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XPS and ^{125}Te NMR Studies of Organotellurium Compounds. 1. Tellurapyrans, Tellurapyranones, Tellurapyrylium Salts, and Their Benzo Analogues in Both the Tellurium(II) and Tellurium(IV) Oxidation States

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^{125}Te NMR and XPS (X-ray photoelectron spectroscopy or ESCA, electron specroscopy for chemical analysis) analyses of several series of tellurapyran, tellurapyranone, and tellurapyrylium compounds were carried out. In the tellurium(II) oxidation state of these compounds, the chemical shifts in the ^{125}Te NMR of these compounds were sensitive to the presence of a formal positive charge. 2,6-Di-*tert*-butyltellurapyrylium hexafluorophosphate (**23**) had the furthest downfield chemical shift in this study at δ 1304 ppm (dimethyl telluride, δ 0.0 ppm) with a Te($3d_{5/2}$) binding energy of 575.2 eV. Introduction of a methyl substituent at the 4-position resulted in a more electron-rich tellurium center as evidenced by an upfield shift to δ 1185 ppm and a Te($3d_{5/2}$) binding energy of 574.9 eV. In tellurapyrylium dye chromophores where the positive charge could be shared by more that one heteroatom, the ^{125}Te NMR chemical shifts were even further upfield in the range δ 784–934 ppm with Te($3d_{5/2}$) binding energies from 573.1 to 574.1 eV. A linear correlation was found between the ^{125}Te NMR chemical shift and the Te($3d_{5/2}$) binding energies on comparison of seven closely related cationic Te(II) compounds with a least-squares correlation coefficient of 0.98. A linear correlation was also found on the comparison of the ^{125}Te NMR chemical shift and the Te($3d_{5/2}$) binding energies of six closely related neutral Te(II) compounds with a least-squares correlation coefficient of 0.91. The neutral Te(II) tellurapyranones have ^{125}Te NMR chemical shifts that are downfield of their neutral Te(II) tellurapyran analogues by 139–188 ppm. Contributions from resonance forms that give a tellurapyrylium ring in the tellurapyranones, placing a partial positive charge on the tellurium center, could be responsible, in part, for the downfield shifts. The examination of a series of Te(IV) compounds, with Te($3d_{5/2}$) binding energies from 575.8 to 576.4 eV, did not find a correlation with the ^{125}Te NMR chemical shift. As expected, the ^{125}Te NMR chemical shift was found to be sensitive to changes which affect the paramagnetic screening constant in these compounds.

Two trends that have emerged in the study of ^{125}Te NMR chemical shifts of organotellurium compounds are that the chemical shift moves downfield as the oxidation state increases from Te(II) to Te(IV) and as the electronegativity of the ligands attached to tellurium increases.[2] Since relatively few ^{125}Te NMR chemical shifts have been reported,[3] the generality of these trends has not been unequivocally established. The range of chemical shifts in ^{125}Te NMR covers several thousand parts per million, and one expects factors in addition to the electronegativity of the ligands attached to the tellurium center and the oxidation state of the tellurium center to be important contributors to the changes observed in chemical shift.

The effect of charge in organotellurium compounds on ^{125}Te NMR chemical shifts has not been addressed extensively. The addition of methyl iodide to dimethyl telluride to give the telluronium salt $Me_3Te^+I^-$ gives a 443

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(1) Division of Organic Chemistry of the American Chemical Society Fellow sponsored by the Rohm & Haas Company, 1986–1987. General Electric Co. Fellow, 1985–1986.

(2) Zumbulyadis, N.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *192*, 183.

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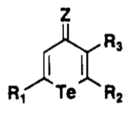
ppm downfield shift in the ^{125}Te NMR spectrum of the telluronium salt relative to the telluride.[4] In contrast to this result, the increased formal positive charge per tellurium in comparing Te_6^{4+} with Te_4^{2+}, systems in which charge is delocalized, is not reflected in chemical shifts. The ^{125}Te NMR chemical shift of Te_6^{4+} is over 2500 ppm upfield of the ^{125}Te NMR chemical shift of Te_4^{2+}.[5]

The electronic factors that contribute to the binding energy shifts observed in X-ray photoelectron spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis) are primarily inductive in nature while NMR chemical shifts are sensitive to both the diamagnetic screening and the paramagnetic screening of the nucleus.[6] However, in some closely related organometallic systems, linear correlations between XPS binding energies and NMR chemical shifts have been observed.[7] The comparison of tellurium XPS binding energies with ^{125}Te NMR chemical shifts in a series of related organotellurium compounds lends a better understanding of the effects of charge, oxidation state, and the ligands attached to tellurium with respect to both binding energies and NMR chemical shifts. We wish to report our results on XPS and ^{125}Te NMR investigations of a series of tellurapyran, tellurapyranone, and tellurapyrylium compounds in both the tellurium(II) and tellurium(IV) oxidation states.

Results and Discussion

Tellurium(II) compounds of the general structures 1–3, and three-center, four-electron tellurium(IV) compounds of the general structure 4, were studied by both XPS and ^{125}Te NMR.[8] The rationalization for the choice of structure is based both in the ease of synthetic accessibility and in the diversity of substitution patterns available. For example, with the methylene unit at the 4-position of 1, extensive delocalization into the carbon π-framework, as shown for 2, is precluded. The tellurapyranones of structure 2 and their benzo analogues should have more extensive delocalization of the carbon π-framework as exemplified in the resonance form shown with separation of charge. Tellurapyrylium compounds 3 are Hückel aromatic systems with a formal positive charge in the ring delocalized to the carbons at positions 2, 4, and 6 in addition to the tellurium atom at position 1. The analysis of tellurapyrylium salts, such as 3, allows the contribution of the resonance form with separation of charge, as in 2, to be assessed. Oxidative addition of halogen to the tellurium atoms of structures 1, 2, and 3 is possible to give tellurium(IV) analogues 4 of the tellurapyrans,[9] tellurapyranones,[9] and tellurapyrylium compounds.[10]



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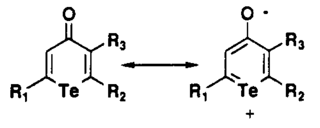

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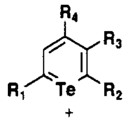

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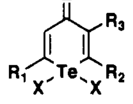

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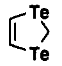
The interaction of tellurium with the carbon π-framework and the inductive effects of the hydrocarbon backbone with tellurium are demonstrated by the tellurium–carbon bond lengths in these systems. 1,3-Ditellurole (5) is a good model for a vinyl telluride with a carbon (sp^2)–tellurium bond length of 2.090 Å.[11] In tellurapyrylium dye 6, the tellurium–carbon bond lengths are shorter at 2.068 Å, as would be expected, from partial double-bond character in these bonds.[12] Oxidative addition of bromine to 2,6-di-*tert*-butyl-4-(4-(dimethylamino)phenyl)tellurapyrylium perchlorate (7) gave the tellurium dibromide 8 with tellurium–carbon bond lengths of 2.115 Å.[10] We sought to develop an understanding of the relationship between the interaction of tellurium with the hydrocarbon backbone through the analysis with XPS and ^{125}Te NMR of a series of Te(II) and Te(IV) tellurapyrans, tellurapyranones, and tellurapyrylium salts.



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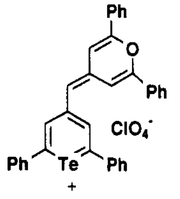

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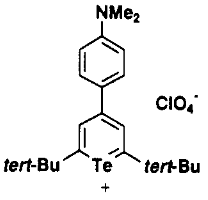

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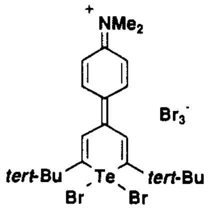

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Organotellurium(II) compounds chosen for study by ^{125}Te NMR spectroscopy and XPS include the following: the monocyclic 2,6-di-*tert*-butyl-substituted tellurapyran 9 and its dimer linked at the 4-position, 10; the bicyclic benzo[*b*]tellurapyrans 11 and 12 and the chlorine and bromine oxidative addition products of 11, 13 and 14, respectively; tellurapyranones 15 and 16 and their products of oxidative halogenation, chlorination and bromination of 15 to give 17 and 18, respectively, and bromination of 16 to give 19; tellurapyranones 20 and 21 and the oxidative chlorination product of 20, 22 (Chart I). Tellurapyrylium salts that were also included in the study include the following: the monocyclic 2,6-di-*tert*-butyl-substituted tellurapyrans 23 and 24 and the bis(tellurapyrylium) salt 25; the benzo[*b*]tellurapyrylium salts 26 and 27; tellurapyrylium dyes 7, 28, and 29 (Chart I), which have a dimethylaniline substituent at the 4-position and vary in the groups attached at carbon positions 2 and 6. Compounds 12, 19, 21, and 27 were not included in the XPS study. This set of three series of compounds allows the gross

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(8) We are avoiding the use of the term "hypervalent" in the discussion of organotellurium compounds which have linear three-center, four-electron bonds such as in 4. These compounds have been found to not "exceed the octet" and are thus not *hypervalent*, see: Gassman, P. G.; Callstrom, M. R.; Martin, J. C.; Rongione, J. C. *J. Am. Chem. Soc.*, in press.

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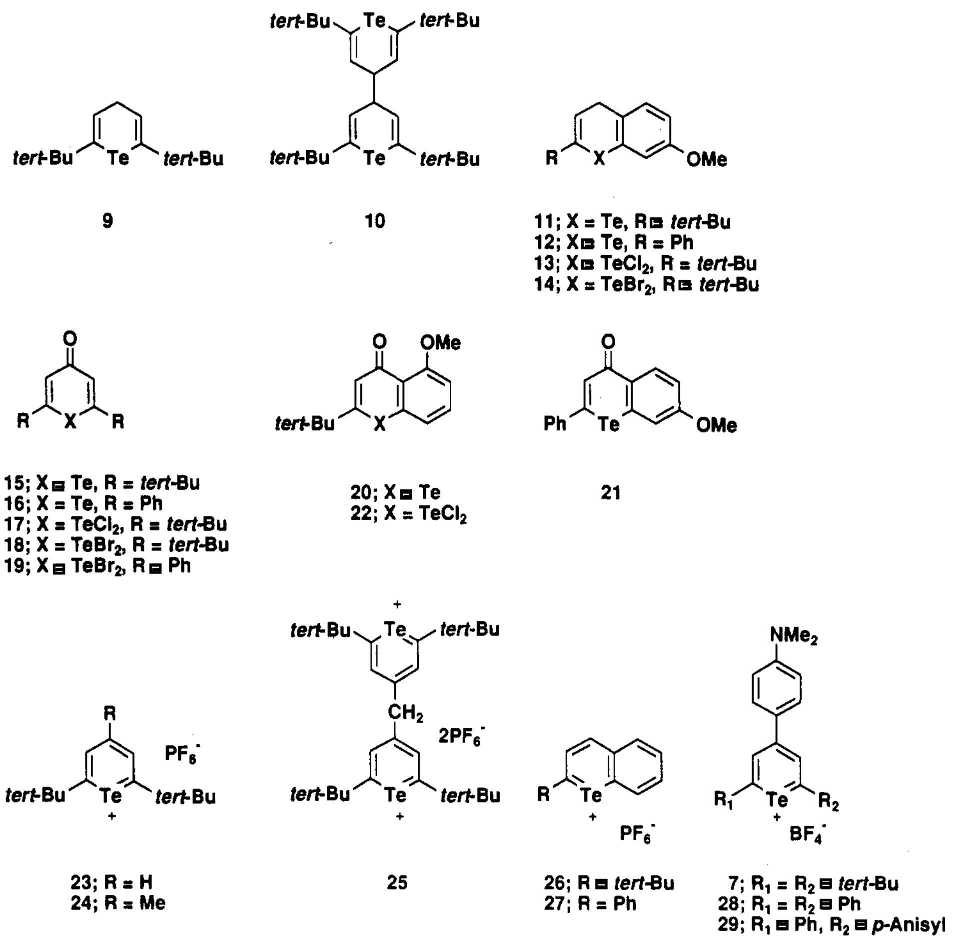
Chart I



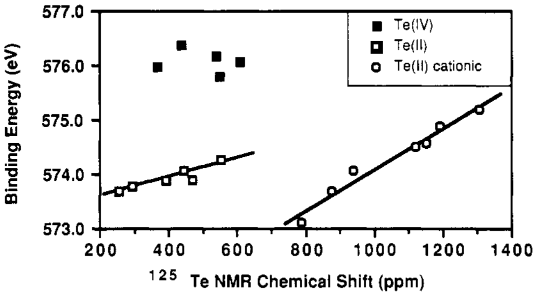


Figure 1. The Te($3d_{5/2}$) binding energies versus the ^{125}Te NMR chemical shifts for 7, 9–11, 13–18, 20, 22–26, 28, and 29.

changes in ^{125}Te NMR chemical shifts and Te($3d_{5/2}$) binding energies to be followed from tellurium(II) tellurapyrans and tellurapyranones to tellurapyrylium salts to tellurium(IV) tellurapyrans and tellurapyranones.

The tellurium(II) compounds 1–3 of this study have resonance forms that involve conjugative interaction of tellurium with the carbon π-framework. The conjugation of a tellurium 5p orbital with the 2p orbitals of the carbon π-framework can be eliminated by the oxidative addition of halogens such as chlorine and bromine to these compounds. The oxidative addition involves the $5p_z$ orbital of tellurium forming a linear, three-center, four-electron bond (the X–Te–X bond) in the tellurium(IV) compounds.[8,13] Consequently, pπ-conjugation of tellurium with the carbon π-framework in the tellurium(IV) compounds 4 of this study is not possible.

(i) Relationship between XPS Binding Energies and ^{125}Te NMR Chemical Shifts. Both the XPS binding energies and ^{125}Te NMR chemical shifts (~7 % natural abundance, $I = {}^1/_2$, parts per million relative to $TePh_2$ at δ 688 relative to $TeMe_2$ at δ 0.0 ppm) of the organotellurium compounds 7 and 9–29 are listed in Table I. These data, taken as a whole, are best compared by ex-

Table I. XPS Te($3d_{5/2}$) Binding Energies and ^{125}Te NMR Chemical Shifts for 7 and 9–29

compd	binding energy Te($3d_{5/2}$) (±0.1 eV), eV	chem shift[a] ^{125}Te, δ (ppm)
7	574.1	934
9	573.7	257
10	573.8	296
11	573.9	391
12		380
13	576.1	611
14	575.8	550
15	574.1	445
16	574.3	553
17	576.4	434
18	576.0	363
19		424
20	573.9	465
21		519
22	576.2	541
23	575.2	1304
24	574.9	1185
25	574.6	1150
26	574.5	1124
27		1086
28	573.7	875
29	573.1	784

[a] Diphenyl telluride was used as an external standard (δ 688 ppm relative to dimethyl telluride δ 0.0 ppm). NMR spectra were measured in CD_2Cl_2. [b] All binding energies are calibrated versus C(1s) of polyethylene (284.6 eV).

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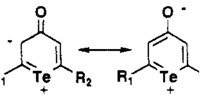
amination of the Te($3d_{5/2}$) binding energy versus the ^{125}Te NMR chemical shift as shown in Figure 1. Clearly, the data are broken up into three sets of points with separate relationships of ^{125}Te NMR chemical shift versus at Te($3d_{5/2}$) binding energy. On one line lie the Te(II) neutral compounds **9**–**11**, **15**, **16**, and **20** and on another line lie the Te(II) cationic compounds **7**, **23**–**26**, **28**, and **29**. The line containing the neutral Te(II) compounds had a least-squares correlation coefficient of 0.91 while the line containing the Te(II) cationic compounds had a least-squares correlation coefficient of 0.98. Obviously, there is no correlation between the Te($3d_{5/2}$) binding energy and the ^{125}Te NMR chemical shift for the three-center, four-electron bonded Te(IV) compounds **13**, **14**, **17**, **18**, and **22**. However, the Te(IV) compounds all fall within a fairly narrow range, distinct from the Te(II) and Te(II) cationic compounds in Figure 1.

The lack of a linear relationship between NMR chemical shift and XPS binding energies is not unexpected. Siegbahn and co-workers[6] have noted that there is no general relationship between the two spectroscopies. However, as was previously mentioned, linear correlations have been observed between NMR chemical shifts and XPS binding energies for narrow, well-defined classes of compounds.[7] The reason that there is not a general, linear correlation between these two spectroscopies, both of which measure the electronic environment of the atom in question, lies in the contributions to the NMR chemical shift. In an NMR experiment, the external applied magnetic field induces currents in the electron cloud of the molecule and these currents create a shielding field at the nucleus. This shielding field, or screening constant for a nucleus, is an average over all directions in a molecule. The screening constant is composed of both a diamagnetic and a paramagnetic contribution. The diamagnetic screening constant is a description of the screening at the nucleus due to currents created by the external magnetic field which are spherically symmetric. The paramagnetic screening constant is a description of asymmetry of the electron distribution as this asymmetry hinders the creation of shielding current.

For compounds which are closely related in structure, as are the compounds in this study, a linear relationship of XPS binding energy to NMR chemical shift may be observed. We have found that dramatic changes in structure result in the Te(II) compounds on one line, the Te(II) cationic compounds on another, and the Te(IV) compounds lacking a linear relationship.

(ii) ^{125}Te NMR Chemical Shifts, Te($3d_{5/2}$) Binding Energy, and Structure. Compounds **9**, **11**, and **12** are 4*H*-tellurapyrans without contributions from resonance forms involving charge separation or delocalization of the carbon π-framework. These compounds have binding energies consistent with Te(II) [Te($3d_{5/2}$), 573.7 (**9**), 573.9 eV (**11**)] and ^{125}Te NMR chemical shifts (δ 257 for **9**, δ 391 for **11**, and δ 380 ppm for **12**) that are significantly upfield from the ^{125}Te NMR chemical shifts of the tellurapyranone analogues of these compounds, **15** (δ 445), **16** (δ 553), **20** (δ 465), and **21** (δ 519), respectively. The carbonyl in the 4-position of the tellurapyranones can exert both an inductive effect on the tellurium atom and a mesomeric effect as in resonance forms **30** and **31**. In order to assess whether the resonance form involving separation of charge in **15** is important, it is necessary to compare **15** to **9**, where the 4-position is blocked by a methylene unit. A change of 0.4 eV to higher binding energy from **9** to **15** suggests that the resonance forms shown as **30** needs to be included for a description of the electronic makeup of **15**. Again, the ^{125}Te NMR supports the suggestion that the tellurium in **15** (δ 445) is electron-deficient relative to **9** (δ 257) with a chemical shift difference of 188 ppm. Comparison of the benzo analogues of **9** and **15**, **11**, and **20**, respectively, suggests that the resonance form **31** is not as an important contributor for a description of the structure of **20**. Comparison of the ^{125}Te NMR of **11** (δ 391) and **20** (δ 465) with a chemical shift difference of 74 ppm suggests that the binding energy difference between **11** and **20** should be approximately 0.15 eV (comparison to **9** and **15** with 47 ppm/0.1 eV). Both **11** and **20** had a Te($3d_{5/2}$) binding energy of 573.9 eV. These findings by both XPS and ^{125}Te NMR are consistent with a description of **20** with little or no contribution from a resonance form involving separation of charge.



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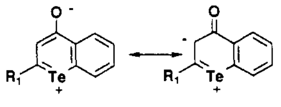

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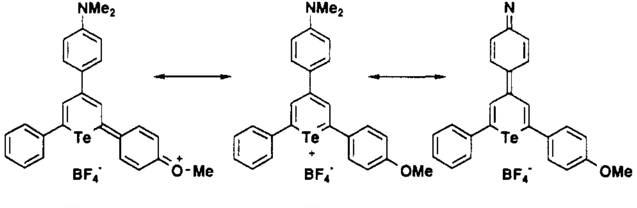
In the tellurapyrylium compounds **23**–**27**, which have a positive charge on the ring containing tellurium, resonance forms which place a positive charge on tellurium are expected to make a greater contribution than in the tellurapyranone system. The Te($3d_{5/2}$) binding energies range from 574.5 to 575.2 eV, a minimum of 0.4 eV higher in binding energy than that found for the analogous tellurapyranone compounds. The ^{125}Te NMR chemical shifts of **23** (δ 1304), **24** (δ 1185), **25** (δ 1150), **26** (δ 1124), and **27** (δ 1086) are hundreds of parts per million downfield of the tellurapyranones. In benzotellurapyrylium salt **26**, one *tert*-butyl group in **23** has been replaced by a fused benzo group. The binding energy of **26** [Te($3d_{5/2}$), 574.5 eV] is a full 0.7 eV lower than the binding energy of **23** [Te($3d_{5/2}$), 575.2 eV]. The positive charge in **26** is delocalized over more of the π-framework resulting in less charge at tellurium. The ^{125}Te NMR chemical shift of **26** is 180 ppm upfield of the chemical shift of **23**, consistent with a more electron-rich tellurium center in **26** relative to **23**.

Tellurapyrylium dyes **7**, **28**, and **29** incorporate a heteroatom in addition to the tellurium in the dye chromophore in the form of a dimethylaniline at the 4-position. The effects of increased conjugation and additional heteroatoms are apparent in these compounds. The ^{125}Te NMR chemical shifts for **7** (δ 934), **28** (δ 875), and **29** (δ 784), with a chemical shift change of 150 ppm suggest that the tellurium center is progressively more electron-rich from **7** to **28** to **29**. The suggestion is confirmed on examination of the binding energies of **7** [Te($3d_{5/2}$), 574.1 eV], **28** [Te($3d_{5/2}$), 573.7 eV], and **29** [Te($3d_{5/2}$), 573.1 eV]. The binding energies of these Te(II) cations varied by 1.0 eV! The binding energies of these compounds when compared to simple Te(II) and Te(II) cationic compounds suggest that the resonance forms **29a** and **29c** contribute significantly to the electronic structure of **29**. For example, **9**, a simple Te(II) compound, had a Te($3d_{5/2}$) binding energy of 573.7 eV. The binding energies for **7**, **28**, and **29** are closer to the binding energies for the uncharged Te(II) compounds than the Te(II) cationic compounds! Also, the



29a **29b** **29c**

donation of electron density to the tellurium atom was much greater for the phenyl-substituted **28** and **29** than the *tert*-butyl-substituted **7**.

The change in binding energy on oxidative addition of chlorine and bromine to tellurapyran **11** [Te(3$d_{5/2}$), 573.9 eV] to give **13** [Te(3$d_{5/2}$), 576.1 eV] and **14** [Te(3$d_{5/2}$), 575.8 eV] was found to be 2.2 and 1.9 eV, respectively, forming linear, three-center, four-electron bonds (X–Te–X). The change in binding energy on oxidative addition of chlorine and bromine to tellurapyranone **15** [Te(3$d_{5/2}$), 574.1 eV] to give **17** [Te(3$d_{5/2}$), 576.4 eV] and **18** [Te(3$d_{5/2}$), 576.0 eV], respectively, was found to be 2.3 and 1.9 eV, respectively. Examination of the ^{125}Te NMR chemical shifts of these Te(IV) compounds in comparison to the neutral Te(II) compounds in Figure 1 finds only small changes in the NMR chemical shifts in contrast to the 1.9–2.3 eV changes in XPS binding energies.

Conclusion

Clearly, in the tellurapyran and tellurapyranone systems, increasing the oxidation state of tellurium by oxidative addition of halogen does not necessarily lead to a downfield shift in ^{125}Te NMR chemical shifts as has been reported in other systems.[2] Structural features are important contributors to the ^{125}Te NMR chemical shifts. Important contributions include the presence of a formal positive charge in the molecule that can be placed on tellurium and the contribution of other resonance forms involving separation of charge. XPS binding energies are useful in describing the electronic environment at tellurium in organotellurium compounds. In closely related systems, linear correlations have been observed for XPS binding energies and NMR chemical shifts. In the analysis of organotellurium compounds, we have found that changes in structure markedly affect the relationship of the Te-(3$d_{5/2}$) binding energies to the ^{125}Te NMR chemical shifts. In comparing the cationic tellurium(II) systems with the neutral tellurium(II) systems with XPS and NMR spectroscopies it is evident that ligand changes in the cationic ring systems resulted in dramatic differences in the electronic environment of the tellurium center. As described above, conjugation and charge delocalization were found to be more extensive in the cationic tellurapyrylium systems than in the neutral tellurapyran and tellurapyranone systems. Neutral tellurium(II) compounds lie on one line, the cationic tellurium(II) compounds lie on another, and the tellurium(IV) compounds show no apparent relationship between XPS and NMR spectroscopies.

Experimental Section

The NMR solvent was CD_2Cl_2 which was used as received from Aldrich Chemical Co. ^{125}Te NMR spectra were recorded on a Varian Automated XL 300 NMR spectrometer at 94.704 MHz with a 5-mm broad-band probe (25–150 mg of sample/0.5 mL of solvent, probe temperature of 22 °C); samples were referenced to $^{125}TePh_2$ (at δ 688 relative to $^{125}TeMe_2$ at δ 0.0), as an external standard run as a neat liquid. The spectra were collected over 100–5000 transients by using a 100 000 Hz sweep width, a pulse time of 10 μs, and a delay time of 1.0 s. The spectra were proton decoupled with WALTZ decoupling using 1.5 W of power centered at 5 ppm in the proton window. The ESCA analyses were carried out with a Physical Electronics Industries, Inc., ESCA-Auger-SIMS Model 555 spectrometer equipped with a Model 15-770 specimen introduction/reaction chamber. All reported values are ±0.1 eV. Both Mg Kα and Al Kα radiation were used. Samples were run with a polyethylene backing, allowing an internal calibration against the C(1s) binding energy (284.6 eV). Compounds **7**, **24**, and **28** were prepared according to ref **12**. Compounds **9–12**, **23**, **26**, and **27** were prepared according to ref 14. Compounds **15–19** were prepared according to ref 9. Compounds **20** and **21** were prepared according to ref 15. The remaining compounds were new materials prepared for this study.

4-(*p*-*N*,*N*-Dimethylanilino)-2-phenyl-6-(*p*-anisyl)tellurapyrylium Tetrafluoroborate (29). A solution of *p*-bromo-*N*,*N*-dimethylaniline (0.31 g, 1.5 mmol) in 7 mL of dry tetrahydrfuran (THF) was added to magnesium turnings (0.040 g, 1.5 mmol) under a nitrogen atmosphere. A small crystal of iodine (~5 mg) was added. The mixture was stirred at reflux for 3 h. 2-Phenyl-6-(*p*-anisyl)tellurapyranone (0.30 g, 0.77 mmol) in 7 mL of dry THF was added dropwise over 10 min. The mixture was stirred at reflux for 1.5 h. The reaction mixture was added to a solution of 18 mL of 49% fluoroboric acid in 60 mL of ice water. The precipitate was collected by filtration and was recrystallized from acetonitrile to give 0.11 g (25%) of **29** as a dark green solid: mp 206–208 °C; IR (KBr) 2930 (w), 1615, 1545, 1510, 1490, 1460, 1445, 1400, 1310, 1275, 1210, 1175, 1055 (br), 960, 820 cm^{-1}; λ_{max} (log ϵ) 655 nm (4.80 in dichloromethane). Anal. Calcd for $C_{26}H_{24}NOTe{\cdot}BF_4$: C, 53.7; H, 4.2; N, 2.4. Found: C, 54.0; H, 4.1; N, 2.4.

***Te*,*Te*-Dichloro-4*H*-7-methoxy-2-*tert*-butylbenzo[*b*]tellurapyran (13).** Chlorine gas was bubbled into a dichloromethane solution of **11** (0.33 g, 1.0 mmol) until the color of the solution was pale yellow (from gold). The reaction mixture was concentrated. The yellow crystalline solid was recrystallized from acetonitrile to give 0.32 g (80%) of **13** as a pale yellow solid: mp 163–164 °C; ^{1}H NMR (CD_2Cl_2) δ 7.45 (d, J = 9 Hz, 1 H), 7.36 (d, J = 3 Hz, 1 H), 7.05 (dd, J = 3 Hz, J = 9 Hz, 1 H), 6.27 (t, J = 4.5 Hz, 1 H), 4.20 (d, J = 4.5 Hz, 2 H), 3.84 (s, 3 H). Anal. Calcd for $C_{14}H_{18}Cl_2OTe$: C, 41.95; H, 4.5. Found: C, 41.9; H, 4.4.

***Te*,*Te*-Dibromo-4*H*-7-methoxy-2-*tert*-butylbenzo[*b*]tellurapyran (14).** Bromine (0.18 g, 1.1 mmol) in 5 mL of dichloromethane was added dropwise to a solution of **11** (0.33 g, 1.0 mmol) in 5 mL of dichloromethane. After addition was complete, the reaction mixture was concentrated and the residue was recrystallized from acetonitrile to give 0.45 g (92%) of **13** of a tan solid: mp 177–179 °C; ^{1}H NMR (CD_2Cl_2) δ 7.44 (d, J = 9 Hz, 1 H), 7.34 (d, J = 3 Hz, 1 H), 7.06 (dd, J = 3 Hz, J = 7 Hz, 1 H), 6.18 (t, J = 4.5 Hz, 1 H), 4.18 (d, J = 4.5 Hz, 2 H), 3.83 (s, 3 H). Anal. Calcd for $C_{14}H_{18}Br_2OTe$: C, 34.3; H, 3.7. Found: C, 34.5; H, 3.8.

***Te*,*Te*-Dichloro-4*H*-5-methoxy-2-*tert*-butylbenzo[*b*]tellurapyran-4-one (22).** Chlorine gas was bubbled into a dichloromethane solution of **20** (0.34 g, 1.0 mmol) until the color of the solution faded to pale yellow. The reaction mixture was concentrated and the residue was recrystallized from pentane–ether to give 0.39 g (95%) of **22** as bright yellow crystals: mp 199–202 °C; ^{1}H NMR (CD_2Cl_2) δ 7.63 (dd, J = 8 H, J = 9 Hz, 1 H), 7.46 (d, J = 8 Hz, 1 H), 7.25 (d, J = 9 Hz, 1 H), 6.65 (s, 1 H), 3.93 (s, 3 H). Anal. Calcd for $C_{14}H_{16}Cl_2O_2Te$: C, 48.9; H, 4.7. Found: C, 48.8; H, 4.5.

Preparation of 25. An acetic acid solution of 2,6-di-*tert*-butyl-4-(2,6-di-*tert*-butyltellurapyranyl-4-methylidenyl)tellurapyrylium hexafluorophosphate (100 mg in 5 mL was treated with 250 μL of 50% aqueous HPF_6. The resulting solution was heated for 1 h on a steam bath at which point the reaction mixture had changed color from green to yellow. The reaction mixture was diluted with 10 mL of ether, and the resulting solution was chilled. The bright yellow precipitate was collected by filtration, washed with ether, and dried to give 88 mg of material, mp 232–242 °C with decomposition: ^{1}H NMR (CD_2Cl_2) δ 8.60 (s, 4 H), 4.56 (s, 2 H), 1.65 (s, 36 H). Anal. Calcd for $C_{27}H_{42}Te_2{\cdot}2PF_6$: C, 35.6; H, 4.6. Found: C, 36.1; H, 4.8.

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