Acknowledgment. We thank the U.S. Army Research Office for the support of this work. We also acknowledge the assistance of Dr. M. Parvez with parts of the crystallographic work.

Registry No. 1b, 86727-36-8; **4**, 21229-71-0; **6a**, 104323-06-0; **7a**, 104323-02-6; **7b**, 104323-03-7; **7c**, 104323-04-8; **7d**, 88043-06-5; **7e**, 104323-05-9; $FeCp(CO)_2I$, 12078-28-3; $CrCp(CO)_3I$, 32628-88-9; $MoCp(CO)_3I$, 12287-61-5; $WCp(CO)_3I$, 31870-69-6; $RuCp(CO)_2I$, 31781-83-6.

Supplementary Material Available: Tables of atomic positional and thermal parameters and bond distances and angles for **7a**, **7b**, **7d**, and **7e** (18 pages); listings of structure factor amplitudes for **7a**, **7b**, **7d**, and **7e** (49 pages). Ordering information is given on any current masthead page.

Tellurapyrylium Dyes. 3. Oxidative Halogen Addition and Tellurium–Halogen Exchange

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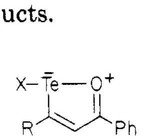
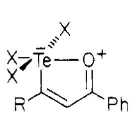
Received February 19, 1986

The oxidative addition of halogens to tellurapyrylium dyes gives 10-Te-4 telluranes. The absorption maxima of the oxidative addition products are shifted hypsochromically relative to the parent tellurapyrylium salt. The structure of the oxidative addition products was determined unambiguously for one dye by single-crystal X-ray crystallography. Fluxional behavior was observed in the ^1H NMR spectra of one of the products as a result of tellurium–halogen exchange. The exchange was first-order with respect to the dye in CD_3CN and second-order in $CDCl_2CDCl_2$. In $CDCl_3$, the exchange was a mixture of first- and second-order processes. The line shapes from variable-temperature ^1H NMR were matched to line shapes generated by computer simulation with the program DNMR3 to give the kinetics of the exchange. The oxidative addition products are easily reduced, as shown by cyclic voltammetry.

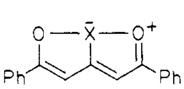
Organotellurium compounds easily exchange halogen ligands with other halogens or with other organotellurium compounds in which the Te atoms are in a lower oxidation state. For example, the addition of 1 equiv of bromine to oxatellurolylium chlorides **1** gives a 2:1 mixture of pertellurane trihalides **2** and **3**, respectively.[1] Similarly, the addition of chlorine to oxatellurolylium bromides **4** gives a 1:2 mixture of **2** and **3**, respectively.[1] The addition of bromine to oxatellurolylium iodides **5** gives pertellurane tribromides **2** plus iodine. The dioxatellurapentalene dibromide **6** reacts with diphenyltelluride to give dioxatellurapentalene **7** and diphenyltellurium dibromide.[2] These exchanges are rapid and are completely driven to products.



1, X = Cl
4, X = Br
5, X = I



2, X = Br
3, X = Cl



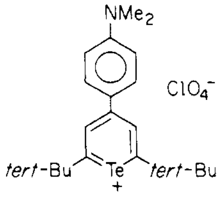
6, X = $TeBr_2$
7, X = Te

In a series of studies, Nefedov et al. used isotopic labeling to follow halogen exchange between diphenyltellurium dihalides and diphenyltelluride.[3] The exchange reactions involving diphenyltellurium dichloride, dibromide, and diiodide were second-order reactions, first-order with respect to both dihalide and diphenyl telluride. A change in mechanism was observed for the halogen exchange between diphenyltellurium difluoride and diphenyl telluride. This exchange was a first-order reaction with respect to the difluoride.[3a]

We wish to report the synthesis, structure, and properties of a new class of 10-Te-4 telluranes formed by the oxidative addition of a halogen molecule across a Te atom of a tellurapyrylium dye. Some of the resulting dyes display fluxional behavior, as shown by ^1H NMR, resulting from Te–halogen exchange. The kinetics and activation parameters for the exchange for one dye were determined by variable-temperature ^1H NMR and computer-simulated line-shape matching using the program DNMR3.[4]

Results and Discussion

Preparation and Structure. The addition of bromine to a solution of tellurapyrylium dye **8** in CH_2Cl_2 gave a red solution. The black solid isolated from this solution gave shiny, black needles of **9** upon recrystallization from CH_3CN. The structure of **9** was determined unambiguously by single-crystal X-ray crystallography.



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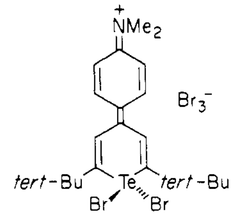

9

Figure 1 shows a plot of the molecule with atomic labeling. For clarity, only the A positions for the disordered methyls are shown. The thermal ellilpsoids were plotted at the 40% probability level. Tables of bond distances and angles, least-squares planes, and positional and thermal parameters are given in the supplementary material.

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(1) Detty, M. R.; Luss, H. R.; McKelvey, J. M., Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692.

(2) Detty, M. R.; Luss, H. R. *J. Org. Chem.* **1983**, *48*, 5149.

(3) (a) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Kolobov, E. A.; Kapustin, V. K. *Radiokhimiya* **1971**, *13*, 435. (b) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Timofev, S. A. *Ibid.* **1969**, *11*, 154.

(4) Klein, D. A.; Bensch, G. *J. Magn. Reson*, **1970**, *3*, 146.

Table I. Physical and Spectral Properties of Telluropyrylium Dyes

compd	mp, °C	λ_{max},[a] nm (log E)	molecular formula	anal. calcd C	calcd H	calcd N	calcd Te	found C	found H	found N	found Te
8	195–197	611 (4.82)	$C_{21}H_{30}NTeBF_4$	48.2	5.8	2.7	24.4	47.8	5.7	2.6	25.1
11	192–195	655 (4.82)	$C_{25}H_{22}NTeBF_4$	54.5	4.0	2.5		54.7	4.1	2.8	
13	219–222	508 (4.94)	$C_{17}H_{28}NTeBF_4$	44.3	6.1	3.0	27.7	44.3	6.1	3.4	27.1
16	225–227	759 (5.20)	$C_{35}H_{25}Te_2BF_4$	53.4	3.2		32.4	53.1	3.3		31.1
17	205–208	830 (5.52)	$C_{29}H_{43}Te_2BF_4$	47.5	5.9		34.8	47.4	6.2		33.9
22	199–202	786 (5.45)	$C_{29}H_{43}SeTeBF_4$	50.8	6.3		18.6[b]	51.1	6.7		18.9

[a] In CH_2Cl_2. [b] Calcd: Se, 11.5; F, 11.1. Found: Se, 11.3; F, 10.9.

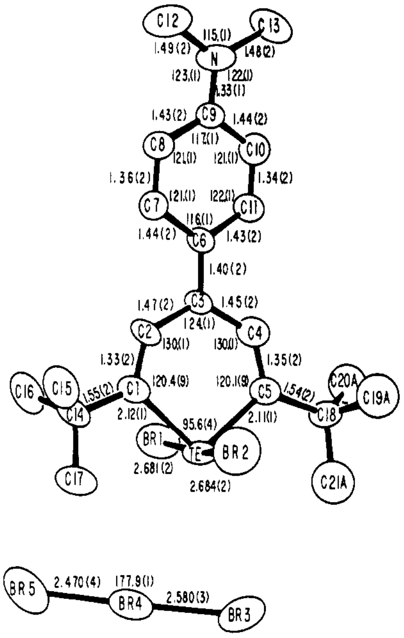
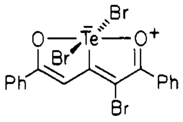


Figure 1. Plot of **9** with selected bond distances and angles.

The Te–C and Te–Br bond distances are similar to those found in 12-Te-5 pertellurane **10**.[2] The distances of the C–C bonds alternate between near-single-bond (1.48 Å) and double-bond (1.34 Å) values. The N–C9 bond length is between those of a single bond (1.45 Å) and a double bond (1.27 Å).[5] These results show that the positive charge is located primarily on N, as shown in **9**.



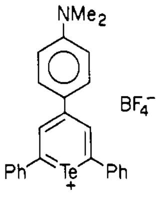
10

The Br–Te–Br angle (173.22°) deviates from linearity with the Br's bending toward the ring much like those in **10**, suggestive of some Te lone-pair stereochemical activity. The Br_3 anion is located near Te, as shown in Figure 1, and probably involves a weak Te···Br_3 interaction (3.837 Å). This distance is slightly less than the sum of the van der Waals radii (3.91 Å).[6] The Br_3 anion is only 0.01 Å out of the plane through C1, C5, and Te. The asymmetry of the Br–Br bonds also suggests interaction with Te.

The two six-membered rings are only approximately planar and are each folded about the Te···N axis, forming dihedral angles of 3.0° and 5.5° for the Te heterocyclic and phenyl rings, respectively. The dihedral angles defined by the least-squares planes through the heterocyclic ring (plane 1), the phenyl ring (plane 2), and the dimethylamino group (plane 3) are 10.0° (angle between planes 1 and 2) and 6.8° (angle between planes 2 and 3).

The isolation of the Br_3^- salt of **9** was not surprising, since an excess of bromine was used. When 1.1 molar equiv of bromine was added to **8**, the perchlorate salt was isolated.

The addition of bromine and iodine to tellurapyrylium dyes containing an N in conjugation with the π framework appears to be a general reaction. The addition of bromine to **11** gave tellurapyrylium dibromide **12**, and the addition of bromine and iodine to **13** gave iminium dyes **14** and **15**, respectively.



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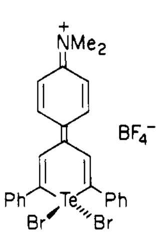
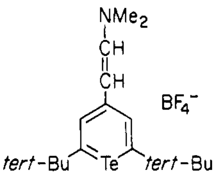
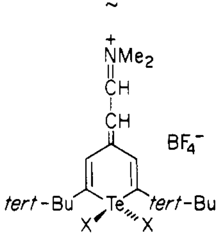


12

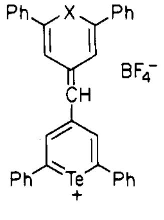


13

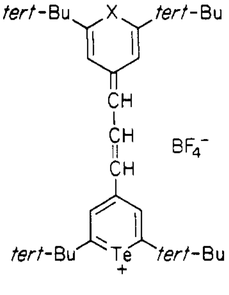


14, X = Br
15, X = I

The symmetrical tellurapyrylium monomethine and trimethine dyes **16** and **17** offered the possibility of the oxidative addition of halogen to each of two Te atoms in the dye molecule. With 1.1 equiv of halogen, the oxidative addition of chlorine, bromine, and iodine across only one Te was achieved to give **18**–**21**. The physical and spectral properties for the tellurapyrylium dyes are listed in Table I and for the tellurapyrylium dihalides in Table II.



16, X = Te
18, X = $TeCl_2$
19, X = $TeBr_2$
20, X = TeI_2



17, X = Te
21, X = $TeBr_2$

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(5) Burke-Laing, M.; Laing, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32B*, 3216.

(6) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table II. Physical and Spectral Properties of Tellurapyrylium Dihalide Dynes

				anal.							
				calcd				found			
compd	mp, °C	λ_{max},[a] nm (log *E*)	molecular formula	C	H	N	Te	C	H	N	Te
9	177	496 (4.48)	$C_{21}H_{30}Br_2NTeBr_3$	30.6	3.7	1.7		30.3	3.6	1.6	
12	218–219	522 (4.26)	$C_{25}H_{22}Br_2NTeBF_4$	42.2	3.1	2.0		41.9	3.1	2.1	
14	232–233	388 (4.48)	$C_{17}H_{28}Br_2NTeBF_4$	31.9	4.5	2.3	20.6	32.5	4.5	2.5	19.8
15	108–112		$C_{17}H_{28}I_2NTeBF_4$	28.6	3.9	2.0		28.8	3.9	1.9	
18	178–197 dec	497 (4.41)	$C_{35}H_{25}Cl_2Te_2BF_4$	49.0	2.9		29.7	49.4	3.1		31.0
19	222–224	525 (4.45)	$C_{35}H_{25}Br_2Te_2BF_4$	44.4	2.7			44.0	2.6		
20	209–210		$C_{35}H_{25}I_2Te_2x$[b,c]	35.4	2.1		21.5	35.1	2.1		23.4
21	199–200	565 (4.81)	$C_{29}H_{43}Br_2Te_2BF_4$	39.0	4.9		28.6	38.7	4.9		29.3
23	205–207	543 (4.74)	$C_{29}H_{43}Br_2SeTeBF_4$	40.6	5.1			40.8	5.0		

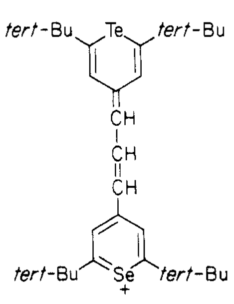
[a] In CH_2Cl_2. [b] Analyzed as a 1:1 mixture of I_3 and BF_4 salts. [c] Calcd for F in $0.5BF_4$: 3.2. Found: 3.2.

Table III. Oxidation and Reduction Potentials of Tellurapyrylium Dyes and Their Dihalide Complexes as Determined by Cyclic Voltammetry[a]

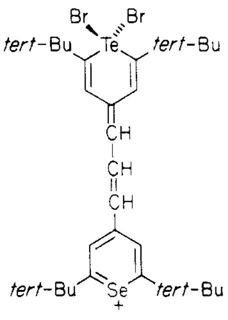
		reduction					
		E_1		E_2		oxidation	
compd	E_{p_c}, V	E_{p_c}, V	E_{p_a}, V	E_{p_c}, V	E_{p_a}, V	E_{p_a}, V	E_{p_a}, V
8		–0.48	–0.41				
9	+0.48	–0.485	–0.41			+0.80	
16		–0.16	–0.08	–1.04	–0.96		
17		–0.33	–0.25				
18	+0.28	–0.17	–0.06	–1.05	–0.94	+0.58	
19	+0.35	–0.16	–0.08	–1.04	–0.96	+0.62	
20	+0.58[b]	–0.16	–0.08	–0.98[c]		+0.39	+0.70
21	+0.17	–0.33	–0.25			+0.68	

[a] Approximately 5 × 10^{-4} M in CH_2Cl_2 with 0.1 M TBAF as supporting electrolyte vs. SCE at a Pt disk with a scan speed of 0.1 V/s. [b] E_{p_c} = +0.10 V also observed. [c] Irreversible.

If the halogens were added in excess (more than 2 equiv) to **16** and **17**, insoluble polyhalogenated materials were obtained. However, the addition of 2 equiv of bromine to selenapyranyl tellurapyrylium dye **22** gave only oxidative addition across one heteroatom, presumably Te, to produce **23**.[7]



22



23

The diiodides **15** and **20** were quite insoluble. Compound **20** was isolated as a 1:1 mixture of BF_4 and I_3 salts. In solution, the diiodides apparently are not stable, since all attempts to obtain the absorption spectra of **15** and **20** gave only the absorption spectra of **13** and **16**, respectively, in a variety of solvents including CH_3CN, CH_2Cl_2, and $HCON(CH_3)_2$.

Absorption Properties. The data in Tables I and II show that all the dihalide dyes are shifted hypsochromically relative to the tellurapyrylium dyes. This is consistent with the Te $5p_z$ orbital being removed from the chromophore by oxidative addition of halogen.

Perhaps the most interesting feature of the absorption spectra is the difference in absorption maxima between dichloride **18** and dibromide **19** (28 nm), taken with the apparent dissociation of **20**. The data suggest that the Te–Cl bonds are stronger (more covalent) than the Te-Br bonds, whereas the Te–I bonds are weak. In solution, the tellurapyrylium diiodides may be molecular complexes of iodine and Te rather than 10-Te-4 telluranes,[8] since the observed absorption spectra of the diiodides appear to be those of the parent tellurapyrylium dyes.

Electronegativity arguments have been used to explain the reluctance of selenides to form selenuranes by the oxidative addition of iodine.[8,9] Iodine is more electropositive than Se and would be expected to be a poor donor to Se. Tellurium is more electropositive than Se or I and forms tellurane complexes with iodine,[9,10] although these complexes have Te–I bonds that are weaker than the Te–Cl and Te–Br bonds.[8-10]

The presence of a positive charge in the tellurapyrylium dyes should effectively increase the electronegativity of the Te atom.[1,8] Consequently, the ability of I to act as a donor ligand to Te to form telluranes would be diminished, as is observed.

Electrochemical Properties. The oxidation and reduction potentials for the tellurapyrylium dyes **8**, **16**, and **17** and their dihalide complexes **9** and **18–21** were determined by cyclic voltammetry (CV). The results are compiled in Table III. The dihalide complexes are easily reduced, regenerating the starting tellurapyrylium dyes and 2 equiv of halide. The oxidation waves observed at potentials more anodic than +0.30 V (vs. SCE) in **9** and **15–18** were observed only after reduction had occurred and correspond to oxidation of the halide produced by reduction of the dihalide complexes. Coulometric reduction of **9** at +0.1 V (vs. SCE) required 1.9 faradays/mol and

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[7] Selenuranes are formed by the oxidative addition of halogens to selenides: Clayman, D. L.; Gunther, W. H. H. *Organic Selenium Compounds: Their Chemistry and Biology*; Wiley: New York, 1973.

[8] Nakanishi, W.; Yamamoto, Y.; Kusuyama, Y.; Ikeda, Y.; Iwamura, H. *Chem. Lett.* **1983**, *675.*

[9] Baenziger, N. C.; Bucklen, R. E.; Maner, R. J.; Simpson, T. D. *J. Am. Chem. Soc.* **1969**, *91*, 5749.

[10] Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: London, 1974.

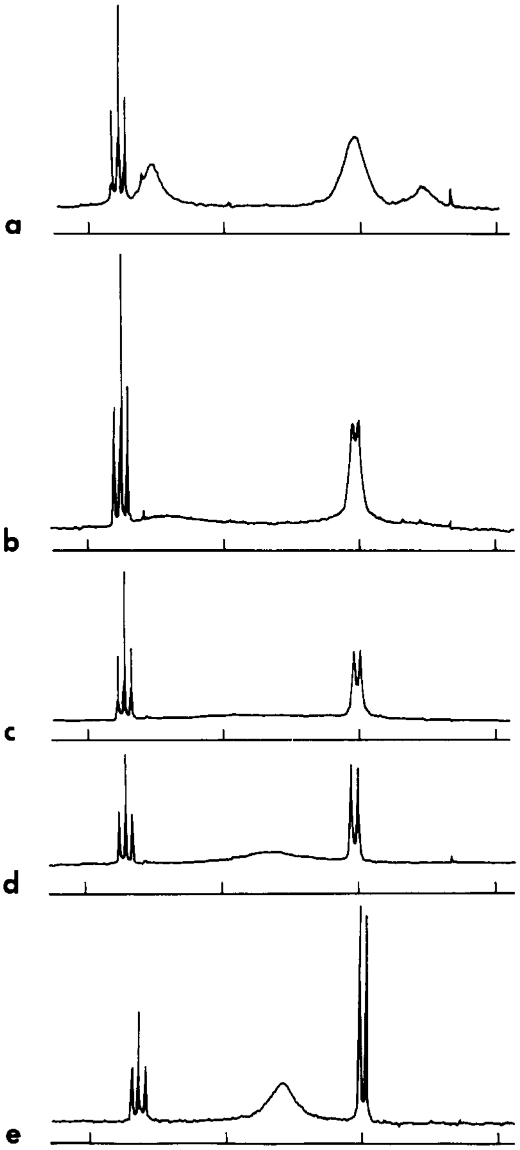
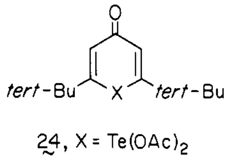


Figure 2. Variable-temperature ^1H NMR spectra of **21** in CD_3CN at 0.007 M concentration at (a) 233 K, (b) 253 K, (c) 273 K, (d) 303 K, and (e) 348 K. The grids are δ 9.0–6.0 for the olefinic protons.

generated the absorption spectrum of **8** (λ_{max} = 611 nm).

The ease of reduction of the tellurapyrylium dihalides is even more remarkable when compared to the reduction potentials of other 10-Te-4 telluranes. The telluranes **24–27** prepared by the oxidative addition of peracetic acid and halogens to 2,6-di-*tert*-butyltelluropyran-4-one (**28**)[11] show E_{p_c} of −1.14, −0.68, −0.46, and +0.04 V (vs. SCE), respectively. The tellurapyrylium dihalides should function as oxidizing agents and are being investigated in this capacity.



24, X = $Te(OAc)_2$
25, X = $TeCl_2$
26, X = $TeBr_2$
27, X = TeI_2
28, X = Te

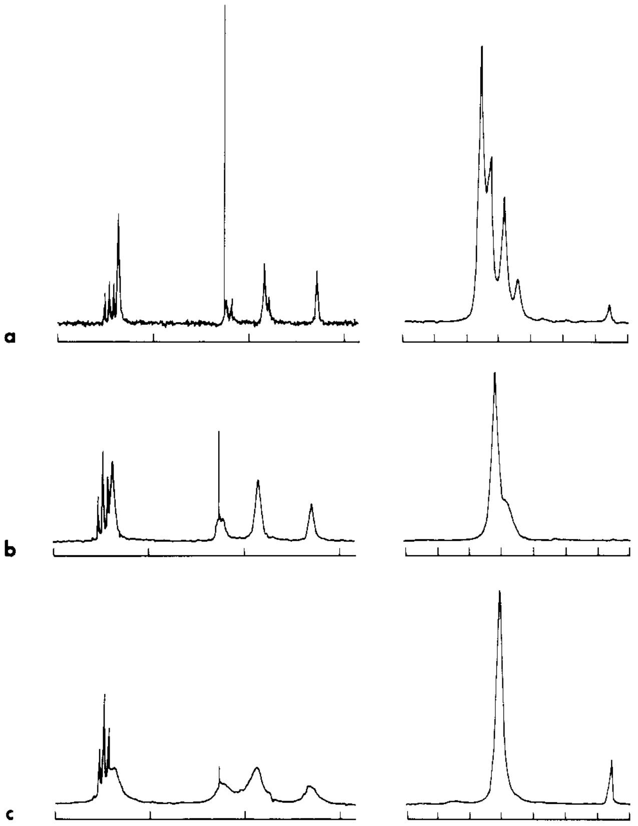


Figure 3. Concentration-dependent ^1H NMR spectra of **21** in $CDCl_3$ at 303 K at (a) 0.0046 M, (b) 0.023 M, and (c) 0.070 M. The grids are δ 9.0–6.0 for the olefinic protons and δ 1.9–1.2 for the *tert*-butyl protons.

Fluxional ^1H NMR Behavior. The tellurapyrylium dibromide dye **21** was observed to have fluxional ^1H NMR behavior in CD_3CN, $CDCl_3$, and $CDCl_2CDCl_2$. The two Te atoms of **21** presumably become equivalent by some temperature-dependent exchange process of bromide ligands. The dibromotellurapyranyl tellurapyrylium dye **19** also showed fluxional ^1H NMR behavior but was too insoluble for convenient study.

In CD_3CN the bromine exchange reaction of **21** was first-order with respect to **21** over the concentration range 0.001–0.07 M and the temperature range 233–348 K. The experimental spectra were matched with the calculated exchange-broadened NMR line shapes by using DNMR3[4] at eight temperatures between (and including) 233 and 348 K. As shown in Figure 2, the protons on the trimethine bridge appear as a one-proton triplet and two one-proton doublets (J = 15.3 Hz) at slow-exchange rates and as a one-proton triplet and a two-proton doublet (J = 15.3 Hz) at fast exchange. The ring protons on the pyrylium ring appear as a two-proton singlet and the ring protons on the tellurapyranyl dihalide ring as two one-proton singlets at slow exchange. These four protons collapse to a four-proton singlet at fast-exchange rates. The *tert*-butyl groups are similarly separated at slow exchange but collapse at fast exchange. The relative thermodynamic and activation parameters were determined to be E_a = 5.62 ± 0.20 kcal/mol, $\Delta H^\ddagger$ = 5.06 ± 0.25 kcal/mol, $\Delta S^\ddagger$ = −26 ± 2 cal K^{-1} mol^{-1}, and $\Delta G^\ddagger_{298}$ = 12.8 kcal/mol.

In $CDCl_3$ solution, the bromine exchange in **21** was higher order with respect to **21** over the concentration range 0.001–0.07 M. The exchange reaction appeared to be complicated by a mixture of first- and second-order processes. Figure 3 shows the effect of concentration on the ^1H NMR line shapes.

In $CDCl_2CDCl_2$, the bromine exchange rate for **21** at 303

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[11] Detty, M. R.; Murray, B. J., submitted for publication in *J. Org. Chem.*

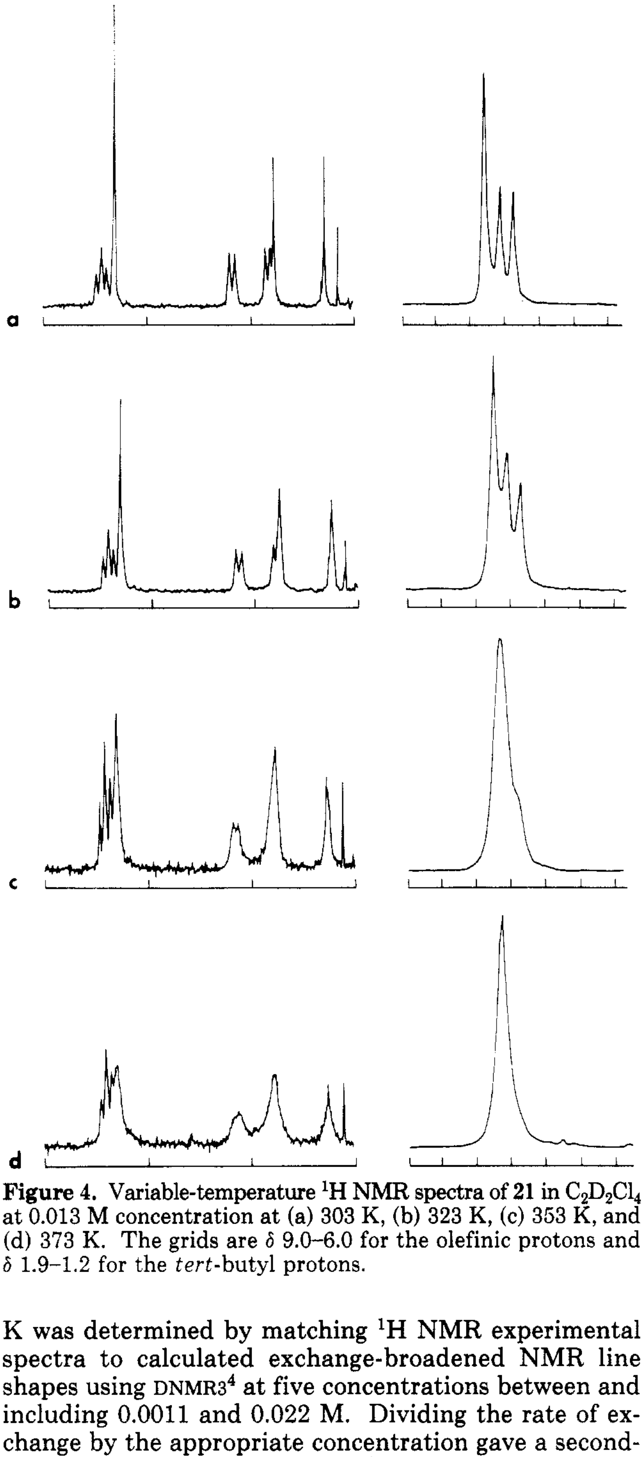


Figure 4. Variable-temperature ^{1}H NMR spectra of **21** in $C_2D_2Cl_4$ at 0.013 M concentration at (a) 303 K, (b) 323 K, (c) 353 K, and (d) 373 K. The grids are δ 9.0–6.0 for the olefinic protons and δ 1.9–1.2 for the *tert*-butyl protons.

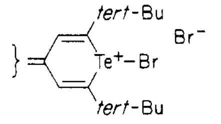
K was determined by matching ^{1}H NMR experimental spectra to calculated exchange-broadened NMR line shapes using DNMR3[4] at five concentrations between and including 0.0011 and 0.022 M. Dividing the rate of exchange by the appropriate concentration gave a second-order rate constant of 3.0×10^3 mol^{-1} s^{-1} in each case.

Figure 4 shows the variable-temperature ^{1}H NMR spectra for a 0.013 M solution of **21** in $CDCl_2CDCl_2$ between and including 303–373 K. The *tert*-butyl region of these spectra were matched with calculated spectra by using DNMR3.[4] The frequency separation of the *tert*-butyl singlets at slow exchange was determined from the experimental spectrum at 283 K. The calculated exchange rates were divided by the concentration to give second-order rate constants of 3.0, 7.4, 44.6, and 149×10^3 mol^{-1} s^{-1} at temperatures of 303, 323, 353, and 373 K, respectively. The relative activation parameters were determined to be $E_a = 12.5 \pm 0.4$ kcal/mol, $\Delta H^{\ddagger} = 11.8 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -22 \pm 3$ cal K^{-1} mol^{-1}, and $\Delta G_{298}{}^{\ddagger} = 18.3$ kcal/mol.

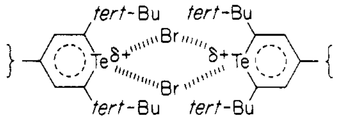
Although the kinetic behavior of **21** in $CDCl_3$ was not strictly first- or second-order, an approximation of $\Delta G^{\ddagger}$ can be obtained from the coalescence of the two one-proton doublets ($J = 15.3$ Hz, $\nu_A = 1945$ Hz, $\nu_B = 1839$ Hz) observed in Figure 3. At a concentration of 0.07 M **21** in $CDCl_3$, coalescence of the two one-proton doublets was observed at 316 K from which $\Delta G_{316}{}^{\ddagger}$ was calculated to be 14.9 kcal/mol.[12]

The first-order behavior observed in polar CD_3CN argues for a rate-determining dissociation of one Te–Br bond in **21** to give Br$^-$ and a telluronium species (**29**) followed by a rapid loss of Br$^+$ to generate bromine, which could then readd to either Te atom in the resulting tellurapyrylium dye **17** to regenerate **21**. This is similar to the argument put forth by Nefedov et al. to account for the first-order behavior of fluoride exchange in diphenyltellurium difluoride.[3a]

In less polar solvents, the rate of the dissociation to give bromide and telluronium species should be lowered, allowing a competing second-order process to occur, which should be favored by higher concentrations. The second-order process might involve a four-center exchange mechanism as in **30** or exchange between two head-to-tail stacked molecules of **21**.



29



30

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^{1}H NMR spectra were recorded on Varian EM-390 or IBM WP270SY spectrophotometers. IR spectra were recorded on a Beckman IR4250 instrument. UV-visible–near-IR spectra were recorded on a Cary 17 spectrophotometer. Tellurium shot and selenium shot were purchased from Ventron. Solvents (Kodak Laboratory Chemicals) were dried over 3A molecular sieves before use. Microanalyses were obtained with a Perkin-Elmer C, H, and N analyzer. Tellurium and selenium analyses were obtained by atomic absorption spectroscopy with ±1% accuracy. A Princeton Applied Research Model 173 potentiostat/galvanostat and a Model 175 Universal programmer were used for the cyclic voltammetry studies. The working electrode was a Pt disk. All samples were run in J. T. Baker HPLC-grade dichloromethane that had been stored over 3A sieves. Electrometric-grade tetrabutylammonium fluoroborate (Southwestern Analytical Chemicals, Inc.), recrystallized from ethyl acetate/pentane, was used as supporting electrolyte at 0.1 M concentration. Argon was used for sample deaeration. Tellurapyrylium dyes **11** and **16** were prepared by the literature method.[13]

Preparation of 2,6-Di-*tert*-butyltellurapyran-4-one (28). A 1-L flask equipped with a water-cooled reflux condenser, a magnetic stirring bar, and a dry-nitrogen inlet was charged with 12.76 g (0.100 mol) of tellurium shot and 300 mL of 0.5 M sodium ethoxide in ethanol. Sodium borohydride (3.80 g, 0.100 mol) was added in three portions of 15-min intervals (mildly exothermic) to the gently refluxing reaction mixture. After the final addition, the reaction mixture was stirred for 2 h at ambient temperature until a clear, colorless solution was obtained. 2,2,9,9-Tetramethylnona-3,6-diyn-5-one (19.0 g, 0.100 mol) was dissolved in 200 mL of 0.005 M sodium ethoxide in ethanol. The resulting

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(12) Martin, M. L.; Delpuech, J.-J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: Philadelphia, 1980. The coalescence temperature approximations are given by

$$\nu = (\sqrt{2}\pi\Delta\nu)^{-1} \qquad K_r = (2\nu)^{-1}$$

$$\Delta G_c{}^{\ddagger} = 4.57T_c[9.96 + \log(T_c/\Delta\nu)] \quad K = 1$$

$$\Delta G_c = 4.57T_c[9.67 + \log(T_c/\Delta\nu)] \quad K = 0.5$$

where T_c = coalescence temperature in kelvin and $\Delta\nu$ = peak separation in hertz at slow exchange. For an AB system, $\Delta\nu = (\Delta\nu_{AB}{}^2 = +6J_{AB}{}^2)^{1/2}$.

(13) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 5235.

solution was added to the disodium telluride. The solution was stirred for 1 h at ambient temperature. The reaction mixture was diluted with 500 mL of ice water. The mixture was stirred for 1 h at 0 °C, and the crystalline **28** was removed by filtration. Recrystallization from CH_3CN gave 19.2 g (60%) of **28**: mp 83.5–84 °C; ^1H NMR ($CDCl_3$) δ 6.90 (s, 2 H), 1.33 (s, 18 H); IR (KBr) 2985, 1600, 1575, 1330, 1275, 895 cm^{-1}; field-desorption mass spectrum (FDMS), *m/e* 322 ($C_{13}H_{20}O^{130}Te$). Anal. Calcd for $C_{13}H_{20}OTe$: C, 48.8; H, 6.3; Te, 39.9. Found: C, 48.9; H, 6.4; Te, 38.5.

2,6-Di-*tert*-butyl-4-(4-(dimethylamino)phenyl)tellurapyrylium Perchlorate Perchlorate (8). *p*-Bromo-*N*,*N*-dimethylaniline (6.00 g, 30.0 mmol) and magnesium turnings (0.96 g, 40 mmol) in 140 mL of dry THF were heated at reflux for 2 h under argon. The reaction mixture was cooled to ambient temperature, and 6.40 g (20.0 mmol) of **25** in 30 mL of THF was added. The mixture was heated for 1 h at reflux. The reaction mixture was filtered through a pad of glass wool and concentrated. The residue was taken up in 50 mL of acetic acid, and 5 mL of 70% perchloric acid was added, followed by 100 mL of 80% aqueous methanol. The solution was chilled at −20 °C for 16 h, precipitating a golden brown crystalline solid. The solid was collected by filtration, washed with cold aqueous methanol, and dried, to give 7.6 g (72%) of **8**: mp 195–197 °C; ^1H NMR ($CDCl_3$) δ 8.40 (s, 2 H), 8.00 (d, 2 H, *J* = 9 Hz), 6.95 (d, 2 H, *J* = 9 Hz), 3.14 (s, 6 H), 1.63 (s, 18 H); IR (KBr) 2990, 1610, 1545, 1280, 1080, 823, 775 cm^{-1}.

Preparation of 2,6-Di-*tert*-butyl-4-methyltellurapyrylium Fluoroborate (31). Tellurapyrone 8 (23.0 g, 0.0719 mol) was added to 92 mL of ethyl fluorosulfonate under an argon atmosphere. The mixture was warmed on a steam bath for 5 min and cooled to ambient temperature. Anhydrous ether (1 L) was added, precipitating the fluorosulfonate salt. The chalky gray salt was washed with ether (2 × 500 mL) and collected by filtration. The material was used without further purification: FDMS, *m/e* 351 ($C_{15}H_{25}OTe$).

Meldrum's acid (23.0 g, 0.0720 mol) was dissolved in 230 mL of pyridine, and the fluorosulfonate was added as a powder. The mixture was stirred for 5 min at ambient temperature and concentrated. The residue was dissolved in 250 mL of dichloromethane. The solution was washed with 5% HCl, dried over $MgSO_4$, and concentrated to give 24.5 g (78%) of the Meldrum's acid adduct as an orange crystalline solid: mp 155–158 °C; ^1H NMR ($CDCl_3$) δ 9.25 (s, 2 H), 1.53 (s, 6 H), 0.48 (s, 18 H); IR (KBr) 2970, 1672, 1580, 1295, 1190 cm^{-1}; FDMS, *m/e* 448 ($C_{19}H_{26}O_4Te$). Anal. Calcd for $C_{19}H_{26}O_4Te$: C, 51.2; H, 5.9; Te, 28.6. Found: C, 51.4; H, 6.2; Te, 27.8.

The Meldrum's acid adduct (24.5 g, 0.0561 mol) was dissolved in 500 mL of 88% formic acid. The solution was warmed on a steam bath until gas evolution ceased (~20 min). Fluoroboric acid (49%, 11.2 g, 0.062 mol) was added, and the solution was concentrated. The residue was dissolved in 100 mL of acetonitrile. The solution was filtered through a pad of Celite, the filtrate was diluted with 1 L of ether, and a tan solid precipitated. The material was collected by filtration to give 13.6 g (60%) of **31**: mp 185–187 °C dec; ^1H NMR ($CDCl_3$) δ 8.30 (s, 2 H), 2.53 (s, 3 H), 1.63 (s, 18 H); IR (KBr) 2970, 1575, 1445, 1390, 1378, 1090 (br), 1040 cm^{-1}; FDMS, *m/e* 321 ($C_{14}H_{23}Te$). Anal. Calcd for $C_{14}H_{23}BF_4Te$: C, 41.4; H, 5.7; B, 2.7; F, 18.7; Te, 31.4. Found: C, 41.7; H, 5.8; B, 2.1; F, 18.6; Te, 29.9.

Preparation of Tellurapyrylium Dye 17. A mixture of 7.00 g (17.2 mmol) of 2,6-di-*tert*-butyl-4-methyltellurapyrylium fluoroborate (**31**) and 7.5 g (22 mmol) of 2,6-di-*tert*-butyl-4-(formylmethylene)-4*H*-tellurapyran (**32**) in 35 mL of acetic anhydride was heated for 2 min on a steam bath. The reaction mixture was cooled to room temperature, and 150 mL of ether was added. Upon chilling, **17** precipitated as shiny red crystals: mp 205–208 °C; ^1H NMR ($CDCl_3$) δ 8.75 (t, 1 H, *J* = 13.5 Hz), 7.70 (s, 4 H), 6.87 (d, 2 H, *J* = 13.5 Hz), 1.51 (s, 36 H); IR (KBr) 2995, 1460, 1155 cm^{-1}.

2,6-Di-*tert*-butyl-4-(formylmethylene)-4*H*-tellurapyran (32) and Imminium Dye 13. A mixture of **31** (2.50 g, 6.16 mmol) and 1.5 mL of *N*,*N*-dimethylthioformamide in 20 mL of acetic anhydride was heated for 1.5 h on a steam bath. The reaction mixture was cooled to ambient temperature, and ether (100 mL) was added. Chilling the solution precipitated bright orange crystals, which were collected by filtration, washed with cold ether, and dried to give 2.59 g (91%) of the iminium dye **13**: mp 219–222 °C; IR (KBr) 2960, 1635, 1480, 1405, 1262, 1090 (br), 1035 cm^{-1}.

Table IV. Crystal Data for 9

formula	$TeBr_5NC_{21}H_{30}$
M_r	823.62
space group	$P2_1/n$
extinctions	$h0l$, $h + l$ odd; $0k0$, k odd
cell const	
a, Å	8.895 (2)
b, Å	15.713 (2)
c, Å	19.670 (2)
β, deg	94.70 (1)
V, Å^3	2740 (1)
no. of molecules/unit cell (Z)	4
D(calcd), g cm^{-3}	1.996
D(obsd), g cm^{-3}	1.99
F(000)	1560
abs coeff (μ, Mo Kα), cm^{-1}	83.2
temp, °C	22 (1)
scan technique	-2θ
scan rate, deg 2θ min^{-1}	1.7–20
2θ limit, deg	50
no. of unique reflct ns measd	4812
no. of reflctns used in refinement	2750 ($I > \sigma(I)$)
no. of variable parameters	250
cryst dimens, mm	0.15 × 0.17 × 0.41

Compound **13** was dissolved in acetonitrile (20 mL), and 20 mL of saturated sodium bicarbonate solution was added. The mixture was heated on a steam bath for 1 h. The mixture was diluted with water and extracted with dichloromethane. The dichloromethane extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel to give aldehyde **32** as an oil that was used without further purification.

Preparation of Tellurapyrylium Dye 22. Tellurapyrylium **31** (4.98 g, 0.0123 mol) and 2,6-di-*tert*-butyl-4-(formylmethylene)-4*H*-selenapyran (**33**)[14] (3.80 g, 0.0128 mol) in 30 mL of acetic anhydride were heated on a steam bath for 2.5 min. The reaction mixture was cooled to ambient temperature, and 65 mL of ether was added. Chilling the solution precipitated large copper-bronze crystals. The crystals were collected by filtration, washed with ether, and dried to give 7.01 g (83%) of **22**: mp 199–202 °C; IR (KBr) 2990, 1475, 1175 cm^{-1}.

General Procedure for Preparing Tellurapyrylium Dibromides. A stock solution of 1.60 g (0.0100 mol) of bromine in 20 mL of CCl_4 was prepared. The tellurapyrylium dye was dissolved in dichloromethane (1 mmol/10 mL), and 1.1 equiv of the bromine in CCl_4 solution was added via syringe. The solution was allowed to stand for 1 min at ambient temperature and then concentrated in vacuo. The residue was recrystallized from CH_3CN.

For **9**: 90% yield; IR (KBr) 2980, 1635, 1595, 1085 cm^{-1}.

For **12**: 97% yield; IR (KBr) 1625, 1590, 1195, 1080 cm^{-1}.

For **14**: 91% yield; IR (KBr) 2980, 1650, 1620, 1585, 1270, 1075 cm^{-1}.

For **19**: 75% yield; IR (KBr) 1560, 1540, 1125, 1085 cm^{-1}.

For **21**: 81% yield; IR (KBr) 2990, 1560, 1130, 1080 cm^{-1}.

For **23**: 62% yield; IR (KBr) 2860, 1560, 1550, 1470 cm^{-1}.

General Procedure for Preparing Tellurapyrylium Diiodides. Iodine (1.1 equiv) was added to a solution of tellurapyrylium dye in dichloromethane (1 mmol/10 mL). The reaction mixture was diluted with an equal volume of ether and allowed to stand for 2 h. The crystalline products were filtered, washed with ether, and dried.

For **15**: 67% yield; IR (KBr) 2980, 1635, 1570, 1400, 1260, 1125, 1080, 1035 cm^{-1}.

For **20**: 75% yield (1:1 $BF_4 \cdot I_3$ salts); IR (KBr) 1565, 1510, 1500, 1235 cm^{-1}.

Preparation of Tellurapyrylium Dichloride 18. Chlorine gas was bubbled into CCl_4 to give a ~0.10 M solution. Dye **16**

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[14] Wadsworth, D. H.; Detty, M. R.; Murray, B. J.; Weidner, C. H.; Haley, N. F. *J. Org. Chem.* **1984**, *49*, 2676.

Table V. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Te	0.00678 (9)	0.31585 (6)	0.16852 (4)	4.26 (2)
Br1	−0.2175 (2)	0.2431 (1)	0.23077 (9)	6.66 (4)
Br2	0.2432 (2)	0.3957 (2)	0.1208 (1)	9.02 (5)
Br3	0.6136 (3)	0.7147 (2)	0.5050 (1)	10.36 (6)
Br4	0.5638 (2)	0.5936 (1)	0.4175 (1)	8.34 (5)
Br5	0.5221 (3)	0.4805 (2)	0.3308 (2)	11.56 (8)
N	0.122 (1)	0.6838 (7)	0.5191 (5)	5.1 (2)
C1	0.139 (1)	0.3085 (8)	0.2632 (6)	3.9 (3)
C2	0.130 (1)	0.3695 (7)	0.3097 (6)	4.2 (3)
C3	0.039 (1)	0.4476 (7)	0.3077 (6)	3.6 (2)
C4	−0.059 (1)	0.4742 (8)	0.2485 (6)	4.6 (3)
C5	−0.091 (1)	0.4347 (8)	0.1879 (6)	4.0 (3)
C6	0.051 (1)	0.5027 (7)	0.3641 (6)	3.4 (2)
C7	0.162 (1)	0.4902 (8)	0.4207 (6)	4.3 (3)
C8	0.183 (1)	0.5487 (9)	0.4717 (6)	4.8 (3)
C9	0.096 (1)	0.6248 (8)	0.4712 (6)	4.2 (3)
C10	−0.024 (2)	0.6338 (8)	0.4180 (6)	4.9 (3)
C11	−0.044 (1)	0.5757 (8)	0.3679 (6)	4.6 (3)
C12	0.236 (2)	0.673 (1)	0.5780 (8)	8.0 (5)
C13	0.042 (2)	0.767 (1)	0.5158 (9)	7.6 (4)
C14	0.236 (2)	0.2273 (9)	0.2746 (7)	5.4 (3)
C15	0.401 (2)	0.256 (1)	0.295 (1)	7.5 (5)
C16	0.180 (2)	0.177 (1)	0.336 (1)	7.9 (5)
C17	0.233 (2)	0.172 (1)	0.2114 (9)	10.1 (5)
C18	−0.197 (2)	0.4734 (9)	0.1303 (7)	6.1 (4)
C19A	−0.130 (5)	0.562 (3)	0.103 (2)	10 (1)*
C19B	−0.114 (4)	0.477 (2)	0.068 (2)	7.9 (9)*
C20A	−0.344 (4)	0.505 (2)	0.156 (2)	8.3 (9)*
C20B	−0.265 (3)	0.555 (2)	0.151 (2)	6.7 (7)*
C21A	−0.207 (5)	0.423 (3)	0.063 (2)	10 (1)*
C21B	−0.325 (4)	0.401 (2)	0.113 (2)	6.7 (7)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)*[a^2*B(1,1) + b^2*B(2,2) + c^2*\mathrm{B}(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2.3)]$.

(0.394 g, 0.500 mmol) was dissolved in 5 mL of CH_2Cl_2, and 5 mL of the chlorine–CCl_4 solution was added, giving a deep magenta solution. The reaction mixture was concentrated. The residue was recrystallized from 10 mL of CH_3CN to give 0.34 g (79%) of **18**: mp 178–197 °C dec; IR (KBr) 1560, 1495, 1450, 1240, 1090 cm^{-1}.

Crystal Data Collection. A six-sided needle crystal of **9** was mounted on a thin glass rod and used for data collection on an Enraf-Nonius CADC4 diffractrometer using graphite-monochromated Mo Kα radiation. Unit cell parameters obtained by least-squares refinement of the setting angles for 25 computer-centered reflections are given in Table IV along with other pertinent information.

Each reflection was scanned from 2θ(Mo Kα_1) − 0.75° to 2θ(Mo Kα_2) + 0.75°. The scan width was extended 25% at each end to measure background intensities. As a check on experimental stability, the intensities of three reflections were remeasured every hour. No significant change in these intensities was noted.

The net intensities were calculated according to $I = ASK(C - RB)$, and the standard deviations were $\sigma^2(I) = (ASK)^2(C + R^2B)$ and $\sigma(F_o) = [I + \sigma(I)/Lp]^{1/2} - F_o$, where A is the attenuator factor, S is the scale, C is the total integrated peak count, $(Lp)^{-1}$ is the Lorentz–polarization correction, and $F_o = (I/Lp)^{1/2}$ is the observed structure factor. An empirical absorption correction was made.[15] Correction factors on F_o ranged from 0.941 to 0.999.

Structure Solution and Refinement. The structure was solved by direct methods using MULTAN 11/82. An E map calculated with the best phase set (279 E's ≥ 1.94) gave the Te, Br1, and Br2 positions. Subsequent difference electron density maps revealed the remaining nor-hydrogen atoms. The C18 *tert*-butyl group is disordered, with the methyls C19, C20, and C21 each occupying two positions (A and B). The occupancy was fixed at 0.5 for each disordered site.

Refinement was by the full-matrix least-squares method. The function minimized was $\sum w(|F_o| - K|F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2 + 1.0$. Scattering factors and anomalous dispersion corrections were from ref 16. The agreement indices are $R = \sum||F_o| - K|F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - K|F_c|)^2/\sum wF_o^{\,2})^{1/2}$.

In the final stages, anisotropic thermal parameters were applied to all but the disordered carbons, and refinement converged to give $R = 0.062$, $R_w = 0.068$, and $K = 0.4365$ (3). The final difference electron density map contained residual electron density between −0.76 and +0.99 e/Å^3, with the largest positive peaks near the Br_3 anion. Final positional parameters and their estimated standard deviations are given in Table V.

Registry No. **8**, 103817-74-9; **9**, 103817-98-7; **11**, 84790-57-8; **12**, 103817-82-9; **13**, 103817-76-1; **14**, 103817-84-1; **15**, 103817-86-3; **16**, 83710-79-6; **17**, 103817-78-3; **18**, 103817-88-5; **19**, 103817-90-9; **20**, 103834-86-2; **21**, 103818-00-4; **22**, 103817-80-7; **23**, 103834-88-4; **25**, 103817-94-3; **28**, 86029-92-7; **31**, 103817-93-2; 32, 103817-95-4; **33**, 103817-96-5; Te, 13494-80-9; $(H_3C)_2CHCH_2C{\equiv}CCOC{\equiv}C\text{-}C(CH_3)_3$, 103817-91-0; *p*-bromo-*N,N*-dimethylaniline, 586-77-6; *N,N*-dimethylthioformamide, 758-16-7.

Supplementary Material Available: Tables of crystal data for bond distances, bond angles, general temperature factors, refined temperature factors, and least-squares planes (5 pages); a table of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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(15) Programs used for the X-ray study were part of the Structure Determination Package, SDP-PLUS V1.0, Enraf-Nonius Corp., Delft, Holland.

(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, Chapter 2.