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# $^{125}$Te Nuclear Magnetic Resonance Study and X-ray Crystal Structures of Organotelluronium Salts

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The proton-noise-decoupled tellurium-125 NMR spectra of a series of organotelluronium salts $R_2Te^+R'\ X^-$ are reported, including the precursors of nonstabilized, semistabilized, and stabilized telluronium ylides (R = *n*-Bu, *i*-Bu, Me, and Ph; $R' = C_nH_{2n+1}$ ($n$ = 1–6), Ph, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CSiMe_3$, $CH_2CH{=}CHSiMe_3$, $CH_2CH{=}CHCO_2Et$, $CH_2CO_2CH_3$, $CH_2CO_2C_2H_5$, $CH_2CONHBu$-*i*, $CH_2CO\overline{N(CH_2)_3C}H_2$, $CH_2CO\overline{N(CH_2)_4C}H_2$, and $CH_2CN$; X = Cl, Br, I, and $BPh_4$). The $^{125}$Te NMR chemical shifts are measured in $CDCl_3$, DMSO-$d_6$, or solution relative to neat $Me_2Te$ and range from 418 ppm for $(CH_3)_3Te^+\ I^-$ to 675 ppm for $(C_6H_5)_2Te^+CH_3\ ^-BPh_4$. The coupling constants of Te–C and Te–H of several telluronium salts are also reported. Furthermore, X-ray crystals structures of $(CH_3)_2Te^+CH_3\ I^-$ (**14**), *i*-$Bu_2Te^+C_6H_5\ Br^-$ (**4**), and $(C_6H_5)_2Te^+CH_3\ ^-BPh_4$ (**23**) are reported. Compound **14** belongs to the monoclinic system, space group $P2_1/n$, with $Z = 4$, $a = 7.123(2)$ Å, $b = 9.675(3)$ Å, $c = 11.334(3)$ Å, and $\beta = 107.71(3)°$. Compound **4** crystallizes also in the monoclinic system, space group $P2_1/c$, with $Z = 4$, $a = 9.161(4)$ Å, $b = 14.496(8)$ Å, $c = 13.198(6)$ Å, and $\beta = 106.86(3)°$. Compound **23** belongs to an orthorhombic system, space group $P2_12_12_1$, with $Z = 4$, $a = 8.777(5)$ Å, $b = 16.689(5)$ Å, and $c = 20.523(8)$ Å.

## Introduction

Recently there has been remarkable interest in the synthetic application of organotellurium reagents.[1] In our previous communication, we found that diphenyltelluronium methylide, the first nonstabilized telluronium ylide generated from methyldiphenyltelluronium tetraphenylborate, reacted with aldehydes or ketones to form substituted oxiranes.[2] Later on, we described the applications of several moderately stabilized telluronium ylides and silylated telluronium ylides in organic synthesis.[3] However, the reactions of trimethyl- and methyldiphenyltelluronium salts (precursors of nonstabilized telluronium ylides) with aromatic aldehydes gave secondary alcohols with the use of alkyl- or aryllithium reagent.[4] We also reported that the reactions of carbonyl compounds with benzyldibutyltelluronium bromide (precursor of semistabilized telluronium ylide) and dibutyl(cyanomethyl)telluronium chloride (precursor of stabilized telluronium ylide) afforded homobenzylic alcohols and $\beta$-hydroxy nitriles respectively promoted by alkyl- or aryllithium reagents.[5] As a new type of organometallic reagent, these telluronium salts are expected to find further use in organic synthesis.

Because of the large number of resonances and complex coupling patterns inherent in proton NMR, $^{125}$Te NMR is a more efficient method for the identification of unknown tellurium compounds, the determination of reaction mechanisms, and the elucidation of catalytic properties of tellurium derivatives. The wider use of $^{125}$Te NMR will be realized only after the chemical shifts of a sufficient number of representative classes of tellurium derivatives have been measured. Although there has been an increasing use of direct $^{125}$Te NMR measurements with broad-band probes in the characterization of tellurium compounds,[6–19] few data have been reported for organo-

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**Table 1. Organotelluronium Salts Studied: $R_2Te^+R'\ X^-$ [a]**

| no. | R | R′ | X | no. | R | R′ | X |
|---|---|---|---|---|---|---|---|
| **1** | $i$-$C_4H_9$ | $CH_2CN$ | Cl | **15** | $n$-$C_4H_9$ | $CH_3$ | I |
| **2** | $n$-$C_4H_9$ | $CH_2CN$ | Cl | **16** | $n$-$C_4H_9$ | $CH_2CN$ | I |
| **3** | $i$-$C_4H_9$ | $CH_2CH{=}CH_2$ | Cl | **17** | $i$-$C_4H_9$ | $CH_2CH{=}CH_2$ | I |
| **4** | $i$-$C_4H_9$ | $C_6H_5$ | Br | **18** | $n$-$C_4H_9$ | $CH_2CH_3$ | I |
| **5** | $n$-$C_4H_9$ | $CH_2C_6H_5$ | Br | **19** | $n$-$C_4H_9$ | $CH_2CH_2CH_3$ | I |
| **6** | $n$-$C_4H_9$ | $CH_2CN$ | Br | **20** | $n$-$C_4H_9$ | $n$-$C_4H_9$ | I |
| **7** | $i$-$C_4H_9$ | $CH_2CH{=}CH_2$ | Br | **21** | $n$-$C_4H_9$ | $n$-$C_5H_{11}$ | I |
| **8** | $i$-$C_4H_9$ | $CH_2CH{=}CHSiMe_3$ | Br | **22** | $n$-$C_4H_9$ | $n$-$C_6H_{13}$ | I |
| **9** | $i$-$C_4H_9$ | $CH_2C{=}CSiMe_3$ | Br | **23** | $C_6H_5$ | $CH_3$ | $BPh_4$ |
| **10** | $n$-$C_4H_9$ | $CH_2CO_2CH_3$ | Br | **24** | $n$-$C_4H_9$ | $CH_2CN$ | $BPh_4$ |
| **11** | $n$-$C_4H_9$ | $CH_2CO_2C_2H_5$ | Br | **25** | $i$-$C_4H_9$ | $CH_2CH{=}CH_2$ | $BPh_4$ |
| **12** | $n$-$C_4H_9$ | $CH_2CONHBu$-$i$ | Br | **26** | $n$-$C_4H_9$ | $CH_2CH{=}CHCO_2Et$ | $BPh_4$ |
| **13** | $n$-$C_4H_9$ | $CH_2CH{=}CH_2$ | Br | **27** | $n$-$C_4H_9$ | $CH_2CON(CH_2)_3CH_2$ | $BPh_4$ |
| **14** | $CH_3$ | $CH_3$ | I | **28** | $n$-$C_4H_9$ | $CH_2CON(CH_2)_4CH_2$ | $BPh_4$ |

[a] All the telluronium salts gave satisfactory FAB-MS, $^1H$ NMR, and elemental analysis.

telluronium salts.[20-23] Earlier shift measurements were obtained with double-resonance techniques.[20] The chemical shift range for tellurium is quite large, from the highly deshielded tellurium–selenium dication (2600–3300)[24-25] to the much more shielded lithium alkanetellurolates and arenetellurolates (117–725).[11] However, the limited data so far reported have been for compounds of such widely different structures that little is known concerning the response of the tellurium chemical shifts to structural changes in the organic moiety of similar tellurium compounds.

## Results and Discussion

In our previous paper, we reported the fast atom bombardment mass spectra of organotelluronium salts.[26] We report herein the $^{125}Te$ chemical shifts for a large number of organotelluronium salts. The structures of these telluronium salts studied are given in Table 1.

The $^{125}Te$ chemical shifts, $^1J_{TeC}$ and $^2J_{TeH}$, of some organotelluronium salts are given in Table 2. As shown in Table 2, one can see that the $^{125}Te$ chemical shifts span a range from 418 ppm ($(CH_3)_2Te^+CH_3\ I^-$) to 675 ppm ($(C_6H_5)_2Te^+CH_3\ ^-BPh_4$) with respect to $Me_2Te$. Negative chemical shifts are upfield from $Me_2Te$.

**Table 2. $^{125}Te$ Chemical Shifts, $^1J_{TeC}$ and $^2J_{TeH}$, for Some Organotelluronium Salts[a,b]**

| entry | telluronium salt | $^{125}Te^c$ (ppm) | $^1J_{TeC}$ (Hz) | $^2J_{TeH}$ (Hz) |
|---|---|---|---|---|
| 1 | $(CH_3)_3Te^+\ I^-$ (**14**) | 418 | 153 | $25^d$ |
| 2 | $i$-$Bu_2Te^+C_6H_5\ Br^-$ (**4**) | 543 | | |
| 3 | $(C_6H_5)_2Te^+CH_3\ ^-BPh_4$ (**23**) | 675 | | 25 |
| 4 | $i$-$Bu_2Te^+CH_2CH{=}CH_2\ Br^-$ (**7**) | 476 | | 20 |
| 5 | $n$-$Bu_2Te^+CH_2Ph\ Br^-$ (**5**) | 589 | 160 | 28 |
| 6 | $i$-$Bu_2Te^+CH_2C{\equiv}CSiMe_3\ Br^-$ (**9**) | 496 | | 21 |
| 7 | $i$-$Bu_2Te^+CH_2CH{=}CHSiMe_3\ Br^-$ (**8**) | 475 | | 26 |
| 8 | $i$-$Bu_2Te^+CH_2CH{=}CHCO_2Et\ ^-BPh_4$ (**26**) | 502 | | 26 |
| 9 | $n$-$Bu_2Te^+CH_2CO_2CH_3\ Br^-$ (**10**) | 582 | | |
| 10 | $n$-$Bu_2Te^+CH_2CO_2C_2H_5\ Br^-$ (**11**) | 579 | 150 | 28 |
| 11 | $n$-$Bu_2Te^+CH_2CN\ Cl^-$ (**2**) | 543 | 154 | $21^e$ |
| 12 | $n$-$Bu_2Te^+CH_2CONHBu$-$i\ Br^-$ (**12**) | 547 | | 28 |
| 13 | $n$-$Bu_2Te^+CH_2CON(CH_2)_3CH_2\ ^-BPh_4$ (**27**) | 522 | | 24 |
| 14 | $n$-$Bu_2Te^+CH_2CON(CH_2)_4CH_2\ ^-BPh_4$ (**28**) | 522 | | 25 |

[a] All tellurium-125 spectra were obtained at 94.69 MHz. [b] The spectra were recorded in $CDCl_3$ or DMSO-$d_6$ solution except where specially indicated and were referenced to neat $Me_2Te$. [c] Chemical shifts are downfield relative to $Me_2Te$. [d] The spectrum was recorded in $D_2O$. [e] The spectrum was recorded in $(CD_3)_2CO$.

**Table 3. $^{125}Te$ Chemical Shifts, $^1J_{TeC}$ and $^2J_{TeH}$, of Various Cyanomethyltelluronium Salts[a]**

| entry | telluronium salt | $^{125}Te^b$ (ppm) | $^1J_{TeC}$ (Hz) | $^2J_{TeC}$ (Hz) |
|---|---|---|---|---|
| 1 | $i$-$Bu_2Te^+CH_2CN\ Cl^-$ | 478 | 130 | 21 |
| 2 | $n$-$Bu_2Te^+CH_2CN\ Cl^-$ | 543 | 154 | 21 |
| 3 | $n$-$Bu_2Te^+CH_2CN\ Br^-$ | 548 | 154 | |
| 4 | $n$-$Bu_2Te^+CH_2CN\ I^-$ | 602 | 154 | 23 |
| 5 | $n$-$Bu_2Te^+CH_2CN\ ^-BPh_4$ | 572 | | |

[a] The spectra were recorded in $CDCl_3$ or DMSO-$d_6$ solution and were referenced to neat $Me_2Te$. [b] Chemical shifts are downfield relative to $Me_2Te$.

**Table 4. $^{125}Te$ Chemical Shifts, $^1J_{TeC}$ and $^2J_{TeH}$, of Various Allyltelluronium Salts[a]**

| entry | telluronium salt | $^{125}Te$-$125^b$ (ppm) | $^1J_{TeC}$ (Hz) | $^2J_{TeH}$ (Hz) |
|---|---|---|---|---|
| 1 | $n$-$Bu_2Te^+CH_2CH{=}CH_2\ Br^-$ | 522 | 130 | 21 |
| 2 | $i$-$Bu_2Te^+CH_2CH{=}CH_2\ Cl^-$ | 281 | 152 | 24 |
| 3 | $i$-$Bu_2Te^+CH_2CH{=}CH_2\ Br^-$ | 476 | | 20 |
| 4 | $i$-$Bu_2Te^+CH_2CH{=}CH_2\ I^-$ | 508 | 152 | |
| 5 | $i$-$Bu_2Te^+CH_2CH{=}CH_2\ ^-BPh_4$ | 518 | | |

[a] The spectra were recorded in $CDCl_3$ or DMSO-$d_6$ solution and were referenced to neat $Me_2Te$. [b] Chemical shifts are downfield relative to $Me_2Te$.

Tables 3 and 4 show the effect of the counterion on the $^{125}Te$ chemical shifts of (cyanomethyl)- and allyltelluronium salts, respectively.

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**Table 5. $^{125}$Te Chemical Shifts for $n$-Bu$_2$Te$^+$C$_n$H$_{2n+1}$ I$^-$ [a]**

| entry | telluronium salt | solvent | $^{125}$Te[b] (ppm) |
|---|---|---|---|
| 1 | $n$-Bu$_2$Te$^+$CH$_3$ I$^-$ | CDCl$_3$ | 475 |
| 2 | $n$-Bu$_2$Te$^+$CH$_3$ I$^-$ | DMSO-$d_6$ | 475 |
| 3 | $n$-Bu$_2$Te$^+$CH$_2$CH$_3$ I$^-$ | CDCl$_3$ | 522 |
| 4 | $n$-Bu$_2$Te$^+$CH(CH$_3$)$_2$ I$^-$ | CDCl$_3$ | 508 |
| 5 | $n$-Bu$_2$Te$^+$CH$_2$CH$_2$CH$_3$ I$^-$ | DMSO-$d_6$ | 543 |
| 6 | $n$-Bu$_2$Te$^+$CH$_2$(CH$_2$)$_2$CH$_3$ I$^-$ | DMSO-$d_6$ | 552 |
| 7 | $n$-Bu$_2$Te$^+$CH$_2$(CH$_2$)$_3$CH$_3$ I$^-$ | DMSO-$d_6$ | 547 |
| 8 | $n$-Bu$_2$Te$^+$CH$_2$(CH$_2$)$_4$CH$_3$ I$^-$ | DMSO-$d_6$ | 544 |

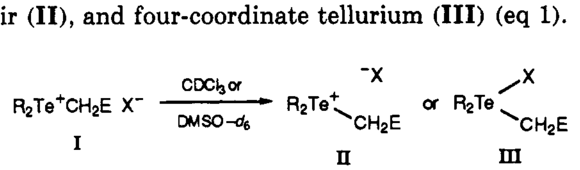
[a] The spectra were recorded in CDCl$_3$ solution and were referenced to neat Me$_2$Te. [b] Chemical shifts are downfield relative to Me$_2$Te.

As shown in Tables 3 and 4, the counterion has nothing to do with $^1J_{TeC}$ (entries 2–4 in Table 3 and entries 2 and 4 in Table 4), which has small influence on $^2J_{TeH}$. For the same kinds of telluronium salts, the $^{125}$Te chemical shifts of the diisobutyl-ligand salts are more upfield compared with the dibutyl-ligand ones due to the donor property of the isobutyl group. For example, the $^{125}$Te chemical shift of (cyanomethyl)diisobutyltelluronium chloride ($i$-Bu$_2$Te$^+$CH$_2$CN Cl$^-$) is 478 ppm, while that of (cyanomethyl)dibutyltelluronium chloride ($n$-Bu$_2$Te$^+$CH$_2$CN Cl$^-$) is 543 ppm. Similarly, the $^{125}$Te chemical shift of allyldiisobutyltelluronium bromide ($i$-Bu$_2$Te$^+$CH$_2$CH=CH$_2$ Br$^-$) is 476 ppm, while that of allyldibutyltelluronium bromide ($n$-Bu$_2$Te$^+$CH$_2$CH=CH$_2$ Br$^-$) is 522 ppm. For the same category of telluronium salts, changing the halogen in the counterion results in the expected deshielding of the tellurium as the halogen ion radius increases. For the allyltelluronium salts, a downfield change of the $^{125}$Te chemical shift is observed. For example, the $^{125}$Te chemical shift of $i$-Bu$_2$Te$^+$CH$_2$CH=CH$_2$ $^-$BPh$_4$ is 518 ppm, while that of $i$-Bu$_2$Te$^+$CH$_2$CH=CH$_2$ Br$^-$ is 476 ppm. For the (cyanomethyl)telluronium salts, the change of the $^{125}$Te chemical shift is not regular. For example, the $^{125}$Te chemical shift of $n$-Bu$_2$Te$^+$CH$_2$CN $^-$BPh$_4$ is 572 ppm, while that of $n$-Bu$_2$Te$^+$CH$_2$CN I$^-$ is 602 ppm and that of $n$-Bu$_2$Te$^+$CH$_2$CN Br$^-$ is 548 ppm.

In order to study the effect of the length of the carbon chain on the $^{125}$Te chemical shift of trialkyltelluronium salts, we synthesized six trialkyltelluronium iodides. The $^{125}$Te chemical shifts of these telluronium salts are given in Table 5. Figure 1 shows the effect of the number of carbon atoms on the $^{125}$Te chemical shift of trialkyltelluronium iodides $n$-Bu$_2$Te$^+$C$_n$H$_{2n+1}$ I$^-$.

As shown in Figure 1, the $^{125}$Te resonance of methyldibutyltelluronium iodide ($n$-Bu$_2$Te$^+$CH$_3$ I$^-$) appeared the most upfield (475 ppm); lengthening the carbon chain results in downfield shift changes. When the number of carbon atoms is 3, the $^{125}$Te NMR chemical shift becomes nearly a constant (entries 5–7 in Table 5). In fact, this phenomenon is also observed in other kinds of telluronium salts. For example, the $^{125}$Te chemical shift of $n$-Bu$_2$Te$^+$-$\overline{\mathrm{N(CH_2)_3C}}$H$_2$ $^-$BPh$_4$ is 522 ppm, while that of $n$-Bu$_2$Te$^+$-CH$_2\overline{\mathrm{N(CH_2)_4C}}$H$_2$ $^-$BPh$_4$ is 522 ppm (entries 13 and 14 in Table 2).

It is known that the telluronium salts may be present in three different forms: free cation and anion (**I**), ion pair (**II**), and four-coordinate tellurium (**III**) (eq 1).



$$R_2Te^+CH_2E\ X^- \xrightarrow[\text{DMSO-}d_6]{\text{CDCl}_3\text{ or}} R_2Te^+\cdots X^-(CH_2E)\ \text{or}\ R_2Te(X)(CH_2E) \quad (1)$$

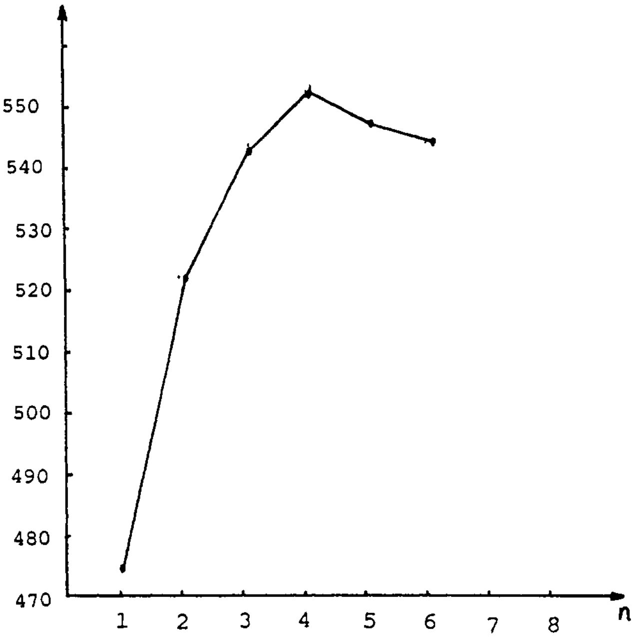


**Figure 1.** Effect of the length of the carbon chain on the $^{125}$Te chemical shifts of $n$-Bu$_2$Te$^+$C$_n$H$_{2n+1}$ I$^-$.

In fact, whether telluronium salt form **II** or form **III** is present may reflect the mechanism of the salt-forming reaction. Diorganyl telluride (R$_2$Te) reacts with the corresponding halides (XCH$_2$E) through an S$_N$2 mechanism to give **II**, while it reacts through the oxidative-addition mechanism to form **III**. Although the structures of many stibonium salts have been described in the literature,[27–32] little attention has been paid to the X-ray structures of telluronium salts. Einstein and co-workers described the crystals of the complex (CH$_3$)$_3$TeI·CH$_3$TeI$_3$.[33] To this purpose, we report herein the X-ray structures of Me$_3$Te$^+$ I$^-$ (**14**), $i$-Bu$_2$Te$^+$C$_6$H$_5$ Br$^-$ (**4**), and Ph$_2$Te$^+$CH$_3$ $^-$BPh$_4$ (**23**). Relevant crystallographic data of these telluronium salts are given in Table 6.

Final fractional atomic coordinates of compounds **14**, **4**, and **23** are given in Tables 7, 8, and 9, respectively. Selected bond distances and angles are described in Tables 10, 11, and 12, respectively. Thermal ellipsoid diagrams are presented in Figures 2, 3, and 4, respectively.

As shown in Figures 2–4, the telluronium salts are present in the ion-pair form (**II**) and do not contain four-coordinate tellurium (**III**), because the tellurium and the counterion atom have not formed the chemical bond. This means that the salt-forming reaction may be through a normal S$_N$2 mechanism, not through the oxidative-addition mechanism. The distance between tellurium and the counterion atom is much longer than that of a normal chemical bond. The Te···I, Te···Br, and Te···B distances are 3.702, 3.293, and 4.690 Å, respectively. It is known that the Te–Br bond distance found in (C$_6$H$_5$)$_2$TeBr$_2$[34,35] is 2.682 Å, and that of Te–I bond in (4-ClC$_6$H$_4$)$_2$TeI$_2$[36] is

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**Table 6. Crystallographic Data and Measurements for $Me_3Te^+$ $I^-$ (14), *i*-$Bu_2Te^+C_6H_5$ $Br^-$ (4), and $Ph_2Te^+CH_3$ $^-BPh_4$ (23)**

| | $Me_3Te^+$ $I^-$ | *i*-$Bu_2Te^+C_6H_5$ $Br^-$ | $Ph_2Te^+CH_3$ $^-BPh_4$ |
|---|---|---|---|
| mol formula | $C_3H_9ITe$ | $C_{14}H_{23}BrTe$ | $C_{37}H_{33}BTe$ |
| formula wt | 299.6 | 398.8 | 616.0 |
| cryst syst | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/n$ | $P2_1/c$ | $P2_12_12_1$ |
| *a*, Å | 7.123(2) | 9.161(4) | 8.777(5) |
| *b*, Å | 9.675(3) | 14.496(8) | 16.689(5) |
| *c*, Å | 11.334(3) | 13.198(6) | 20.523(8) |
| *β*, deg | 107.71(3) | 106.86(3) | |
| *V*, Å$^3$ | 744.0(4) | 1677.3(4) | 30006(2) |
| *Z* | 4 | 4 | 4 |
| $D_{calcd}$, mg m$^{-3}$ | 2.675 | 1.579 | 1.361 |
| cryst size, mm | 0.3 × 0.3 × 0.5 | 0.6 × 0.5 × 0.5 | 0.45 × 0.40 × 0.50 |
| *F*(000) | 528 | 776 | 1248 |
| *μ*, mm$^{-1}$ | 7.998 | 4.116 | 1.012 |
| scan type | $2\theta-\theta$ | $2\theta-\theta$ | *ω* |
| $2\theta_{max}$, deg | 50.0 | 50.0 | 50.0 |
| scan rate | variable 4.51–29.30°/min in *ω* | variable 4.88–29.30/min in *ω* | variable 4.1–29.30°/min in *ω* |
| scan width | 0.60 plus K*α* sep | 1.20 plus K*α* sep | 0.70 |
| *R* | 0.0639 | 0.0618 | 0.0297 |
| goodness of fit | 0.59 | 1.06 | 1.33 |
| range of rflns measd | | | |
| *h* | 0–8 | 0–10 | 0–10 |
| *k* | 0–11 | 0–17 | 0–19 |
| *l* | (13)–(+12) | (−15)–(+15) | 0–24 |

**Table 7. Non-Hydrogen Atom Fractional Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (×10$^3$) for $Me_3Te^+$ $I^-$ with Estimated Standard Deviations in Parentheses**

| atom | *x* | *y* | *z* | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Te | 4688(1) | 1153(1) | 8208(1) | 31(1) |
| I | −268(1) | 2273(1) | 6194(1) | 44(1) |
| C(1) | 4730(15) | 404(11) | 6464(8) | 46(3) |
| C(2) | 7756(14) | 849(10) | 9106(8) | 45(3) |
| C(3) | 5127(17) | 3268(10) | 7815(9) | 49(4) |

**Table 8. Non-Hydrogen Atom Fractional Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (×10$^3$) for *i*-$Bu_2Te^+C_6H_5$ $Br^-$, with Estimated Standard Deviations in Parentheses**

| atom | *x* | *y* | *z* | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Te | 4306(1) | 822(1) | 1283(1) | 75(1) |
| Br | 5477(2) | 1882(1) | −546(1) | 112(1) |
| C(1) | 3639(14) | 291(9) | 2573(9) | 66(5) |
| C(2) | 3667(18) | 800(11) | 3445(12) | 89(6) |
| C(3) | 3221(20) | 356(14) | 4260(13) | 104(8) |
| C(4) | 2752(20) | −520(13) | 4219(15) | 106(9) |
| C(5) | 2753(23) | −997(11) | 3382(18) | 124(11) |
| C(6) | 3134(20) | −598(11) | 2558(16) | 106(9) |
| C(7) | 6416(18) | 1335(11) | 2257(12) | 93(7) |
| C(8) | 7678(20) | 625(15) | 2636(19) | 163(13) |
| C(9) | 7974(35) | −116(23) | 1937(26) | 266(27) |
| C(10) | 8953(27) | 1109(21) | 3455(18) | 217(20) |
| C(11) | 3184(20) | 2095(11) | 1294(14) | 107(9) |
| C(12) | 1455(24) | 1972(16) | 922(22) | 186(18) |
| C(13) | 775(27) | 1653(23) | −213(21) | 231(23) |
| C(14) | 848(41) | 2871(19) | 1215(29) | 589(68) |

**Table 9. Non-Hydrogen Atom Fractional Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (×10$^3$) for $Ph_2Te^+CH_3$ $^-BPh_4$, with Estimated Standard Deviations in Parentheses**

| atom | *x* | *y* | *z* | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Te | 7777(1) | 571(1) | 9132(1) | 46(1) |
| B | 9490(7) | 2826(3) | 7982(3) | 36(2) |
| C(1) | 8869(8) | −209(3) | 8455(3) | 63(2) |
| C(2) | 8731(6) | 37(4) | 9977(3) | 47(2) |
| C(3) | 9236(7) | 515(4) | 10475(3) | 66(2) |
| C(4) | 9847(9) | 155(5) | 11023(3) | 86(3) |
| C(5) | 9959(8) | −633(6) | 11073(3) | 83(3) |
| C(6) | 9411(9) | −1125(5) | 10585(3) | 77(3) |
| C(7) | 8792(8) | −782(4) | 10034(3) | 66(2) |
| C(8) | 5727(6) | −93(3) | 9246(2) | 45(2) |
| C(9) | 5014(8) | −43(4) | 9850(3) | 64(2) |
| C(10) | 3692(8) | −475(5) | 9958(3) | 82(3) |
| C(11) | 3109(8) | −941(5) | 9474(4) | 83(3) |
| C(12) | 3812(9) | −988(5) | 8883(4) | 86(3) |
| C(13) | 5135(7) | −551(4) | 8764(3) | 67(2) |
| C(14) | 10388(6) | 2425(3) | 8603(2) | 35(2) |
| C(15) | 11076(6) | 1672(3) | 8557(3) | 44(2) |
| C(16) | 11750(6) | 1283(3) | 9082(3) | 54(2) |
| C(17) | 11788(7) | 1651(4) | 9673(3) | 70(3) |
| C(18) | 11113(9) | 2383(4) | 9756(3) | 78(3) |
| C(19) | 10417(7) | 2763(3) | 9228(2) | 55(2) |
| C(20) | 10434(6) | 2693(3) | 7292(2) | 38(2) |
| C(21) | 9727(7) | 2628(3) | 6686(2) | 48(2) |
| C(22) | 10500(9) | 2535(3) | 6107(3) | 65(2) |
| C(23) | 12089(9) | 2517(3) | 6108(3) | 70(2) |
| C(24) | 12825(8) | 2590(3) | 6689(3) | 67(2) |
| C(25) | 12030(7) | 2679(3) | 7269(3) | 49(2) |
| C(26) | 9335(6) | 3807(3) | 8045(2) | 37(2) |
| C(27) | 10498(7) | 4286(3) | 8311(2) | 48(2) |
| C(28) | 10376(9) | 5111(3) | 8346(3) | 63(3) |
| C(29) | 9123(8) | 5484(3) | 8108(3) | 61(2) |
| C(30) | 7988(8) | 5053(3) | 7819(3) | 58(2) |
| C(31) | 8099(6) | 4223(3) | 7793(2) | 44(2) |
| C(32) | 7854(6) | 2374(3) | 7988(2) | 33(1) |
| C(33) | 7596(6) | 1649(3) | 7665(2) | 39(2) |
| C(34) | 6245(6) | 1224(3) | 7721(3) | 50(2) |
| C(35) | 5074(6) | 1498(3) | 8118(3) | 50(2) |
| C(36) | 5287(7) | 2207(3) | 8450(3) | 51(2) |
| C(37) | 6642(6) | 2618(3) | 8390(2) | 43(2) |

2.922 Å. However, the Te–C distances formed here are typical of Te–alkyl or Te–aryl bonds. For example, the Te–C distances in compound $Me_3Te^+I^-$ are 2.114, 2.132, and 2.138 Å, respectively, those in compound 4 are 2.113, 2.114, and 2.122 Å, respectively, and those in compound 23 are 2.122, 2.127, and 2.131 Å, respectively, very similar to those in $(C_6H_5)_2TeBr_2$ and $(4\text{-}ClC_6H_4)_2TeI_2$.

On the other hand, in chloroform solution, the conductance ratio of telluronium salts is very small, similar to that of conductivity water. This indicates that, in the solution, the telluronium salts may be still in the form of an ion pair, not free cations and anions. The interaction of tellurium and the counterion results in an upfield or downfield change when the counterion changes.

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(34) Christofferson, G. D.; McCullough, J. D. *Acta Crystallogr.* **1958**, *11*, 249.

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(36) Chao, G. Y.; McCullough, J. D. *Acta Crystallogr.* **1962**, *15*, 887.

**Table 10. Bond Distances (Å) and Angles (deg) for $Me_3Te^+ I^-$, with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Te–C(1) | 2.114(10) | Te–C(2) | 2.132(9) |
| Te–C(3) | 2.138(10) | | |
| | Bond Angles | | |
| C(1)–Te–C(2) | 95.4(4) | C(1)–Te–C(3) | 95.1(4) |
| C(2)–Te–C(3) | 92.1(4) | | |

**Table 11. Bond Distances (Å) and Angles (deg) for $i$-$Bu_2Te^+C_6H_5$ $Br^-$, with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Te–C(1) | 2.113(14) | Te–C(7) | 2.122(14) |
| Te–C(11) | 2.114(17) | C(1)–C(2) | 1.362(21) |
| C(8)–C(9) | 1.491(43) | C(8)–C(10) | 1.514(30) |
| | Bond Angles | | |
| C(1)–Te–C(7) | 93.7(5) | C(1)–Te–C(11) | 93.3(7) |
| C(7)–Te–C(11) | 92.8(6) | Te–C(1)–C(2) | 123.1(11) |
| Te–C(1)–C(6) | 120.5(12) | C(2)–C(1)–C(6) | 116.4(15) |
| Te–C(7)–C(8) | 115.8(12) | Te–C(11)–C(12) | 110.9(12) |
| C(11)–C(12)–C(13) | 116.3(22) | C(11)–C(12)–C(14) | 124.3(17) |

**Table 12. Bond Distances (Å) and Angles (deg) for $Ph_2Te^+CH_3$ $^-BPh_4$, with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Te–C(2) | 2.122(6) | Te–C(1) | 2.131(6) |
| Te–C(8) | 2.127(5) | C(33)–C(32) | 1.399(6) |
| C(32)–B | 1.622(8) | C(14)–B | 1.640(7) |
| C(2)–C(3) | 1.370(8) | B–C(20) | 1.655(7) |
| B–C(26) | 1.648(7) | | |
| | Bond Angles | | |
| C(2)–Te–C(1) | 95.7(2) | C(2)–Te–C(8) | 91.5(2) |
| C(1)–Te–C(8) | 97.7(2) | C(33)–C(32)–C(37) | 114.0(4) |
| C(33)–C(32)–B | 122.8(4) | C(37)–C(32)–B | 122.7(4) |
| C(32)–C(37)–C(36) | 124.1(5) | C(15)–C(14)–B | 121.5(4) |
| B–C(14)–C(19) | 123.8(4) | Te–C(2)–C(7) | 120.1(4) |
| Te–C(2)–C(3) | 119.5(5) | C(7)–C(2)–C(3) | 120.3(5) |
| Te–C(8)–C(9) | 116.6(4) | Te–C(8)–C(13) | 122.6(4) |
| C(32)–B–C(14) | 103.3(4) | C(32)–B–C(20) | 112.8(4) |
| C(14)–B–C(20) | 111.7(4) | C(32)–B–C(26) | 112.8(4) |
| C(14)–B–C(26) | 112.6(4) | C(20)–B–C(26) | 103.9(4) |
| C(9)–C(8)–C(13) | 120.9(5) | C(25)–C(20)–B | 122.1(4) |
| B–C(20)–C(21) | 123.4(5) | C(8)–C(9)–C(10) | 119.3(6) |
| B–C(26)–C(27) | 122.3(4) | B–C(26)–C(31) | 122.2(4) |

## Experimental Section

Telluronium salts were prepared by the reaction of organic halides with diphenyl telluride or dialkyl telluride, and the telluronium tetraphenylborate salts were prepared by anion exchange from the corresponding telluronium iodides or bromides with sodium tetraphenylborate.[26] It is noteworthy that phenyldiisobutyltelluronium ($i$-$Bu_2Te^+C_6H_5$ $Br^-$) (4) cannot be synthesized via the above described procedure. The synthesis of compound 4 is according to the literature procedure.[3e] Crystals suitable for X-ray examination were grown from solutions in water for $Me_3Te^+$ $I^-$ and in petroleum/ether acetate for $i$-$Bu_2Te^+C_6H_5$ $Br^-$ and $Ph_2Te^+CH_3$ $^-BPh_4$.

**$i$-$Bu_2Te^+CH_2CN$ $Cl^-$ (1):**[26] white solid; mp 100–102 °C; $^1H$ NMR ($CDCl_3$/TMS, 200 MHz) $\delta$ 1.14 (d, $J$ = 6 Hz, 12H), 2.42 (m, 2H), 3.16 (d, $J$ = 7 Hz, 4H), 3.71 (s, 2H); FAB-MS $m/z$ (rel intensity) 284 ([C]$^+$, 100), 282 (93), 280 (58), 603 ([M + C]$^+$, 2), 601 (4), 599 (3); IR (KBr) 2985 (m), 2945 (w), 2245 (m), 1425 (m), 1360 (s) cm$^{-1}$. Anal. Calcd for $C_{10}H_{20}ClNTe$: C, 37.85; H, 6.35; N, 4.41; Cl, 11.17. Found: C, 37.34; H, 6.01; N, 4.20; Cl, 11.25.

**$n$-$Bu_2Te^+CH_2CN$ $Cl^-$ (2):**[37] white solid; mp 93–94 °C; $^1H$ NMR ($CDCl_3$/TMS, 60 MHz) $\delta$ 1.05 (t, $J$ = 6 Hz, 6H), 1.50 (m, 4H), 2.10 (m, 4H), 3.10 (s, 2H), 3.15 (t, $J$ = 6 Hz, 4H); FAB-MS $m/z$ (rel intensity) 284 ([C]$^+$, 100), 282 (96.9), 280 (61.8), 603 ([M + C]$^+$, 1.9), 601 (3.3), 599 (3.3); IR (KCl) 2980 (m), 2950 (w), 2230 (m), 1420 (m), 1360 (s) cm$^{-1}$.

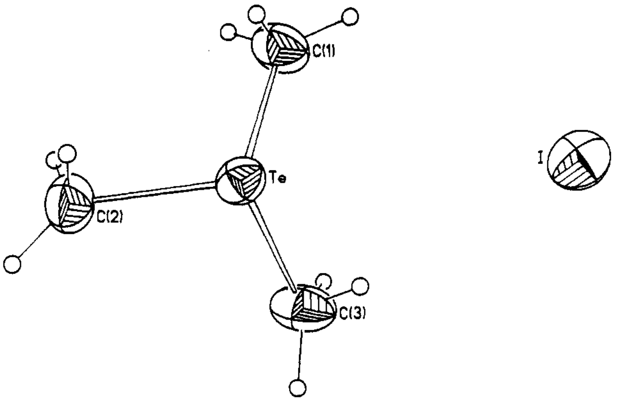

Figure 2. Thermal ellipsoid diagram showing the solid-state conformation of one of the molecules in the crystal unit and the atom-numbering scheme of $Me_3Te^+$ $I^-$ (14).

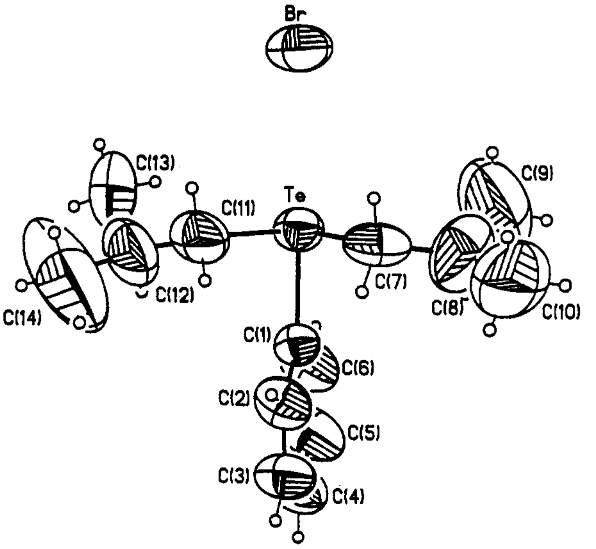

Figure 3. Thermal ellipsoid diagram showing the solid-state conformation of one of the molecules in the crystal unit and the atom-numbering scheme of $i$-$Bu_2Te^+C_6H_5$ $Br^-$ (4).

**$i$-$Bu_2Te^+CH_2CH{=}CH_2$ $Cl^-$ (3):**[26] white solid; mp 30 °C; $^1H$ NMR ($CDCl_3$/TMS, 60 MHz) $\delta$ 1.14 (d, $J$ = 6 Hz, 12H), 2.34 (m, 2H), 2.82 (m, 4H), 3.80 (d, $J$ = 7 Hz, 2H), 5.45 (m, 3H); FAB-MS $m/z$ (rel intensity) 285 ([C]$^+$, 100), 283 (93.1), 281 (57.6), 697 ([M + C]$^+$, 0.9), 695 (1.4), 599 (2.0); IR (KBr) 3034 (w), 2980 (m), 1630 (m), 1465 (m), 1385 (m), 1365 (m), 693 cm$^{-1}$. Anal. Calcd for $C_{11}H_{23}ClTe$: C, 40.98; H, 7.12; Cl, 10.68. Found: C, 41.50; H, 7.28; Cl, 11.14.

**$i$-$Bu_2Te^+C_6H_5$ $Br^-$ (4):**[3e] white solid; mp 136–138 °C; $^1H$ NMR ($CDCl_3$/TMS, 90 MHz) $\delta$ 1.02 (d, $J$ = 7 Hz, 6H), 1.14 (d, $J$ = 7 Hz, 6H), 2.30 (m, 2H), 3.24 (dd, $J_1$ = 11 Hz, $J_2$ = 7 Hz, 2H), 3.80 (dd, $J_1$ = 11 Hz, $J_2$ = 7 Hz, 2H), 7.60 (m, 5H); FAB-MS $m/z$ (rel intensity) 321 ([C]$^+$, 100), 319 (93.1), 317 (59.1), 721 ([M + C]$^+$, 1.1), 719 (1.5), 711 (1.4); IR (KBr) 3010 (m), 1570 (m), 1425 (m), 1380 (s), 1360 (s), 745 (s) cm$^{-1}$. Anal. Calcd for $C_{14}H_{23}BrTe$: C, 41.72; H, 5.70; Br, 20.24. Found: C, 42.16; H, 5.81; Br, 20.03.

**$n$-$Bu_2Te^+CH_2Ph$ $Br^-$ (5):**[26] white solid; mp 120–122 °C; $^1H$ NMR ($CDCl_3$/TMS, 60 MHz) $\delta$ 0.97 (m, 6H), 1.78 (m, 8H), 2.75 (m, 4H), 4.40 (s, 2H), 7.29 (m, 5H); FAB-MS $m/z$ (rel intensity) 335 ([C]$^+$, 100), 333 (90.7), 331 (56.7), 749 ([M + C]$^+$, 2.3), 747 (2.9), 745 (2.3); IR (KBr) 2950 (m), 2850 (m), 1600 (w), 1495 (s), 1170 (m), 760 (s), 700 (s) cm$^{-1}$. Anal. Calcd for $C_{15}H_{25}BrTe$: C, 43.44; H, 6.00; Br, 19.46. Found: C, 43.58; H, 6.05; Br, 19.37.

**$n$-$Bu_2Te^+CH_2CN$ $Br^-$ (6):**[26] white solid; mp 76–78 °C; $^1H$ NMR ($CDCl_3$/TMS, 60 MHz) $\delta$ 0.98 (t, $J$ = 7 Hz, 6H), 1.52 (m, 4H), 2.02 (m, 4H), 3.25 (m, 4H), 3.60 (s, 2H); FAB-MS $m/z$ (rel intensity) 284 ([C]$^+$, 100), 282 (92.8), 280 (59.9), 647 ([M + C]$^+$, 2.8), 645 (3.8), 643 (3.3); IR (KBr) 2985 (m), 2950 (w), 2240 (m), 1425 (m),

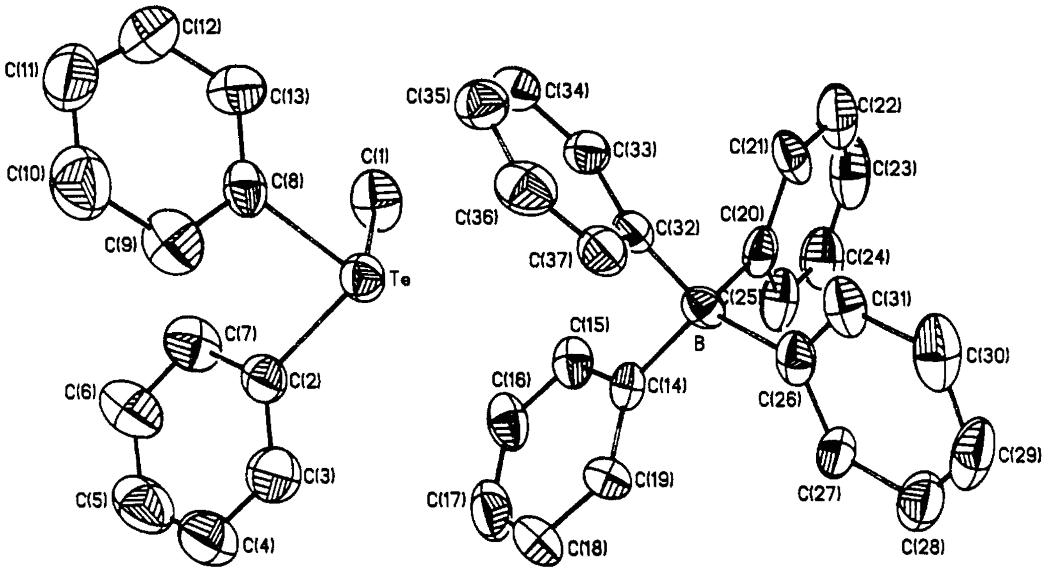

**Figure 4.** Thermal ellipsoid diagram showing the solid-state conformation of one of the molecules in the crystal unit and the atom-numbering scheme of $\text{Ph}_2\text{Te}^+\text{CH}_3\ {}^-\text{BPh}_4$ (**23**).

1380 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{BrNTe}$: C, 33.43; H, 5.38; N, 4.07; Br, 21.63. Found: C, 33.20; H, 5.57; N, 3.87; Br, 22.08.

**$i$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CH}{=}\text{CH}_2\ \text{Br}^-$ (7):**[26] white solid; mp 94–95 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 90 MHz) $\delta$ 1.12 (d, $J$ = 6 Hz, 12H), 2.32 (m, 2H), 2.80 (m, 4H), 4.00 (d, $J$ = 8 Hz, 2H), 5.32 (m, 3H); FAB-MS $m/z$ (rel intensity) 285 ([C]$^+$, 100) 283 (96.6), 281 (5918), 649 ([M + C]$^+$, 2.5), 647 (3.3), 645 (3.5); IR (KCl), 3050 (w), 2900 (m), 1630 (m), 1460 (m), 1385 (m), 1365 (m) cm$^{-1}$.

**$i$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CH}{=}\text{CHSiMe}_3\ \text{Br}^-$ (8):**[26] white solid; mp 90–92 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 200 MHz) $\delta$ 0.12 (s, 9H), 1.13 (d, $J$ = 7 Hz, 12H), 2.34 (m, 2H), 2.66 (m, 2H), 2.93 (m, 2H), 3.80 (d, $J$ = 8 Hz, 1H), 3.90 (d, $J$ = 8 Hz, 1H), 5.96 (d, $J$ = 18 Hz), 6.10 (dt, $J_1$ = 18 Hz, $J_2$ = 8 Hz, 1H); FAB-MS $m/z$ (rel intensity) 357 ([C]$^+$, 100), 355 (90.0), 353 (56.9), 793 ([M + C]$^+$, 0.9), 791 (1.1), 789 (1.0); IR (KBr) 2980 (m), 1610 (m), 1385 (w), 1365 (w), 1250 (s), 1000 (m), 880 (s), 840 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{14}\text{H}_{31}\text{BrSiTe}$: C, 38.74; H, 7.02; Br, 18.59. Found: C, 38.66; H, 7.18; Br, 18.37.

**$i$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{C}{\equiv}\text{CSiMe}_3\ \text{Br}^-$ (9):**[26] white solid; mp 102–104 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 90 MHz) $\delta$ 0.10 (s, 9H), 2.02 (d, $J$ = 7 Hz, 6H), 2.04 (d, $J$ = 7 Hz, 6H), 2.30 (m, 2H), 3.00 (d, $J$ = 7 Hz, 4H), 3.58 (s, 2H); FAB-MS $m/z$ (rel intensity) 355 ([C]$^+$, 100), 353 (92.8), 351 (57.6), 789 ([M + C]$^+$, 0.8), 787 (1.0), 785 (0.6); IR (KCl) 2950 (s), 2150 (s), 1380 (s), 1360 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{14}\text{H}_{29}\text{BrSiTe}$: C, 38.84; H, 6.75; Br, 18.45. Found: C, 38.50; H, 6.77; Br, 18.52.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CO}_2\text{CH}_3\ \text{Br}^-$ (10):**[37] white solid; mp 68–70 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 60 MHz) $\delta$ 0.97 (t, $J$ = 6 Hz, 6H), 1.43 (m, 4H), 1.80 (m, 4H), 3.13 (t, $J$ = 7 Hz, 4H), 3.52 (s, 2H), 3.70 (s, 3H); FAB-MS $m/z$ (rel intensity) 317 ([C]$^+$, 100), 315 (93.9), 313 (59.3), 713 ([M + C]$^+$, 1.6), 711 (2.4), 709 (2.3); IR (KCl) 2950 (s), 2860 (m), 1720 (s), 1460 (m), 1440 (m), 1380 (s) cm$^{-1}$.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5\ \text{Br}^-$ (11):**[38] white solid; mp 66–68 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 60 MHz) $\delta$ 0.95 (t, $J$ = 6 Hz, 6H), 1.30 (t, $J$ = 7 Hz, 3H), 1.45 (m, 4H), 1.90 (m, 4H), 3.15 (t, $J$ = 7 Hz, 4H), 3.70 (s, 2H), 4.15 (q, $J$ = 7 Hz, 2H); FAB-MS $m/z$ (rel intensity) 331 ([C]$^+$, 100), 329 (97), 327 (60), 741 ([M + C]$^+$, 1.5), 739 (2.2), 737 (1.8); IR (KCl) 2950 (m), 2850 (m), 1710 (s), 1460 (m), 1405 (m), 1380 (s) cm$^{-1}$.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CONHBu}$-$i$ $\text{Br}^-$ (12):**[26] white solid; mp 94–96 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 60 MHz) $\delta$ 0.90 (d, $J$ = 6 Hz, 9H), 0.94 (d, $J$ = 6 Hz, 9H), 1.47–1.77 (m, 9H), 3.87 (s, 2H), 4.59 (br, 1H); FAB-MS $m/z$ (rel intensity) 385 ([C]1+, 100), 356 (96), 354 (62.2), 795 ([M + C]$^+$, 0.3), 793 (0.5), 791 (0.5); IR (KBr) 3300 (s), 2950 (m), 2850 (m), 1620 (s), 1540 (m), 1270 (s) cm$^{-1}$.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CH}{=}\text{CH}_2$** $\text{Br}^-$ **(13):**[38] oil.

**$(\text{CH}_3)_3\text{Te}^+\ \text{I}^-$ (14):**[39] white solid; mp 239–240 °C; $^1$H NMR ($\text{CD}_3\text{OD}/\text{CH}_3\text{OD}$, 200 MHz) $\delta$ 5.04 (s, 9H); FAB-MS $m/z$ (rel intensity) 175 ([C]$^+$, 100), 173 (86.4), 171 (54.5), 477 ([M + C]$^+$, 2.7), 475 (4.4), 473 (4.2); IR (KCl) 2900 (m), 1235 (w), 1208 (m), 900 (m), 530 (m) cm$^{-1}$.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_3\ \text{I}^-$ (15):**[40] white solid; mp 158 °C dec; $^1$H NMR ($\text{CDCl}_3$/TMS, 200 MHz) $\delta$ 0.97 (d, $J$ = 7 Hz, 6H), 1.44 (m, 4H), 1.84 (m, 4H), 2.43 (s, 3H), 3.05 (m, 4H); FAB-MS $m/z$ (rel intensity) 259 ([C]$^+$, 100), 257 (95.3), 255 (58.7), 645 ([M + C]$^+$, 2.4), 643 (4.2), 641 (4.6); IR (KBr) 2900 (m), 1235 (w), 1210 (m), 850 (m), 530 (m) cm$^{-1}$.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CN}\ \text{I}^-$ (16):**[26] white solid; mp 78–80 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 200 MHz) $\delta$ 1.01 (t, $J$ = 7 Hz, 6H), 1.51 (m, 4H), 2.00 (m, 4H), 3.26 (m, 4H), 3.62 (s, 2H); FAB-MS $m/z$ (rel intensity) 284 ([C]$^+$, 100), 282 (92.4), 280 (57.5), 695 ([M + C]$^+$, 2.2), 693 (4.0), 691 (4.3); IR (KBr) 2980 (m), 2940 (w), 2230 (m), 1425 (m), 1365 (s), 1360 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{INTe}$: C, 29.39; H, 4.59; N, 3.29; I, 30.69. Found: C, 29.38; H, 4.93; N, 3.43; I, 31.04.

**$i$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CH}{=}\text{CH}_2\ \text{I}^-$ (17):**[26] white solid; mp 70–72 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 60 MHz) $\delta$ 1.14 (d, $J$ = 6 Hz, 12H), 2.32 (m, 2H), 2.84 (m, 4H), 3.90 (d, $J$ = 6 Hz, 2H), 5.45 (m, 3H); FAB-MS $m/z$ (rel intensity) 285 ([C]1+, 100), 283 (92.8), 281 (59.3), 697 ([M + C]$^+$, 2.0), 695 (3.3), 693 (3.6); IR (KBr) 2980 (m), 1630 (m), 1450 (m), 1385 (s), 1365 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{ITe}$: C, 32.20; H, 5.44; I, 30.96. Found: C, 32.24; H, 5.66; I, 30.99.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\ \text{I}^-$ (20):**[26] white solid; mp 64–66 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 200 MHz) $\delta$ 0.98 (d, $J$ = 7 Hz, 9H), 1.28–2.02 (m, 12H), 3.04 (m, 6H); FAB-MS $m/z$ (rel intensity) 301 ([C]$^+$, 100), 299 (94.1), 297 (59.3), 729 ([M + C]$^+$, 1.1), 727 (2.0), 725 (2.2); IR (KBr) 2950 (m), 1230 (m), 1210 (m), 860 (s), 765 (s) cm$^{-1}$. Anal. Calcd for $\text{C}_{12}\text{H}_{27}\text{ITe}$: C, 33.55; H, 6.40; I, 29.42. Found: C, 33.85; H, 6.39; I, 29.80.

**$n$-$\text{Bu}_2\text{Te}^+\text{CH}_2(\text{CH}_2)_4\text{CH}_3\ \text{I}^-$ (22):**[26] white solid; mp 58–60 °C; $^1$H NMR ($\text{CDCl}_3$/TMS, 90 MHz) $\delta$ 0.98 (d, $J$ = 7 Hz, 9H), 1.28–2.04 (m, 16H), 3.05 (m, 6H); IR (KBr) 2980 (m), 1235 (m), 1208 (w), 850 (m), 740 (m) cm$^{-1}$.

**$\text{Ph}_2\text{Te}^+\text{CH}_3\ {}^-\text{BPh}_4$ (23):**[26] white solid; mp 201–202 °C; $^1$H NMR ($\text{CD}_3\text{COCD}_3$/TMS, 60 MHz) $\delta$ 2.40 (s, 3H), 6.35–7.14 (m, 30 H); FAB-MS $m/z$ (rel intensity) 299 ([C]$^+$, 100), 297 (92.0), 295 (57.5),

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917 ([M + C]$^+$), 915, 913; IR (KCl) 3010 (m), 1570 (m), 1425 (m), 745 (vs), 682 (s) cm$^{-1}$. Anal. Calcd for $C_{37}H_{33}BTe$: C, 72.01; H, 5.43. Found: C, 72.13; H, 5.40.

**$n$-Bu$_2$Te$^+$CH$_2$CN $^-$BPh$_4$ (24)**:[26] white solid; mp 130–132 °C; $^1$H NMR (CDCl$_3$/TMS, 60 MHz) $\delta$ 1.05 (t, $J$ = 7 Hz, 6H), 1.55 (m, 2H), 2.04 (m, 4H), 3.28 (m, 4H), 3.65 (s, 2H), 6.90–7.05 (m, 12H), 7.50 (brs, 8H); FAB-MS $m/z$ (rel intensity) 284 ([C]$^+$, 100), 282 (90.3), 280 (54.5), 887 ([M + C]$^+$, 2.8), 885 (4.2), 883 (5.0); IR (KBr) 3010 (w), 2980 (m), 2945 (w), 2230 (m), 1425 (m), 1360 (s) cm$^{-1}$. Anal. Calcd for $C_{34}H_{40}BNTe$: C, 67.66; H, 6.51; N, 2.21. Found: C, 67.94; H, 6.71; N, 2.33.

**$i$-BuTe$^+$CH$_2$CH=CH$_2$ $^-$BPh$_4$ (25)**:[26] white solid; mp 130–132 °C; $^1$H NMR (CDCl$_3$/TMS, 200 MHz) $\delta$ 0.96 (d, $J$ = 6 Hz, 12H), 2.17 (m, 2H), 2.49 (m, 4H), 3.73 (d, $J$ = 8 Hz, 2H), 5.30 (m, 3H), 6.92–7.07 (m, 12H), 7.50 (brs, 8H); FAB-MS $m/z$ (rel intensity) 285 ([C]$^+$, 100), 283 (91.7), 281 (57.5), 889 ([M + C]$^+$), 887, 885; IR (KCl) 3020 (w), 2900 (m), 1630 (m), 1462 (m), 1385 (m), 1365 (m) cm$^{-1}$. Anal. Calcd for $C_{38}H_{43}BTe$: C, 69.42; H, 7.05. Found: C, 69.82; H, 7.20.

**$n$-Bu$_2$Te$^+$CH$_2$CH=CHCO$_2$Et $^-$BPh$_4$ (26)**:[26] white solid; mp 140–142 °C; $^1$H NMR (CDCl$_3$/TMS, 200 MHz) $\delta$ 0.94 (d, $J$ = 6 Hz, 12H), 1.30 (t, $J$ = 7 Hz, 3H), 1.75 (m, 2H), 2.10 (m, 4H), 2.32 (d, $J$ = 8 Hz, 2H), 4.22 (q, $J$ = 7 Hz, 2H), 5.68 (d, $J$ = 16 Hz, 1H), 6.31 (dt, $J_1$ = 16 Hz, $J_2$ = 8 Hz, 1H), 6.90–7.12 (m, 12H), 7.52 (brs, 8H); FAB-MS $m/z$ (rel intensity) 357 ([C]$^+$, 100), 355 (96.0), 280 (61.1), 1033 ([M + C]$^+$), 1031, 1029; IR (KBr) 3050 (m), 2950 (m), 1720 (s), 1645 (m), 1585 (s), 1480 (s) 1320 (s), 1270 (s), 1040 (s), 980 (s), 850 (s), 720 (s) cm$^{-1}$. Anal. Calcd for $C_{38}H_{47}BO_2Te$: C, 67.55; H, 7.09. Found: C, 67.70; H, 7.03.

**$n$-Bu$_2$Te$^+$CH$_2$CO$\overline{\mathrm{N(CH_2)_3C}}$H$_2$ $^-$BPh$_4$ (27)**:[2]16 white solid; mp 176–177 °C; $^1$H NMR (CDCl$_3$/TMS, 60 MHz) $\delta$ 0.85 (t, $J$ = 6 Hz, 6H), 1.20 (m, 8H), 1.76 (m, 8H), 2.73 (t, $J$ = 6 Hz, 4H), 3.30 (s, 2H), 6.93 (s, 8H), 7.43 (s, 12H); FAB-MS $m/z$ (rel intensity) 356 ([C]$^+$, 100), 354 (94.1), 280 (60.4), 1031 ([M + C]$^+$), 1029, 1027; IR (KBr) 3100 (w), 2980 (m), 2880 (m), 1720 (m), 1620 (s), 1455 (m), 1380 (s) cm$^{-1}$. Anal. Calcd for $C_{38}H_{48}BNOTe$: C, 67.38; H, 7.19; N, 1.93. Found: C, 67.78; H, 7.19; N, 2.08.

**$n$-Bu$_2$Te$^+$CH$_2$CO$\overline{\mathrm{N(CH_2)_4C}}$H$_2$ $^-$BPh$_4$ (28)**:[26] white solid; mp 128–130 °C; $^1$H NMR (CDCl$_3$/TMS, 60 MHz) $\delta$ 0.86 (t, $J$ = 6 Hz, 6H), 1.20 (m, 8H), 1.78 (m, 10H), 2.75 (t, $J$ = 7 Hz, 4H), 3.32 (s, 2H), 6.95 (m, 12H), 7.43 (brs, 8H); FAB-MS $m/z$ (rel intensity) 370 ([C]$^+$, 100), 368 (95.3), 366 (60.4), 1059 ([M + C]$^+$), 1057, 1055; IR (KBr) 3100 (w), 2980 (m), 2880 (m), 1720 (m), 1640 (s), 1455 (m), 1380 (s) cm$^{-1}$.

Solutions for NMR measurements were prepared by dissolving approximately 50 mg of the telluronium salts in 0.5 mL of CDCl$_3$ or DMSO-$d_6$. All tellurium-125 spectra were obtained with a Bruker AM-300 NMR spectrometer equipped with a broad-band probe tuned to 94.69 MHz at ambient temperature, with transmitter offset of 0 and −30.9 KHz. About 1000–3000 average transients were required to obtain satisfactory signal to noise ratios using a sweep width of 160 kHz stored in 32K data points. With these spectral parameters, proton-noise-decoupled tellurium resonances were 5–10 Hz at half-height. All tellurium-125 shifts are referenced to neat dimethyl telluride. Positive shifts are downfield and negative shifts are upfield from dimethyl telluride.

**Structural Analyses for Compounds 14, 4 and 23.** Relevant crystallographic data are given in Table 7. Data were collected on a Siemens R3m/V (Mo K$\alpha$ 0.717 03 Å) diffractometer at 20 °C. The structures were solved by direct methods and refined by Siemens SHELXTL PLUS(VMS) system.

For compounds **14** and **4**, cell constants and an orientation matrix for data collection corresponded to a monoclinic cell. Intensity data in the range $3.0 < 2\theta < 50.0°$ were corrected for the usual Lorentz and polarization effects, and a semiempirical absorption correction was made. Independent reflections totaling 1329 for **14** and 2392 for **4** were collected, of which 1183 with $F > 6.0\sigma(F)$ and 1526 with $F > 6.0\sigma(F)$ were retained for analysis of **14** and **4**, respectively. The structures were solved by direct methods and Fourier synthesis. The non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms, in calculated positions, were included in structure factor calculations. With the weighting scheme ($w^{-1} = \sigma^2(F) + 0.023F^2$ for **14** and ($w^{-1} = \sigma^2(F) + 0.0053F^2$ for **4**), the final $R$ indices were 0.0639 ($R_w$ = 0.0895) for **14** and 0.0618 ($R_w$ = 0.0870) for **4**. The final difference Fourier maps contained maxima of 1.81 and 1.14 e Å$^{-3}$, respectively.

For compound **23**, cell constants and an orientation matrix for data collection corresponded to an orthorhombic cell. Intensity data in the range of $3.0° < 2\theta < 50.0°$ were corrected for the usual Lorentz and polarization effects, and a semiempirical absorption correction was made. A total of 3031 independent reflections for **23** were collected, of which 2714 with $F > 4.0\sigma(F)$ were retained for analysis of **23**. The structures were solved by direct methods and Fourier synthesis. The non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms, in calculated positions, were included in structure factor calculations. With the weighting scheme ($w^{-1} = \sigma^2(F) + 0.002F^2$), the final $R$ indices were 0.0297 ($R_w$ = 0.0333). The final difference Fourier maps contained a maximum of 0.32 e Å$^{-3}$.

## Conclusions

$^{125}$Te NMR of various kinds of telluronium salts was systematically studied, including precursors of nonstabilized, semistabilized, and stabilized telluronium ylides. The $^{125}$Te chemical shifts of all Te salts are downfield with respect to neat Me$_2$Te and range from 418 ppm to 675 ppm due to the electron-deficient character of tellurium in the salts. For the same kind of telluronium salts, the $^{125}$Te resonance of the diisobutyl-ligand salts appeared more upfield compared with that of dibutyl-ligand ones, whereas the $^{125}$Te resonance of tetraphenylborate salts appeared more downfield compared with that of bromide salts. It is interesting to note that the $^{125}$Te chemical shifts of $n$-Bu$_2$Te$^+$C$_n$H$_{2n+1}$ I$^-$ become nearly a constant when $n$ = 3. Furthermore, the X-ray structures of Me$_3$Te$^+$ I$^-$, $i$-Bu$_2$Te$^+$C$_6$H$_5$ Br$^-$, and Ph$_2$Te$^+$CH$_3$ $^-$BPh$_4$ are reported.

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**Supplementary Material Available:** Tables of crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and least squares planes and structures of the complexes (31 pages). Ordering information is given on any current masthead page.

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