TELLURIUM-CONTAINING HETEROCYCLES

MICHAEL R. DETTY and (in Part)
MARIE B. O'REGAN

Office Imaging Research and Technical Development
Kodak Imaging Group
Eastman Kodak Company
Rochester, New York

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TELLURIUM-CONTAINING HETEROCYCLES

This is the fifty-third volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

EDWARD C. TAYLOR, *Editor*

ARNOLD WEISSBERGER, *Founding Editor*

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The Chemistry of Heterocyclic Compounds
Introduction to the Series

The chemistry of heterocyclic compounds constitutes one of the broadest and most complex branches of chemistry. The diversity of synthetic methods utilized in this field, coupled with the immense physiological and industrial significance of heterocycles, combine to make the general heterocyclic arena of central importance to organic chemistry.

The Chemistry of Heterocyclic Compounds, published since 1950 under the initial editorship of Arnold Weissberger, and later, until Dr. Weissberger's death in 1984, under our joint editorship, has attempted to make the extraordinarily complex and diverse field of heterocyclic chemistry as organized and readily accessible as possible. Each volume has dealt with syntheses, reactions, properties, structure, physical chemistry, and utility of compounds belonging to a specific ring system or class (e.g., pyridines, thiophenes, pyrimidines, three-membered ring systems). This series has become the basic reference collection for information on heterocyclic compounds.

Many broader aspects of heterocyclic chemistry are recognized as disciplines of general significance which impinge on almost all aspects of modern organic and medicinal chemistry, and for this reason we initiated several years ago a parallel series entitled *General Heterocyclic Chemistry*, which treated such topics as nuclear magnetic resonance, mass spectra, photochemistry of heterocyclic compounds, the utility of heterocyclic compounds in organic synthesis, and the synthesis of heterocyclic compounds by means of 1,3-dipolar cycloaddition reactions. These volumes are of interest to all organic and medicinal chemists, as well as to those whose particular concern is heterocyclic chemistry.

It has become increasingly clear that this arbitrary distinction created as many problems as it solved, and we have therefore elected to discontinue the more recently initiated series *General Heterocyclic Chemistry* and to publish all forthcoming volumes in the general area of heterocyclic chemistry in *The Chemistry of Heterocyclic Compounds* series.

Part of the fascination of heterocyclic chemistry, and the challenge in studying this discipline, is probing and understanding the role of the heteroatom(s) in determining chemical and physical properties. The impact of the heteroatom could not be more dramatically illustrated than in the case of tellurium, relative to its lighter chalcogens, as detailed so insightfully in this present volume by Michael R. Detty and his coauthor, Marie B. O'Regan.

EDWARD C. TAYLOR

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Preface

For one of us (MRD), chemical efforts with organotellurium chemistry and tellurium heterocycles, in particular, have been a continual source of intellectual pleasure for the past 15 years. The numerous differences between the heterocyclic chemistry of tellurium-containing compounds and the heterocyclic chemistry of compounds containing the lighter chalcogens have challenged the mind to find utilities that exploit the differences. For the other of us (MBO'R), contributing a chapter to this work has enabled a transition-metal organometallic chemist to think about main-group organometallic chemistry. Both of us have enjoyed this opportunity to share our perspective.

The authors thank Barb Maxwell in the Kodak Research Libraries for her efforts to keep us as current as possible with respect to new references and Tim Frade for his efforts in copying many of the older references in the literature. The authors also respect the wishes of all those souls specifically requesting not to be acknowledged (but, thanks anyway).

While both authors work for the Eastman Kodak Company, the ideas expressed in this work should not be construed to define past, current, or future research directions of the Eastman Kodak Company. The ideas conveyed are the authors' alone.

MICHAEL R. DETTY AND MARIE B. O'REGAN

Rochester, New York
September, 1994

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TELLURIUM-CONTAINING HETEROCYCLES

This is the fifty-third volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

CHAPTER I

Tellurium-Containing Heterocycles: Reviews, Distinguishing Features, and Utility

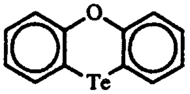
I. HISTORY IN REVIEW(S)

The first organotellurium compound was reported more than 150 years ago with the synthesis of diethyltelluride in 1840.[1] (*Note*: Superscript reference numbers refer to references listed at end of chapter, under "References"; not references listed in text as here.) The area of organotellurium chemistry was slow to develop, but in the last 20 years, numerous reviews have appeared in order to cover the thousands of papers dealing with organo- and organometallic tellurium compounds:

1. Irgolic, K. J. In *Houben-Weyl Methoden der Organischen Chemie: Organo tellurium Chemistry*, Klamann, D., ed., Georg Thieme, New York, 1990, Vol. E12b.
2. Patai, S., ed., *The Chemistry of Organic Selenium and Tellurium Compounds*, J. Wiley, New York, 1987, Vol. 2.
3. Patai, S.; Rappoport, Z., eds., *The Chemistry of Organic Selenium and Tellurium Compounds*, J. Wiley, New York, 1986, Vol. 1.
4. Irgolic, K. J. *The Organic Chemistry of Tellurium*, Gordon and Breach Science Publishers, New York, 1974.
5. Sadekov, I. D.; Rybalkina, L. E.; Movshovich, D. Ya; Bulgarevich, S. B.; Kogan, V. A. *Uspekhi Khimii* **1991**, *60*, 1229.
6. Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 897.
7. Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 793.
8. Sadekov, I. D.; Rivkin, B. B. *Khim. Geterostsikl. Soedin*, **1991**, 291.
9. Sadekov, I. D.; Abakarov, G. M.; Sadekova, Y. I.; Minkin, V. I. *Sulfur Reports* **1986**, *6*, 15.
10. Fringuelli, F.; Marino, G.; Taticchi, A. *Adv. Heterocycl. Chem.* **1977**, *21*, 119.

As the area of organotellurium chemistry has developed, the numbers of papers describing tellurium-containing heterocycles have increased as well. Saturated six-membered rings containing one tellurium atom (tellurane **1**) are among the oldest studied tellurium-containing heterocycles through the research of G. T. Morgan and colleagues in the 1920s.[2,3] Unsaturated analogs of the telluranes, however, were not prepared until the 1980s. Phenoxtellurine (**2**) was first prepared by Drew in 1926,[4] and tetrahydrotellurophene (**3**) was first prepared by Morgan and Burstall in 1931.[5] While these simple tellurium-containing heterocycles have been known for at least 50 years, other simple tellurium-containing heterocycles have only recently been prepared or remain unknown [e.g., monocyclic 1,3-tellurazole (**4**)].

1



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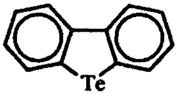
The vagaries of the syntheses of tellurium-containing heterocycles are illustrated by the development of the tellurophene nucleus. Although tetrahydrotellurophene (**3**) was first prepared in 1931[5] and dibenzotellurophene (**5**) was first prepared in 1936,[6] very few papers concerning these molecules have appeared in the ensuing 63 years. Tellurophene (**6**), on the other hand, was first prepared in

1966[7] and a major review (Fringuelli, et al., in the list above) appeared in 8 years. The benzo analog 7, another simple heterocycle, was not prepared until 1971.[8]



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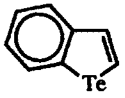

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The development of the chemistry of tellurium-containing heterocycles in the last 25 years has been sufficiently rapid to warrant separate reviews as well as inclusion as discrete sections in other reviews. In the list presented above, the reviews devoted in their entirety to tellurium-containing heterocycles are Sadekov and Rivkin, Sadekov, et al., and Fringuelli, et al. and those with chapters dedicated to tellurium-containing heterocycles include Irgolic (Klamann, ed.); Patai, ed.; and Patai and Rappoport, eds. in the preceding list. The other reviews in the preceding list also describe tellurium-containing heterocycles and their reactions, but not in a systematic way. The series below contains chapters devoted to the synthesis, chemistry, and properties of tellurium- and selenium-containing heterocycles and is developed in a systematic way.

11. Katritzky, A. R.; Rees, C. W., eds.; *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds*, Pergamon, New York, 1984.

What is the need, then, for another review of tellurium-containing heterocycles? The field continues to develop rapidly, and numerous references have appeared since the more recent reviews in the lists presented above. The differences in the properties of series of heterocycles, where only the heteroatom varies, are rapidly becoming clear. Advances in organometallic chemistry have created new types of tellurium-containing heterocycles where tellurium is bonded to other metals and pseudo-metals. Finally, the "real-world use" of tellurium-containing heterocycles is beginning. This is perhaps reflected in the appearance of manuscripts devoted to the applications of tellurium-containing heterocycles and in the appearance of patents, where tellurium-containing heterocycles are not part of a boiler plate, but are described in detail. In these examples, the unique properties of tellurium are necessary for the application.

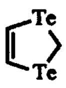
II. DISTINGUISHING CHARACTERISTICS OF THE TELLURIUM ATOM IN TELLURIUM-CONTAINING HETEROCYCLES

A. Electronegativity

Tellurium is the most electropositive of the chalcogen elements with a Pauling electronegativity of 2.1.[9] This value can be compared to electronegativities of 3.5 for oxygen, 2.5 sulfur, and 2.4 for selenium.[9] One consequence of the low electronegativity of tellurium is an inverted polarization of the chalcogen–carbon bond as one moves down the periodic table from oxygen to tellurium. The tellurium–carbon bonds are polarized Te$^{\delta+}$—C$^{\delta-}$, while oxygen–carbon bonds are polarized O$^{\delta-}$—C$^{\delta+}$. Chemically, the difference in polarization of the bond is manifested in differing chemistry between telluro ethers and ethers. As an example, treating anisole with HBr gives phenol and bromomethane, while treating phenyl methyl telluride with HBr gives phenyltellurenyl bromide and methane.

B. Covalent and van der Waals Radii and Inter- and Intramolecular Interactions

Tellurium is significantly larger than the other chalcogen atoms with a covalent radius of 1.36 Å[9] and a van der Waals radius of 2.06 Å.[10] Because the tellurium atoms of tellurium-containing heterocycles are large and polarizable, intermolecular interactions between tellurium atoms tend to be strong, as found in 1,3-ditellurole (**8**). In crystal structures of 1,3-ditellurole (**8**),[11] Te···Te intermolecular interactions result in a three-dimensional polymeric array of tellurium atoms. The distances of the Te···Te interactions are 3.864 and 3.865 Å, which are significantly shorter than twice the van der Waals radius of tellurium: 4.12 Å. In 1,3-ditellurole (**8**), the interacting atoms are also in stereochemically significant positions. These two criteria have been given by Alcock as evidence for the formation of secondary bonds.[12]



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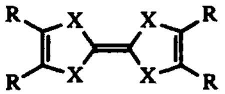

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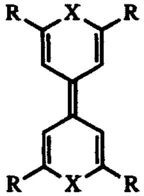

X = O, S, Se, Te

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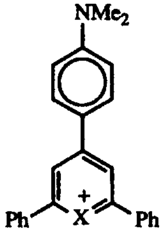
The large size of tellurium also leads to less effective overlap of the heteroatom orbitals with an adjacent carbon π framework, which leads to higher orbital energies. In donor molecules such as the tetrachalcogenafulvalenes (**9**)[13–16] and (chalcogenopyranyl)chalcogenopyrans (**10**),[17,18] the first oxidation potential becomes more positive, and the difference between first and second oxidation potentials decreases as the heteroatom increases in size from oxygen to tellurium. These trends are opposite those expected from electronegativity differences among the heteroatoms, but are consistent with the premise that less effective overlap with the π framework both raises the energy of the first oxidation and promotes less effective communication between the heteroatoms.

In chromophores where the chalcogen atom is in the conjugation with π bonds, the wavelength of the tellurium-containing chromophore is at a longer wavelength than chromophores containing a lighter chalcogen atom. In dye molecules such as the chalcogenapyrylium dyes **11**[19,20] and the cyanine dyes **12**[21,22] raising the energy of the lone pair of electrons on the heteroatom leads to a lower-energy $n-\pi^*$ transition, which leads to longer-wavelength-absorbing dyes. In dyes **11**, for example, the wavelength of the absorption maximum increases from 550 nm for the pyrylium dye to 650 nm for the telluropyrylium analogue.



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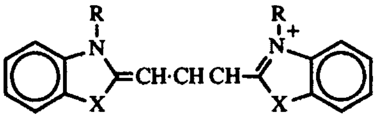

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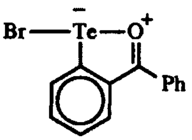
X = O, S, Se, Te

C. Hypervalent Bonding

The metallic character of tellurium dominates the geometry of organotellurium compounds. In organotellurium(II) compounds where one of the ligands is highly electronegative, tellurium(II) is stabilized by forming a bonding arrangement with an additional electronegative ligand to give a three-center, four-electron bond.[23-25] This bonding arrangement requires a nearly linear array of the metal and two ligands and results in approximately half of a covalent bond from tellurium to each ligand. The electronegative ligands occupy axial sites in a trigonal–bipyramidal array, while the equatorial sites are occupied by the bond to carbon and two lone pairs of electrons on tellurium. Such "hypervalent" bonding leads to molecules with cyclic geometry and long bonds, which constitute new classes of tellurium-containing heterocycles.[26] Illustrative examples of these heterocycles with a hypervalent bond in the ring are 2-acetylphenyltellurenyl bromide (**13**),[27] 1,5-diphenyl–dioxatellurapentalene **14**,[28] and oxatellurolylium chloride **15**.[29] Although hypervalent sulfur and selenium analogs are known, they are far fewer in number than the number of hypervalent organotellurium compounds.



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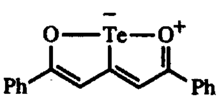

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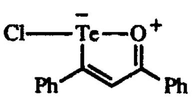

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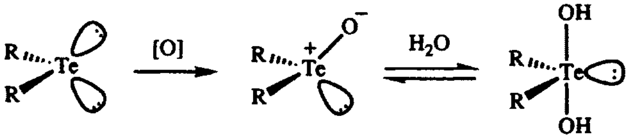
D. Higher Oxidation States, Ligand Exchange, and Reductive Elimination

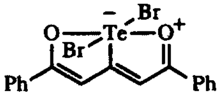
The tellurium atom of tellurium-containing heterocycles is easily oxidized from tellurium(II) to tellurium(IV). A "diagnostic" reaction for the formation of a new tellurium-containing heterocycle is the oxidation of the tellurium atom of the ring with the halogens to give tellurium(IV) derivatives of the heterocyclic ring. The bonds from the halogens to tellurium are linear three-center, four-electron bonds. The geometry around tellurium is trigonal–bipyramidal with the halide ligands occupying axial sites and the ring bonds to tellurium and a lone pair of electrons occupying equatorial sites.

Unlike organosulfur and organoselenium compounds, which have isolable sulfoxide and selenoxide states, respectively, organotellurium compounds rarely have a discrete "oxide" state such as the telluroxide shown in Scheme 1. Typically, the telluroxide is hydrated to give the dihydroxytellurane, which shares the trigonal–bipyramidal geometry of other hypervalent organotellurium compounds.[30]



Scheme 1

Even the hypervalent heterocyles like **14** and **15** can be oxidized to tellurium(IV) derivatives. In the case of trigonal–bipyramidal complexes, oxidative addition of halogens generates an octahedral tellurium(IV) array such as that found in **16**[28] and **17**.[31] In these molecules, 2 three-center, four-electron bonds account for the bonding between the electronegative ligands and tellurium. The tellurium–carbon bond and one lone pair of electrons occupy the remaining octahedral sites.



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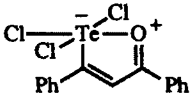

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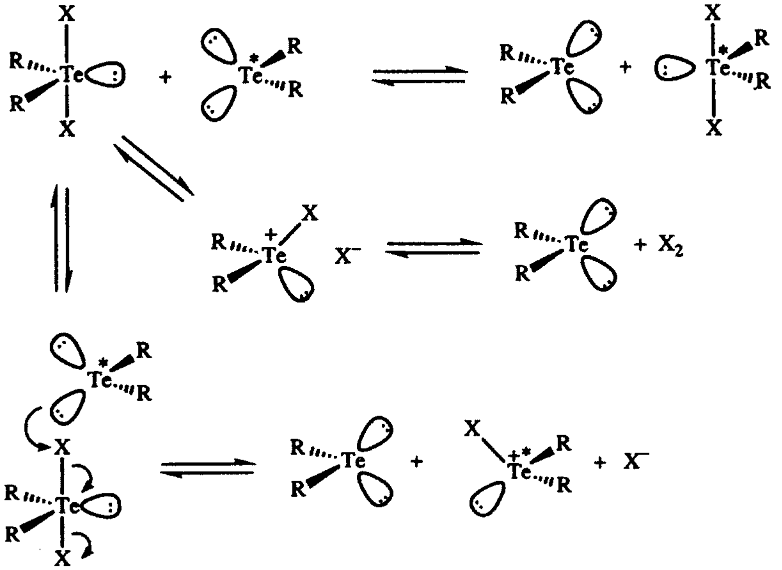
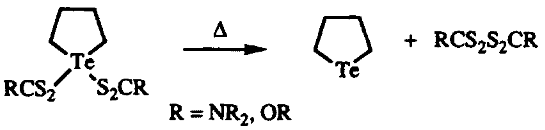
The electronegative ligands to tellurium in tellurium(IV) heterocyclic derivatives and in trigonal–bipyramidal tellurium(II) heterocyclic derivatives undergo nucleophilic ligand-substitution reactions. A variety of different kinds of ligands, which vary in electronegativity, size, thermal stability, and photochemical stability, can be incorporated in the ligand field of these heterocycles. Such variation in structure is not routinely found in analogous selenium- and sulfur-containing heterocyclic compounds.

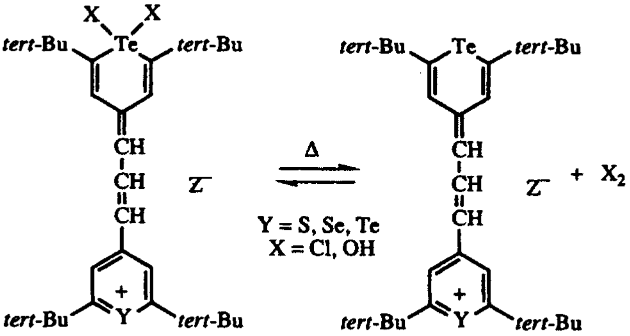
Organotellurium(IV) compounds with highly electronegative ligands can exchange their ligands with a tellurium(II) compound to generate a new tellurium(IV) compound as illustrated in Scheme 2. This process was first observed in dihalodiaryltellurium(IV)/diaryltellurides[32,33] and was subsequently observed in 1,1-dihalotelluropyrans/telluropyrans[34] and 1,1-dihydroxytelluropyrans/telluropyrans.[35] The exchange of oxidation states and ligands in these systems was found to proceed via both first- and second-order processes as illustrated in Scheme 2. The order of the reaction is also dependent on the polarity of the solvent with more polar solvents promoting first-order behavior.



Scheme 2

In addition to exchange of ligands and transfer of oxidation state, tellurium-containing heterocycles with the tellurium(IV) oxidation state can also undergo thermal, reductive elimination of the electronegative ligands to give a tellurium(II) center and coupled, oxidized ligands. As shown in Scheme 3, 1,1-bis(dithiocarbamato)- and 1,1-bis(alkoxydithioxanthato)tetrahydrotellurophenes undergo reductive–elimination reactions on heating to generate tetrahydrotellurophene and a disulfide bond joining the two ligands.[36,37] Reductive elimination of chlorine from 1,1-dichlorotelluropyranyl groups[38] and reductive elimination of hydrogen peroxide from 1,1-dihydroxytelluropyranyl groups[35] generate telluropyrylium dyes as shown in Scheme 3. In the latter two systems, chloride and hydroxide, respectively, were found to act as catalysts for the reductive–elimination reactions. The mechanisms involved in thermal reductive elimination should be similar to the mechanisms of ligand exchange shown in





Scheme 3

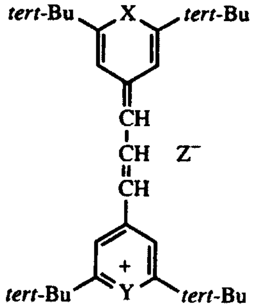
Scheme 2. This rich chemistry is not found in heterocycles based on the lighter chalcogens.

Tellurium(IV) derivatives of heterocyclic systems with halide, hydroxide, or pseudohalide ligands are easily reduced electrochemically to the tellurium(II) analog of the heterocycle and two equivalents of halide, hydroxide, or pseudohalide.[28,31,34,39] The reductions as monitored by cyclic voltammetry are irreversible, two-electron waves.

Kinetically, tellurium-containing heterocycles react much more rapidly with oxidants such as chlorine, bromine, iodine, singlet oxygen, and ozone than the corresponding heterocycles incorporating the lighter chalcogens.[40,41] In the chalcogenopyrylium dye series **18**, the tellurium-containing dyes have second-order rate constants for reaction with these oxidants that are on the order of 10^9 L mol^{-1} s^{-1} or greater. Reaction is at the tellurium atoms to give oxidation to tellurium(IV). With those dyes that do not contain tellurium, second-order rate constants are orders of magnitude smaller and oxidation of the carbon π framework, not oxidation of the heteroatom, is observed.

E. Heavy-Atom Effects on Physical and Photophysical Properties

The spin–orbit coupling constant associated with an atom increases as a function of Z^4, where Z is the atomic number of the atom in question.[42] Obviously, then, the physical and photophysical properties of tellurium-containing heterocycles should reflect large contributions from spin–orbit effects relative to heterocycles containing only the lighter chalcogens. In measurements of excited-state lifetimes of chalcogenopyrylium dyes **18**, both singlet and triplet lifetimes decrease as a function of increased spin–orbit effects.[41] The rates of intersystem crossing in these molecules are affected roughly two orders of magnitude more strongly than rates of internal conversion back to ground state. Thus, even though singlet and triplet lifetimes are short in telluropyrylium compounds relative to other chalcogenopyrylium compounds, triplet yields are large relative to analogs incorporating the lighter chalcogens because of accelerated rates of intersystem crossing.



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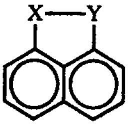

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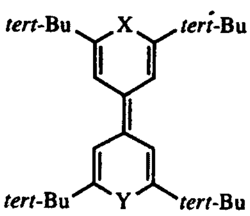

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X, Y = O, S, Se, Te

The quenching of singlet oxygen by organochalcogen compounds was found to be a function of Z^4.[43] Interestingly, the quenching constants, k_Q, for these compounds and the rates of intersystem crossing, k_{isc}, for dyes **18** were found to be identical functions of Z^4 where rates increased with atomic number,[44] which is indicative that spin–orbit interactions are determining in both processes.

Spin–orbit parameters also appear in the EPR (electron paramagnetic resonance) spectra of tellurium-containing heterocycles. In two series of compounds, **19**[45] and **20**,[18] line widths and *g* values of the cation radicals increase as the atomic number of the chalcogen atoms in the molecules increases. The *g* values are linear functions of the spin–orbit coupling constants in these systems, which is indicative that the *g* values are also functions of Z^4. In most examples, EPR hyperfine structure from protons is lost in the line broadening of radical ions of tellurium-containing heterocycles.

F. Isotopes and Mass Spectral Fragmentation

In the mass spectra of tellurium-containing molecules, the tellurium-containing fragments are easy to recognize from the isotope pattern of tellurium. Six major isotopes are observed at *m/e* 122 (2.5% natural abundance), 124 (5%), 125 (7%), 126 (18%), 128 (32%), and 130 (34%) as shown in Figure 1. In tellurium-containing heterocycles incorporating more than one tellurium atom, the tellurium containing fragments have very complicated isotope clusters as illustrated in Figure 2 for Te_2-containing molecules and in Figure 3 for Te_4-containing molecules. The nominal mass in the parent-ion clusters is based on

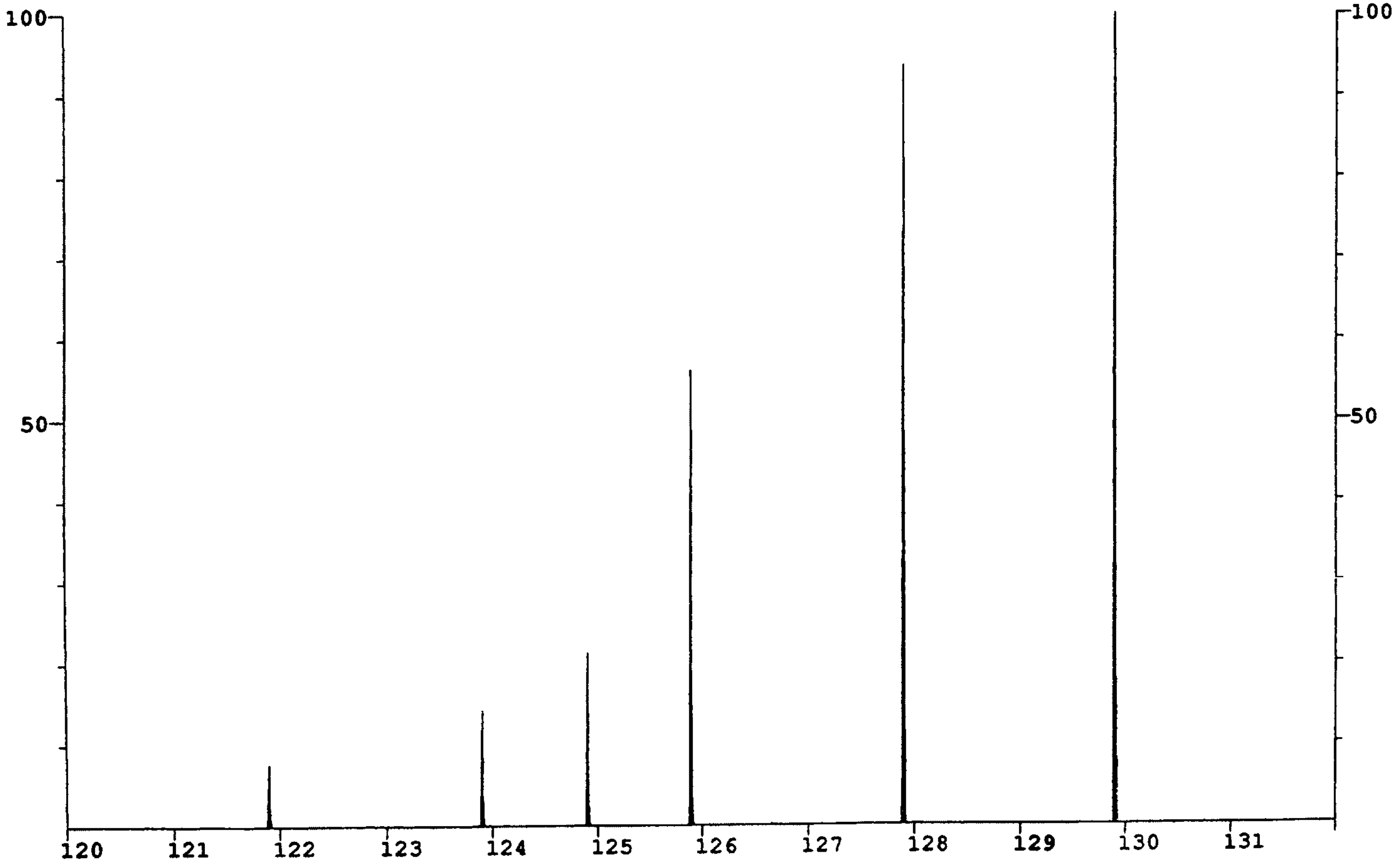


Figure 1. Tellurium isotope pattern for organotellurium compounds containing one tellurium atom.

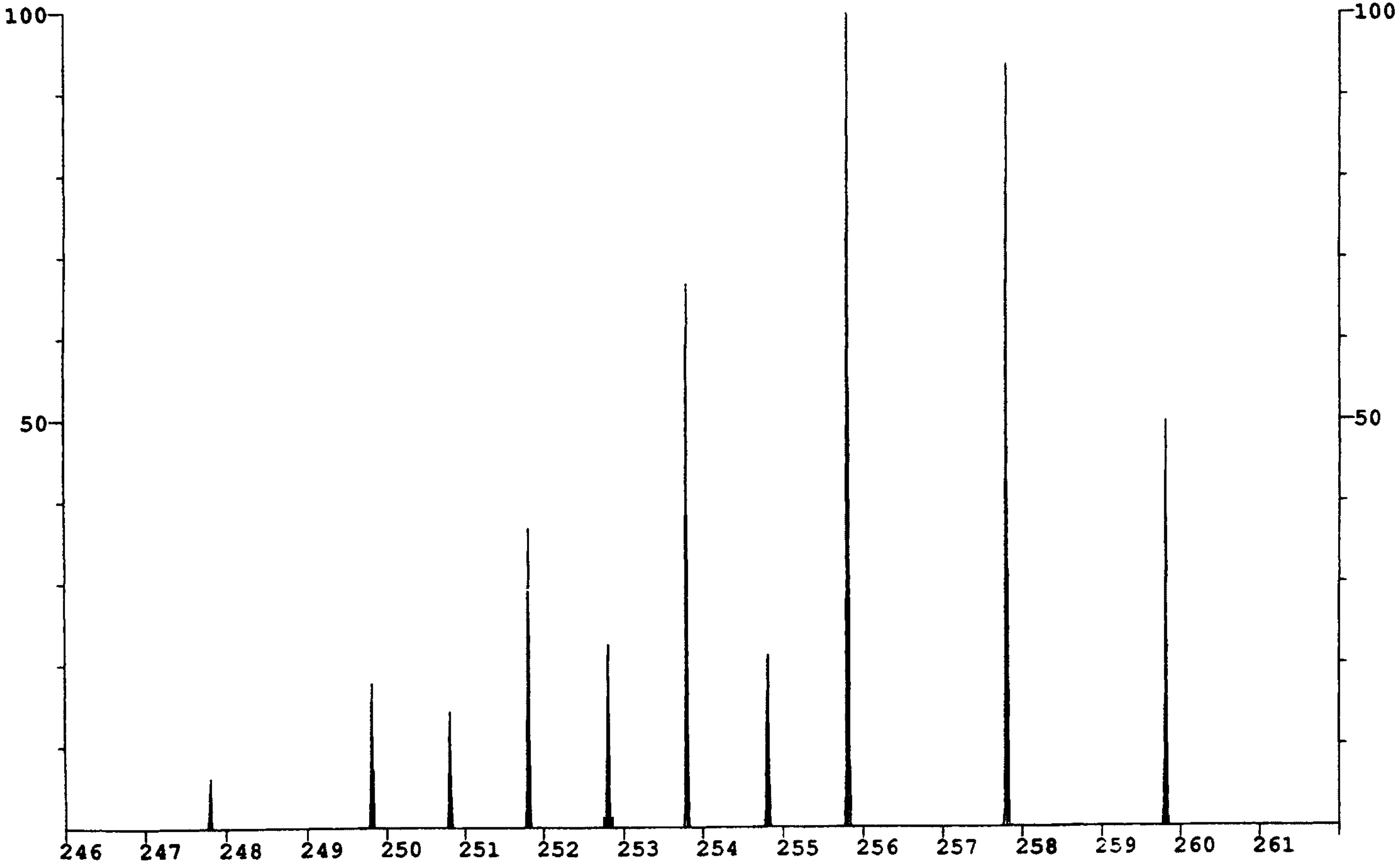


Figure 2. Tellurium isotope pattern for organotellurium compounds containing two tellurium atoms.

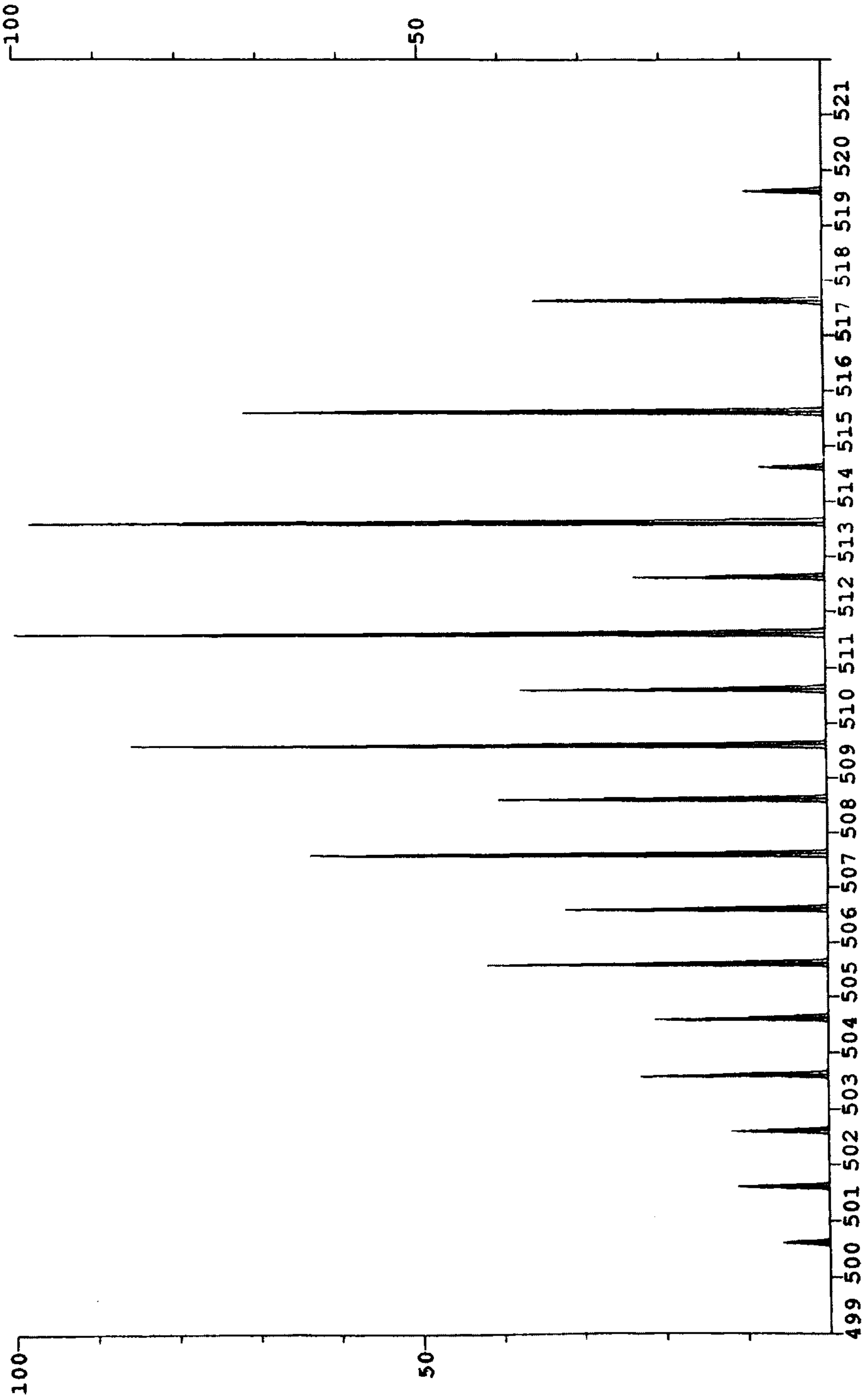


Figure 3. Tellurium isotope pattern for organotellurium compounds containing four tellurium atoms.

^{130}Te for all tellurium atoms in the molecule, but the intensity of this peak diminishes with increasing numbers of tellurium atoms in the molecule as illustrated sequentially in Figures 1–3.

G. Isotopes and Multinuclear Nuclear Magnetic Resonance (NMR)

Tellurium has two isotopes that are NMR-active: ^{123}Te and ^{125}Te.[46,47] The former is weakly radioactive (half-life of approximately 10^{13} years), has a spin $\frac{1}{2}$ nucleus, and is present in about 0.87% natural abundance. The latter is also a spin $\frac{1}{2}$ nucleus but present in nearly 7% natural abundance. The frequency of ^{125}Te is 0.28 that of ^{1}H and has a receptivity 12.5 times that of ^{13}C. In short, ^{125}Te is an easy nucleus to observe with both high receptivity and high natural abundance.

The ^{1}H NMR spectra of organotellurium compounds are characterized by small "side bands" associated with $^{2}J_{\mathrm{Te-H}}$ coupling from the natural abundance of ^{125}Te for those molecules where tellurium is bonded to a proton-bearing carbon. The $^{3}J_{\mathrm{Te-H}}$ coupling is also sometimes observed. In tellurium-containing heterocycles, the natural-abundance ^{125}Te satellites can help assign ^{1}H NMR chemical shifts. The $^{1}J_{\mathrm{Te-C}}$ coupling constants are large (162–531 Hz)[46] and $^{2}J_{\mathrm{Te-C}}$ coupling constants are an order of magnitude smaller, but both can be identified from the natural-abundance ^{125}Te satellites. Ditellurole **8** has been prepared in both mono- and di-^{125}Te-enriched forms, which allowed the detailed analysis of all tellurium couplings in these molecules, including the $^{2}J_{\mathrm{Te-Te}}$ coupling of 260.3 Hz.[48]

8-^{125}*Te*

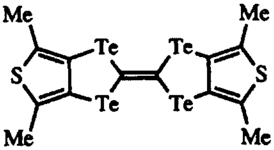
8-^{125}*Te*,^{125}*Te*

III. UTILITY OF TELLURIUM-CONTAINING HETEROCYCLES

In this section, the emerging utilities of tellurium-containing heterocycles are considered. Specifically excluded in this section are the synthetic uses of tellurium-containing heterocycles in organic and organometallic chemistry. These subjects are discussed in the appropriate chapters for the heterocycles.

A. Tellurium-Containing Heterocycles as Organic Conductors

Conducting complexes of tetratellurafulvalenes **9** have been found to display metallic behavior.[49–55] Although superconductivity has not yet been observed in tellurium-containing heterocycles, the metallic behavior of complexes of tetratellurafulvalenes **9** is maintained to 5 K. The extremely short intermolecular tellurium–tellurium contacts in stacks of these molecular systems (3.54 Å for **21** as its 3 : 2 perchlorate complex) may be responsible for the high conductivities of some of these complexes.



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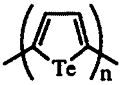
Although the perchlorate salt of **21** is a one-dimensional conductor, there are many contacts between heteroatoms in molecules of this type that are less than van der Waals radii. For the perchlorate complex of **21**, there are no fewer than 14 tellurium–tellurium contacts that are less than van der Waals radii apart. Although the 3 : 2 perchlorate complex is a one-dimensional conductor, the networks of intermolecular tellurium–tellurium contacts in molecules of this type may lead to two- and three-dimensional conductivity. Superconductivity has been observed in tetraselenafulvalenes with extended heteroatom interactions.[56,57]

Conducting polymers of organic and inorganic monomers have attracted considerable attention since the discovery of superconductivity in $(SN)_n$[58] and the insulator–metal transitions in doped polyacetylene $[(CH)_n]$[59]. Heterocyclic polymers such as polypyrrole, polythiophene, and polyselenophene have been prepared with a wide range of electrical properties.[60] The electrical conductivity of polythiophenes has been measured to be as high as 10^2 S cm^{-1}, while the electrical conductivity of polyselenophene was found to be relatively low. Polytellurophene (**22**) has been prepared, and doped films of this material have shown conductivities on the order of 10^{-6} S cm^{-1}.[60] Polybenzotellurophene (**23**) has been prepared, and iodine-doped films have shown conductivities as high as 10^2 S cm^{-1}.[61] Again from the short, intermolecular tellurium–tellurium contacts, polymeric materials based on tellurium-containing heterocycles as monomers may show enhanced multidimensional conducting properties.



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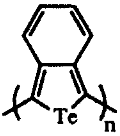

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B. Applications of Infrared-Absorbing Dyes Based on Tellurium-Containing Heterocycles

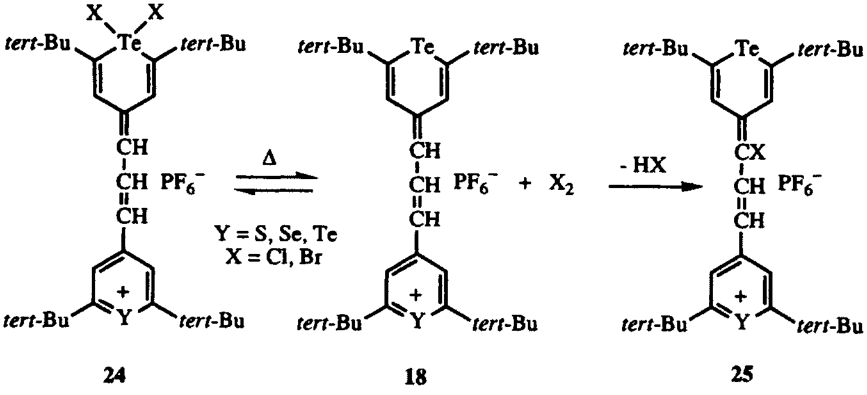
Applications of infrared-absorbing dyes include heat generation in optical recording media and thermal printing, sensitization for charge-generation layers in electrophotographic applications, filter systems for near-infrared-emitting diode lasers, and sensitization for near-infrared silver halide photography and photodynamic therapy.[62] Infrared-absorbing dyes based on tellurium-containing heterocycles have been utilized in all these applications.

1. *Optical Recording*

Tellurium-containing dyes **18** (Te,Te; Te,Se; Te,S) have been utilized in write-once–read-many applications for optical recording.[63] These dyes have extremely high extinction coefficients in solution ($\varepsilon \geq 285{,}000$ L mol^{-1} cm^{-1}) with λ_{max} in the range 770–830 nm. Furthermore, increased spin–orbit interactions improve the efficiency of converting light energy into heat energy. The heat generated by absorption of light from the write laser heats a binder above its glass-transition temperature and creates a "pit." If this chemistry occurs on a highly reflective support, the "pit" changes the reflectivity of the medium and thus can be read as a dark mark on a highly reflective background.

A new method of optical recording in which an infrared-absorbing dye is generated on exposure to the write laser has been demonstrated only with tellurium-containing heterocycles.[64,65] Oxidative addition of chlorine or bromine to tellurium-containing dyes **18** gives the tellurium(IV) dyes **24**. The dyes **24** are coatable from organic solvents, and their absorption maxima are shifted approximately 300 nm to the blue as a consequence of removal of a tellurium *p* orbital from conjugation with the π framework. The oxidized dyes are transparent at wavelengths where gallium arsenide diode lasers emit. Consequently, optical recording media may be highly reflective at the operating wavelengths of the read laser.

Dyes **24** undergo thermal reductive elimination of halogen to generate the corresponding dyes **18** as shown in Scheme 4. At high concentrations in a binder such as those found in optical recording media, the write laser triggers the thermal reductive elimination reaction, and the released halogen is removed irreversibly by reaction with the trimethine bridge to generate the halogen-containing dyes **25**. The dyes **25** are shifted bathochromically by a few nanometers from the corresponding dyes **18** (Te,Y). Optical recording media based on these reactions require a single layer, are first-order in their kinetics with $\Delta H^{\ddagger}$ of approximately 20 kcal mol^{-1} and $\Delta S^{\ddagger}$ of approximately -10 cal mol^{-1} K^{-1},[38] and change reflectivity through increased absorption of the light from the read laser. As shown in Fig. 4 for a series of long and short recorded marks, the carrier : noise ratio is high (≥ 60 dB) with this method.



Scheme 4

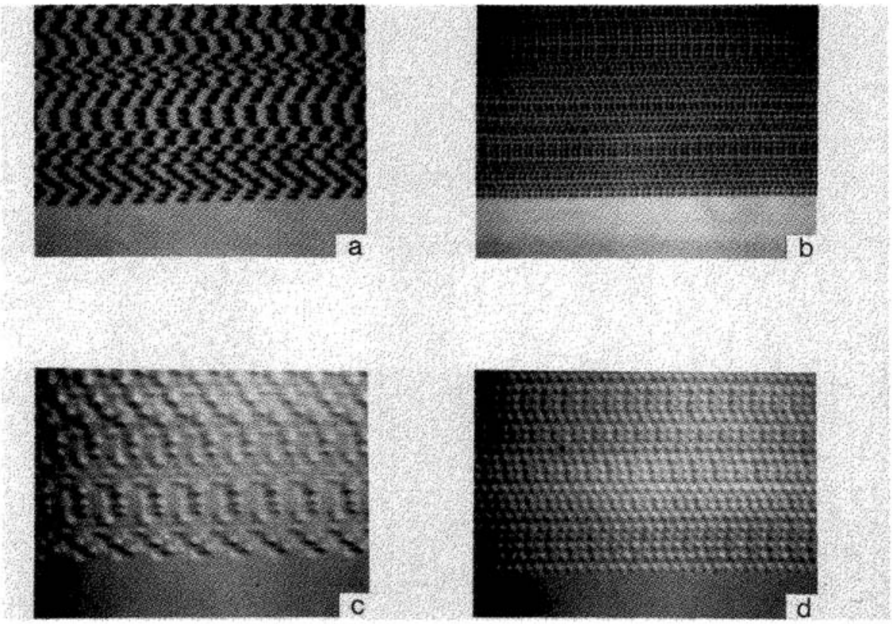


Figure 4. Recorded long [(*a*), 10–15 μm] and short [(*b*), 1–3 μm] marks created by irradiation of **24** (X = Br, Y = S) in a monomeric glass support on a gold reflective layer with a 788-nm diode laser as viewed by brightfield microscopy. The backside of the gold layer for (*a*) is shown in (*c*), and the backside of the gold layer in (*b*) is shown in (*d*) as viewed by DIC microscopy.

2. *Thermal Printing*

In thermal printing applications, three or four different near-infrared-emitting diode lasers are utilized to record the tricolor image. (The fourth is for