toluene solution. In a polar solvent, the hydrogen-bonding interaction of **8a** with the solvent may enable the electrons on the tellurocarboxyl group to delocalize more easily. As in thio- and selenocarboxylic acids, the fact that the equilibrium in eq 3 is shifted to **VI** may be explained by the realization that the proton on the tellurocarboxyl group localizes on the more negative oxygen atom than the tellurium, and this enables the involvement of the C=Te bond in **VI**.

Scheme 2

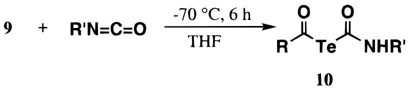




(3)

The resulting tellurocarboxylic acids were extremely sensitive toward oxygen and temperature. Tellurol acids **8** appear to be considerably more labile than telluron acids **9**. For example, when exposed to air, 4-methoxybenzenecarbotelluroic *O*-acid (**9a**) in THF solution immediately liberates black tellurium (tellurium mirror), even at −90 °C.[21] However, under an Ar conditions, no appreciable change in the solution was observed at −78 °C for at least 1 min. In contrast, the tellurol acid **8a** gradually decomposed to change from yellow brown to gray even at −90 °C.

We previously found that dithiocarboxylic acids reacted with aryl isocyanates to give thioacyl carbamoyl sulfides (RCS−S−CONHR′, R, R′ = alkyl, aryl) in good yields, and in which the existence of hydrogen bonding between the NH hydrogen and thiocarbonyl sulfur atoms was suggested by infrared study.[22] Expecting the formation of tellurium analogues, we reacted tellurocarboxylic *O*-acids with aryl isocyanates (eq 4). In fact,



(4)

	R	R'	%
10a	4-$CH_3OC_6H_4$	C_6H_5	81 (71)[a]
10b	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	89
10c	4-$CH_3C_6H_4$	C_6H_5	93

[a] Solvent = CH_2Cl_2

4-methoxybenzenecarbotelluroic *O*-acid (**9a**) reacted with phenyl and 4-methylphenyl isocyanates at −70 °C to give the corresponding acyl carbamoyl tellurides **10a** and **10b** in good yields

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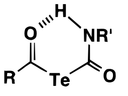
(18) The values of ^{13}C NMR resonances corresponding to C=Te moieties: 4-$CH_3C_6H_4CTeOSi(CH_3)_3$ ($CDCl_3$): δ 223.7[17a]; 4-$CH_3OC_6H_4CTeOSi(CH_3)_3$ ($CDCl_3$): δ 221.6[17b]; *t*-$C_4H_9CTeOSiCH_2$(*t*-Bu) ($CDCl_3$): δ 229.4[18a−c] [(a) Barret, A. G. M.; Barton, D. H. R.; Reed, R. W. *J. Chem. Soc., Chem. Commun.* **1979**, 645−647. (b) Barret, A. G. M.; Reed, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2191−2195. *t*-$C_4H_9CTeOSi(CH_3)_3$ ($CDCl_3$): (c) Severengis, T.; du Mont, W. W. *J. Chem. Soc., Chem. Commun.* **1987**, 820−821].

(19) The values of ^{125}Te NMR resonances corresponding to C=Te moieties. 4-CH_3-$C_6H_4CTeOSiCH_3)_3$ ($CDCl_3$): δ 1438.[17a] 4-$CH_3OC_6H_4CTeOSi(CH_3)_3$ ($CDCl_3$): δ 1303.[17b] *t*-$C_4H_9CTeOSi(CH_3)_3$ ($CDCl_3$): δ 1418.[18c]

(20) The values of n−π* transitions of C=Te group. 4-$CH_3C_6H_4CTeOSi(CH_3)_3$ ($CHCl_3$): 700 nm.[17a] 2-$CH_3OC_6H_4CTeOSi(CH_3)_3$ (CH_3CN): 670 nm.[17b] 4-$CH_3OC_6H_4CTeOSi(CH_3)_3$ ($CHCl_3$): 682 nm.[17b]

(21) Removal of the black tellurium from the decomposition products by filtration, followed by evaporation under reduced pressure, gave a yellow oil in which the presence of bis(4-methoxybenzoyl) telluride was suggested by mass and ^{1}H and ^{13}C NMR spectral studies. Presumably the telluride would be formed by detelluration of the corresponding diacyl ditelluride.

as pale yellow crystals (eq 4). In addition, the reaction with 4-methylbenzenecarbotelluroic *O*-acid (**9b**) under the same conditions gave a good isolated yield of the corresponding addition product **10c** (eq 4). In these reactions, the use of dichloromethane instead of THF as a solvent resulted in analogous yields of **10**. The NH proton chemical shifts of **10** were observed in downfield region below δ 10, suggesting that **10** exists as a strongly intramolecularly hydrogen-bonded species **11**. Recently, analogous intramolecular six-membered-ring structures arising from hydrogen-bonding between the NH hydrogen and the carbonyl oxygen or thiocarbonyl sulfur atom have been observed by X-ray structural analysis for 2,6-dimethoxybenzoyl 4-methylbenzenecarbamoyl selenides[23] and 4-methoxythiobenzoyl 4-methylbenzenecarbamoyl sulfides,[24] respectively.



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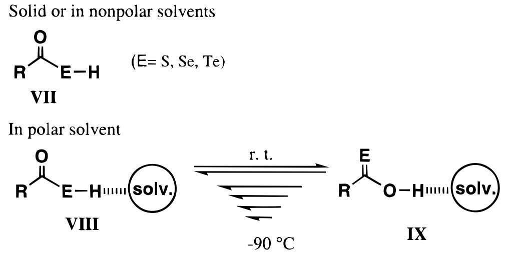
In summary, we have demonstrated the existence of thion acid **2** as a predominat species and have reported the first observation of a tellurocarboxylic acid. Tautomeric equilibrium between the thiol and thioxo forms and between the tellurol and telluroxo forms was demonstrated spectroscopically. These results and those obtained for selenocarboxylic acids[10] lead to the general conclusion that, in monochalcogenocarboxylic acids such as thio-, seleno-, and tellurocarboxylic acids, the chalcogenoxo form **IX** is an actual and predominant species in apolar solvents at low temperature despite the involvement of the energetically unfavorable $C{=}E$ bond (E = S, Se, Te), whereas chalcogenol acid **VII** (chalcogenol form) is a predominant species in both the solid state and nonpolar solvents (Scheme 3). In these classes of compounds involving heteroatom-containing allylic anion systems, electronegativity and hydrogen-bonding interaction may play important roles in controlling the degree of the localization of the electrons and in the formation of double bonding between carbon and third-, forth-, and fifth-row elements. The present findings, 140 years after the first synthesis of a thiocarboxylic acid, have opened up the possibility of a new chemistry for a class of compounds of hitherto unknown *chalcogenon acids* (RCEOH, E = S, Se, Te). In addition, the presence of these acids may be important in understanding not only the role of the chalcogeno elements, especially S and Se, in biological systems but also the results of studies concerning the addition of thiocarboxylic acids to unsaturated bonds.

Scheme 3



R	E	VIII	/	IX
4-$CH_3OC_6H_4$	S	< 1	:	> 99
	Se	< 1	:	> 99
	Te	< 1	:	> 99

Solv. = THF, Temp.= -90 °C.

Experimental Section

General Procedure. Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. The IR spectra were measured on a Perkin-Elmer FT-IR 1640 instrument. The Electron spectra were taken by a JASCO Ubest-55. The ^1H and ^{13}C NMR spectra were recorded in 10% solutions on a JEOL A-400 (400 and 100 MHz, respectively) instrument with tetramethylsilane as an internal standard. The ^{125}Te NMR spectra were recorded on a JEOL A-400 (85.3 MHz) with dimethyl telluride as an external standard. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials. Thioacetic (**1f**) and benzenecarbothioic (**1a**) acids were of commercial grade and distilled before use. 4-Methyl- (**1b**), 4-chloro- (**1c**), 4-methoxy- (**1d**), and 2-methoxybenzenecarbothioic acids (**1e**) were prepared by HCl acidolysis of the corresponding potassium salts which were prepared according to the literature[25a] and purified by vacuum distillation or by recrystallization from ether and/or hexane. C_6H_5COSH (**1a**): liquid; IR (neat) 2582 (SH), 1672 ($C{=}O$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.07 (s, 1H, SH), 7.3−8.1 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) (23 °C) δ 127.9, 128.1, 128.7, 133.9 (Ar), 190.2 ($C{=}O$). 4-$CH_3C_6H_4COSH$ (**1b**): mp 42.5−43 °C (lit.[25c] 43−44 °C); IR (KBr) 2510 (SH), 1651 ($C{=}O$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 4.44 (bs, 1H,SH), 7.14 (d, 2H, Ar, 8.2 Hz), 7.69 (d, 2H, Ar, 8.2 Hz); ^{13}C NMR ($CDCl_3$) (23 °C) δ 21.7 (CH_3), 127.9, 128.0, 129.3, 129.4, 134.1, 144.9 (Ar), 189.7 ($C{=}O$). 4-ClC_6H_4COSH (**1c**): IR (KBr) 2508 (SH), 1658 ($C{=}O$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (s, 1H, SH), 7.34 (d, 2H, Ar, $J = 8.6$ Hz), 7.84 (d, 2H, Ar, $J = 8.6$ Hz); ^{13}C NMR ($CDCl_3$) 129.0, 129.1, 129.2, 129.3, 134.9, 140.7 (Ar), 188.9 ($C{=}O$). 4-$CH_3OC_6H_4COSH$ (**1d**): mp 81−83 °C (lit.[25b] 82−83 °C); IR (KBr) 2512 (SH), 1652 ($C{=}O$); (THF) 3572, 3507 (OH), 2682 (SH), 1670 ($C{=}O$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 4.48 (s, 1H, SH), 6.40 (d, 2H, Ar, 8.4 Hz), 7.87, (d, 2H, Ar, 8.4 Hz); ^{13}C NMR ($CDCl_3$) (23 °C) δ 55.6 (CH_3O), 113.9, 129.5, 130.2, 164.2 (Ar), 189.2 ($C{=}O$) (−50 °C); (CD_2Cl_2) δ 4.49 (SH), 188.7 ($C{=}O$); UV/vis λ_{max} (ϵ) (cyclohexane) 273 (4.40), 283 (4.36); UV/vis λ_{max} (CH_2Cl_2) 279 nm. 2-$CH_3OC_6H_4$-COSH (**1e**): oil; IR (neat) 2552 (SH), 1641 ($C{=}O$); IR (THF) 3571, 3507 (OH), 2682 (SH), 1650 ($C{=}O$); (CD_2Cl_2) 3650 (OH), 2564 (SH), 1645 ($C{=}O$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.96 (s, 3H, CH_3), 4.92 (s, 1H, SH), 7.0−8.0 (m, 4H, Ar); IR (THF-d_8) δ 3.91 (s, 3H, CH_3O), 7.0−7.8 (m, 4H, Ar); ^{13}C NMR (CD_2Cl_2) δ 25.3 (CH_3O), 113.1, 121.1, 130.0, 135.1 (Ar), 159.4 ($C{=}O$). CH_3COSH (**1f**): ^1H NMR ($CDCl_3$) (23 °C) δ 2.39 (s, 3H, CH_3), 4.77 (SH); ^{13}C NMR ($CDCl_3$) (23 °C) δ 32.6 (CH_3), 194.0 ($C{=}O$). 4-methoxybenzenecarboselenoic *O*-acid was prepared by the method described previously.[4] Cesium 2,2-dimethylpropanetelluroates and 4-methyl-, and 4-methoxybenzenecarbotelluroates were prepared by the reaction of the corresponding *O*-trimethylsilyl tellurocarboxylates with cesium fluoride or by the reaction of acyl chlorides with sodium telluride.[17]

Values of ^1H and ^{13}C NMR Corresponding to O*H* and/or SH and *C*═S and/or C═O Moieties of Thiocarboxylic Acids. C_6H_5-CSOH (**1a**): (THF-d_8) (−90 °C) δ 14.28 (O*H*), 213.5 (*C*═S); (−70 °C) 14.68 (O*H*), 213.5 (*C*═S); (−50 °C) 14.52 (O*H*), 213.3 (*C*═S); (CD_3OD) (−80 °C) 15.60 (O*H*), 214.0 (*C*═S). 4-$CH_3C_6H_4$-CSOH (**1b**): (THF-d_8) (−90 °C) δ 14.62 (O*H*), 210.8 (*C*═S); (−70 °C) 14.59 (O*H*), 210.8 (*C*═S); (−50 °C) 14.43 (O*H*), 210.9 (*C*═S) 4-ClC_6H_4CSOH (**1c**): (THF-d_8) (−90 °C) δ 14.90 (O*H*), 212.0 (*C*═S); (−70 °C) 14.80 (O*H*), 212.0 (*C*═S); (−50 °C) 212.2 (*C*═S). 4-$CH_3OC_6H_4CSOH$ (**1d**): (THF) (−90 °C) δ 14.52 (O*H*), 212.3 *C*═S); (−70 °C) 14.37 (O*H*), 212. 2

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(22) For the reaction with RCSSH, see: (a) Kato, S.; Mitani, T.; Mizuta, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3653. We have postulated an analogous intramolecular six-member-ring structure stabilized by hydrogen-bonding between the thiocarbonyl sulfur and NH hydrogen atoms. For the reaction with RCOSH, see: Motoki, S.; Saito, T.; Kagami, H. *Bull. Chem. Soc. Jpn.* **1974**, *44*, 775.

(23) Kageyama, H.; Asada, K.; Maejima, K.; Kanda, T.; Murai, T.; Kato, S. *The 67th Spring Annual Meeting of The Japan Chemical Society, Tokyo, Abstr. II*, March 1994; p 1320, (4HX-07).

(24) Ogawa, T.; Asada, K.; Kageyama, H.; Kanda, T.; Murai, T.; Kato, S. *The 69th Spring Annual Meeting of The Japan Chemical Society, Kyoto, Abstr. II*, March 1995; p 1304, (2HX-30).

(25) (a) Nobel, P. L., Jr.; Tarbel, D. S. *Org. Synth.* **1963**, Collect. Vol. 4, 924. (b) Bloch, I.; Bergmann, M. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 961. (c) Weigert, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 1011.

(*C*═S); (acetone-d_6) (−90 °C) δ 14.60 (O*H*), 193.4 (*C*═O), 211.5 (*C*═S); (C_6D_6) (23 °C) 4.26 (S*H*), 187.8 (*C*O). 2-$CH_3OC_6H_4CSOH$ (**1e**): (THF-d_8) (−90 °C) δ 5.86 (S*H*), 14.68 (O*H*), 188.0 (*C*═O), 217.8 (*C*═S); (−70 °C) 5.71 (S*H*), 188.0 (*C*═O); (−50 °C) 5.71 (S*H*), 188.0 (*C*═O); (−30 °C) 5.71 (S*H*), 188.0 (*C*═O). CH_3CSOH (**1f**): (THF-d_8) (−90 °C) δ 6.44 (S*H*), 14.38 (O*H*), 195.5 (*C*═O), 221.2 (*C*═S); (−70 °C) 6.25 (S*H*), 14.24 (O*H*), 195.2 (*C*═S); (−50 °C) 6.08 (S*H*), 195.0 (*C*═S); (−30 °C) 5.95 (b, S*H*); (0 °C) 5.81 (b, S*H*); (20 °C) 5.84 (b, S*H*).

Values of ^{1}H and ^{13}C NMR Corresponding to O*H* and/or SeH and *C*═Se and/or C═O Moieties of 4-Methoxybenzenecarboselenoic Acid (9a). 4-$CH_3OC_6H_4CSeOH$: (THF-d_8) (−90 °C) δ 15.29 (O*H*), 222.2 (*C*═Se); (−70 °C) 15.16 (O*H*), 222. 2 (*C*═Se); (−50 °C) 15.08 (O*H*), 221.8 (*C*═Se); (−30 °C) 14.7(br) (O*H*), 216.0 (*C*═Se).

Preparation of Tellurocarboxylic Acids. All manipulations were carried out under an argon atmosphere.[26]

Preparation of 4-Methoxybenzenecarbotelluroic *O*-Acid (9a). To a suspension of cesium 4-methoxybenzenecarbotelluroate (**7a**) (0.181 g, 0.45 mmol) in THF-d_8 (5 mL) was added a solution of dry hydrogen chloride (0.9 mmol) in ether (0.9 mL) at −78 °C. The mixture was stirred at this temperature for 1 h. The color of the reaction mixture instantly changed from dark red to dark green. Removal of CsCl by filtration and subsequent evaporation of the excess of hydrogen chloride and ether from the filtrate under reduced pressure afforded a dark green THF-d_8 solution of 4-methoxybenzenecarbotelluroic *O*-Acid (**9a**): ^{1}H NMR (THF-d_8) (−90 °C) δ 3.85 (s, 3H, CH_3O), 6.9−8.3 (m, 4H, Ar), 16.2 (s, 1H, OH); ^{13}C NMR (THF-d_8) (−90 °C) δ 21.7 (CH_3O), 127.9, 134.3, 141.4, 148.2 (Ar), 222.9 (C═Te); ^{125}Te NMR (THF-d_8) (−90 °C) δ 952; UV/vis (THF) (−90 °C) 284, 442.0, 652 nm.

Attempted Preparation of 4-Methoxybenzenecarbotelluroic *Te*-Acid (4-$CH_3OC_6H_4COTeH$) (8a). Dry hydrogen chloride gas (ca. 3 mL) was introduced onto cesium 4-methoxybenzenecarbotelluroate (**7a**) (0.459 g, 1.16 mmol) in an NMR tube (Φ 5 × 150 mm) at −195 °C. The excess of HCl was carefully evaporated upon raising the temperature to −78 °C [the reaction occurred at ca. −110 °C (HCl; mp −114 °C), and the dark brown of the salts changed to a yellow solid of 4-methoxybenzenecarbotelluroic *Te*-Acid (**8a**) containing CsCl]. *Caution: the NMR tube is disrupted explosively by a violent evolution of HCl gas during the preparation of the ^{1}H and ^{13}C NMR samples.* When cooled to −90 °C, toluene-d_8 (3 mL) was added to the yellow solid to give a slightly yellow solution [^{125}Te NMR (toluene-d_8) (−90 °C) δ 535 (*Te*H)]. Upon addition of THF (1 mL) to the toluene-d_8 solution, there was an immediate change to a dark green solution [UV/vis (THF)(−90 °C) 652 nm]. The visible spectrum was consistent with that of the telluron acid **9a**.

Preparation of 4-Methylbenzenecarbotelluroic *O*-Acid (9b). To a suspension of cesium 4-methylbenzenecarbotelluroate (**7b**) (0.181 g, 0.45 mmol) in THF-d_8 (5 mL) was added a solution of dry hydrogen chloride (0.9 mmol) in ether (0.9 mL) at −78 °C. The mixture was stirred at this temperature for 1 h. The color of the reaction mixture instantly changed from a dark red to a dark green. Removal of CsCl by filtration gave a THF solution of 4-methylbenzenecarbotelluroic *O*-acid (**9b**): ^{1}H NMR (THF-d_8) (−90 °C) δ 2.14 (s, 3H, CH_3), 6.94, 6.95 (d, 2H, Ar), 7.71, 7.93 (d, 2H, Ar), 16.48 (s, 1H, OH); ^{13}C NMR (THF-d_8) (−90 °C) δ 57.1 (CH_3O), 115.4, 134.3, 143.1, 148.2 (Ar), 223.1 (C═Te) (?); ^{125}Te NMR (THF-d_8) (−90 °C) δ 1024 (?); UV/vis (THF) (−90 °C) 673 nm.

2,2-Dimethylpropanetelluroic *O*-Acid (9c). To a suspension of cesium 2,2-dimethylpropanetelluroate (**7c**) (0.181 g, 1.40 mmol) in THF-d_8 (5 mL) was added a solution of dry hydrogen chloride (2.8 mmol) in ether (2.8 mL) at −78 °C. The mixture was stirred at this temperature for 1 h. The color of the reaction mixture instantly changed from a yellow brown to blue-violet (a THF solution of 2,2-dimethylpropanetelluroic *O*-acid (**9c**)): UV/vis (THF) (−90 °C) 594 nm.

Reaction of 4-Methoxybenezenecarbotelluroic *O*-Acid (9a) with Phenyl Isocyanate. A solution of dry hydrogen chloride (2.66 mmol) in ether (2.66 mL) was added dropwise to a suspension of cesium 4-methoxybenzenecarbotelluroate (**7a**) (0.181 g, 0.45 mmol) in tetrahydrofuran (7 mL) at −78 °C, and the mixture was stirred at −70 °C for 2 h. The color changed from a dark red to a dark green, indicating the formation of 4-methoxybenzenecarbotelluroic *O*-acid (**9a**). A solution of phenyl isocyanate (0.158 g, 1.33 mmol) in tetrahydrofuran (4 mL) was added dropwise, and the mixture was stirred for 6 h. The insoluble part (CsCl and black tellurium) was filtered off, and the solvent was evaporated under reduced pressure to give 0.138 g (81%, purity >98% by ^{1}H NMR) of 4-methoxybenzoyl phenylcarbamoyl telluride (**10a**) as microfine crystals. Recrystallization of the crystals from a mixed solvent of dichloromethane and hexane (1:6) at −15 °C afforded 0.065 g (38%) of chemically pure **10a** as pale yellow needles: mp 71 °C (dec); IR (KBr) 3324 (NH) 3037, 2985, 1701 (C═O), 1687 (C═O), 1594, 1571, 1545, 1303, 1266, 1165, 1026, 876, 860, 841, 752, 648, 613, 562, 502 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H, CH_3O), 6.80−7.7 (m, 9H, Ar), 10.13 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 55.8 (CH_3O), 114.6, 119.8, 124.8, 129.1, 130.1, 135.2, 137.2, 165.4 (Ar), 148.6 (NCO), 201.5 (C═O); ^{125}Te NMR ($CDCl_3$) δ 891.6.

4-Methoxybenzoyl 4-Methylbenzenecarbamoyl Telluride (10b). In a way similar to the reaction with phenyl isocyanate, the reaction of freshly prepared 4-methoxybenzenecarbotelluroic *O*-acid (**9a**) (0.45 mmol) [from a solution of dry hydrogen chloride (2.66 mmol) in ether (2.66 mL) and cesium 4-methoxybenzenecarbotelluroate (**7a**) (0.181 g, 0.45 mmol) in tetrahydrofuran (10 mL)] with 4-methylphenyl isocyanate (0.100 g, 1.25 mmol) in tetrahydrofuran (4 mL) for 6 h to give 0.256 g (89%, purity >99% by ^{1}H NMR) of 4-methoxybenzoyl 4-methylphenylcarbamoyl telluride (**10b**) as a microfine solid and recrystallization of the solid from a mixed solvent of dichloromethane and hexane (1:6) at −20 °C afforded 0.061 g (21%) of chemically pure **10b** as pale yellow needles: mp 90 °C (dec); IR (KBr) 3345, 3048, 2985, 1690 (C═O), 1593, 1571, 1507, 1432, 1310, 1268, 1220, 1164, 1023, 858, 835, 806, 780, 740, 648, 611, 580, 502, 490, 432 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H, CH_3), 3.79 (s, 3H, CH_3O), 6.90, 6.91, 7.09, 7.11, 7.43, 7.45, 7.69, 7.71 (8H, Ar), 10.05 (s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 21. 0 (CH_3), 55.8 (CH_3O), 114.2, 114.6, 119.8, 129.6, 130.1, 131.1, 132.5 134.9, 135.3 (Ar), 148.5 (NCO), 165.4 (Ar), 201.5 (C═O); ^{125}Te NMR ($CDCl_3$) δ 888.0. Anal. Calcd for $C_{15}H_{15}NO_3Te$: C, 48.42; H, 3.81. Found: C, 48.13; H, 3.69.

4-Methylbenzoyl Phenylcarbamoyl Telluride (10c). In a way similar to the preparation of **10b**, the reaction of freshly prepared 4-methylbenzenecarbotelluroic *O*-acid (**9b**) (1.0 mmol) [from a solution of dry hydrogen chloride (2.66 mmol) in ether (2.66 mL) and sodium 4-methylbenzenecarbotelluroate (0.270 g, 1.0 mmol) in tetrahydrofuran (10 mL)] with phenyl isocyanate (0.122 g, 1.03 mmol) in tetrahydrofuran (5 mL) for 6 h gave 0.358 g (93%, purity >97% by ^{1}H NMR)) of 4-methylbenzoyl phenylcarbamoyl telluride (**10c**) as a white-yellow microfine solid. Recrystallization of the solid from a mixed solvent of dichloromethane and hexane (1:6) at −20 °C afforded 0.091 g (24%) of chemically pure **10c** as pale yellow columns: mp 81 °C (dec); IR (KBr) 3255, 3180, 3048, 2980, 1699 (C═O), 1654, 1597, 1545, 1495, 1444, 1306, 1293, 1236, 1207, 1169, 1142, 1075, 877, 856, 800, 754, 610, 578, 548, 505, 462 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H, CH_3), 7.0−7.7 (9H, Ar), 10.05 (s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 21. 9 (CH_3), 119.8, 124.9, 127.6, 129.1, 130.1, 137.2, 139.9, 146.8 (Ar), 148.8 (NCO), 203.8 (C═O); ^{125}Te NMR ($CDCl_3$) δ 910.2.

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[26] The term “under argon” means that the system was evacuated with an oil pump and refilled with argon at least three times and that a positive (ca. 3 Torr) of argon was maintained during the experiment.