Synthesis and Chemistry of 1,3-Dihydrotellurolo[3,4-*b*]quinoxaline and Derivatives: Crystal and Molecular Structure of 1,3-Dihydro-2,2-di-iodo-2λ^4-tellurolo[3,4-*b*]quinoxaline–2,3-Bis(iodomethyl)quinoxaline (1 : 1) †

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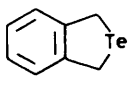
The reaction of 2,3-bis(bromomethyl)quinoxaline with tellurium and sodium iodide (2 h) gave the violet compound 1,3-dihydro-2,2-di-iodo-2λ^4-tellurolo[3,4-*b*]quinoxaline, which may be reduced to 1,3-dihydrotellurolo[3,4-*b*]quinoxaline (m.p. 158—160 °C). The latter compound readily forms a black 1 : 1 complex with 7,7,8,8-tetracyanoquinodimethane. The u.v., n.m.r., i.r., and mass spectra of the new organotellurium heterocycles are presented and discussed. 2,3-Bis(bromomethyl)quinoxaline also reacts with tellurium and potassium iodide (1 h) to give a yellow material for which elemental analysis, n.m.r., and mass spectroscopy suggest a 1 : 1 adduct of the above di-iodo-complex and 2,3-bis(iodomethyl)quinoxaline. Sodium hydrogentelluride reduces 2,3-bis(bromomethyl)quinoxaline to 2,3-dimethylquinoxaline. The crystal and molecular structure of the 1 : 1 adduct of 1,3-dihydro-telluro[3,4-*b*]quinoxaline, $C_{10}H_8I_2N_2Te$, with 2,3-bis(iodomethyl)quinoxaline, $C_{10}H_8I_2N_2$, has been determined. Crystals of the compound are triclinic, space group $P\bar{1}$, with $a = 7.667(2)$, $b = 11.826(4)$, $c = 13.739(4)$ Å, $\alpha = 93.26(3)$, $\beta = 98.37(2)$, $\gamma = 83.29(2)°$, and $Z = 2$. Final $R = 0.059$ for 2 998 observed reflections. The structure consists of discrete molecules of $C_{10}H_8I_2N_2Te$ and $C_{10}H_8I_2N_2$, a pair of each being linked into centrosymmetric dimers by weak Te · · · I linkages. The co-ordination about tellurium is a distorted octahedron with two Te–C bonds [2.14(1) Å], two axial Te–I bonds [2.886(2), 2.911(2) Å] and two longer equatorial Te–I bonds *trans* to Te–C [3.761(2), 3.788(2) Å], the longer contact being to an iodine of the organic di-iodide. Large deviations of bond angle from the ideal octahedral angles occur. A further very weak interaction links the dimers into chains along *x*. No abnormal features are observed in the organic moieties.

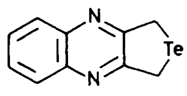
During recent studies [1] of donor–acceptor complexes involving organotellurium donors with 7,7,8,8-tetracyanoquinodimethane (tcnq) as acceptor, it was observed that the 1 : 1 complex with 1,3-dihydro-2-telluraindene (1) was of some interest. The telluride was a good donor (too good from the point of view of obtaining a conducting complex), hence it was decided to investigate further other compounds containing the telluracyclopentane ring.

Attention focused upon 1,3-dihydrotellurolo[3,4-*b*]quinoxaline (2) since the molecule not only contained the telluracyclopentane ring, but also shared some features with 5-methylphenazinium (3) which gives one of the most highly conducting tcnq complexes formed with an organic donor.[2] Furthermore the presence of nitrogen in the molecule may give rise to strong intermolecular interactions such as those observed for 1-tellura-2-azaindene (4) where the very short intermolecular contacts (Te · · · N) of 2.4 Å explain the high melting point and low solubility of the compound.[3] In summary (2) appeared to have sufficient points of interest to make the synthesis worthwhile; not only was it likely to be a reasonable donor, but the possible presence of strong intermolecular interactions might conceivably overcome the normal tendency to form mixed-stack DA, DA, DA . . . donor (D)–acceptor (A) complexes.

In this paper the syntheses of (2) and some derivatives are given. In the case of one compound, it was necessary to turn to *X*-ray crystallography for complete characterisation of the material.



(1)



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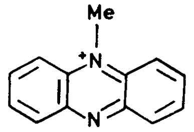

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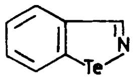

(4)

Experimental

(*a*) *Syntheses*.—1,3-*Dihydro*-2,2-*di-iodo*-2λ^4-*tellurolo*[3,4-b]-*quinoxaline*, (6). A mixture of 2,3-bis(bromomethyl)quinoxaline, (5) (1.58 g, 5 mmol), sodium iodide (3.0 g, 20 mmol), and powdered tellurium (0.64 g, 5 mmol) in 2-methoxyethanol (100 cm^3) was stirred and heated to gentle reflux for 2 h. After cooling the reaction mixture, deionized water (200 cm^3) was added to cause additional precipitation. The precipitate was filtered off, washed with water and dried. The crude material was recrystallized from 2-methoxyethanol to give (6) as a deep violet crystalline solid, m.p. 148—150 °C.

1,3-*Dihydro*-2,2-*di-iodo*-2λ^4-*tellurolo*[3,4-b]*quinoxaline*–2,3-*bis*(*iodomethyl*)*quinoxaline* (1 : 1), (7). In a repeat experiment, 2,3-bis(bromomethyl)quinoxaline (3.16 g, 10 mmol), powdered tellurium (1.28 g, 10 mmol), and potassium iodide (6.54 g, 39 mmol) were stirred and heated gently in 2-ethoxyethanol for 1 h. After the reaction period, deionized water (200 cm^3) was added to the mixture. The yellow precipitate formed was filtered off and air dried. The crude material was dissolved in hot acetone, filtered to remove any unreacted tellurium and the

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† *Supplementary data available* (No. SUP 23737, 22 pp.): structure factors, anisotropic thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

filtrate was set aside to crystallize slowly. The resulting complex, (7), had m.p. 150—152 °C.

1,3-*Dihydrotellurolo*[3,4-b]*quinoxaline*, (2). To a suspension of violet (6) (1.0 g) in ethanol (75 cm^3) and water (15 cm^3) was added dropwise a solution of hydrazine hydrate (0.4 g) in ethanol (15 cm^3). The resulting solution was warmed gently until all the violet crystals of (6) had dissolved, after which the reaction mixture was poured into water (200 cm^3) and extracted into diethyl ether. The ethereal layer was separated, dried over anhydrous Na_2SO_4 and taken to dryness on a rotatory film evaporator. The resulting yellow powder, on treatment with charcoal and ether, gave yellow needles, m.p. 158—160 °C.

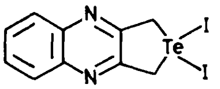
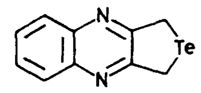
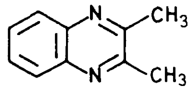
Attempted direct synthesis of 1,3-*dihydrotellurolo*[3,4-b]-*quinoxaline*, (2). A mixture of 2,3-bis(bromomethyl)quinoxaline (1.90 g, 6 mmol), tellurium powder (0.76 g, 6 mmol), and $NaBH_4$ (1.2 g, 32 mmol) in ethanol was stirred and heated for 12 h under dinitrogen. The initial green colour changed to red in 30 min. On completion of the reaction, the mixture was poured into water (500 cm^3) when a yellow precipitate appeared. The colourless material was extracted into ether from which solution colourless needles of 2,3-dimethylquinoxaline, (9), were obtained, m.p. 105—107 °C.

Complex of 1,3-*dihydrotellurolo*[3,4-b]*quinoxaline with tcnq* (1 : 1). To a solution of (2) (0.28 g, 1 mmol) in acetonitrile (20 cm^3) was added a solution of tcnq (0.21 g, 1 mmol) in acetonitrile (30 cm^3). The resulting solution was stirred under reflux for 1 h, after which the volume of the solution was reduced to 10 cm^3 and the residue left to crystallize. Crystals of (8), m.p. 140 °C (decomp.), were obtained.

(*b*) *Physical Measurements*.—Analysis for C, H, and N was by the Analytical Service Unit, University of Aston; tellurium was determined volumetrically.[4] Infrared measurements were carried out using Nujol mulls with a Perkin-Elmer 599 instrument. Mass spectra were determined at 70 eV (1 eV = 96.5 kJ mol^{-1}) with an AEI MS9 instrument. Measurements of u.v. spectra in solution were performed with a Unicam SP8-100 spectrophotometer. ^{1}H N.m.r. spectra were determined with a Perkin-Elmer R14 instrument using $SiMe_4$ as internal standard.

(*c*) X-*Ray Structure Analysis of* 1,3-*Dihydro*-2,2-*di-iodo*-2λ^4-*tellurolo*[3,4-b]*quinoxaline*-2,3-*Bis*(*iodomethyl*)*quinoxaline* (1 : 1), (7).—After preliminary examination by photographic methods, a crystal with dimensions *ca.* 0.26 × 0.18 × 0.03 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and cell dimensions and reflection intensities were measured in the

Table 1. Preparative and analytical data for new compounds

Compound	Colour	M.p. (°C)	Yield (%)	Analysis [a] (%) C	H	N	Te
 (6) $C_{10}H_8I_2N_2Te$	Deep violet	148—150	60	22.5 (22.3)	1.50 (1.50)	5.00 (5.20)	23.2 (23.7)
(7) $C_{10}H_8I_2N_2Te{\cdot}C_{10}H_8I_2N_2$	Yellow	150—152	75	25.4 (25.4)	1.70 (1.70)	5.50 (5.90)	13.4 (13.5)
 (2) $C_{10}H_8N_2Te$	Pale yellow	158—160	60	41.6 (42.3)	2.80 (2.80)	9.50 (9.85)	44.2 (44.9)
(8) $C_{10}H_8N_2Te{\cdot}$tcnq	Black	140 (decomp.)	86	53.8 (54.2)	2.30 (2.45)	16.4 (17.2)	27.0 (26.2)
 (9)	Colourless	105—107 [b]	82	75.0 (75.9)	6.40 (6.35)	17.5 (17.7)	—

[a] Calculated values are given in parentheses. [b] Lit.[8] value = 106 °C.

Table 2. N.m.r., i.r., and u.v. spectral data

Compound	$\lambda_{max.}$ [a]/nm	ν/cm^{-1}	δ(^{1}H) [b]/p.p.m.
(6)	242, 270, 328	514 [ν(TeC)]	4.74 [s, 4 H, *J*(TeH) 31, CH_2], 7.7—8.2 (m, 4 H, aromatic)
(7)	245, 266, 335	512 [ν(TeC)]	4.74 (s, 4 H, CH_2–Te), 4.84 (s, 4 H, CH_2–I), 7.6—8.1 (m, 8 H, aromatic)
(2)	243, 324	500 [ν(TeC)]	4.58 [s, 4 H, *J*(TeH) 23, CH_2], 7.2—8.05 (m, 4 H, aromatic)
(8)	243, 320, 394 (tcnq + tcnq$^{\cdot -}$)	$\left.\begin{matrix}2\,178\\2\,228\end{matrix}\right\}$[ν(CN)] 505 [ν(TeC)]	
(9)	237, 315		2.5 (s, 6 H, CH_3), 7.3—8.1 (m, 4 H, aromatic)
(5)	248, 337		4.92 (s, 4 H, CH_2), 7.5—8.0 (m, 4 H, aromatic)

[a] In CH_2Cl_2. [b] $SiMe_4$ as internal standard; in [$^2H_6$]dimethyl sulphoxide; *J* values in Hz.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for complex (7)

Atom	x	y	z
Te	−2 456(1)	5 292(1)	3 885(1)
I(1)	377(1)	6 735(1)	4 152(1)
I(2)	−5 305(1)	3 833(1)	3 487(1)
I(3)	−5 101(1)	8 140(1)	4 325(1)
I(4)	−9 469(2)	10 387(1)	3 556(1)
C(1)	−801(17)	3 976(11)	3 227(9)
C(2)	−1 179(14)	4 100(10)	2 129(8)
N(3)	−390(13)	3 358(9)	1 578(7)
C(4)	−785(16)	3 477(11)	567(9)
C(5)	−16(19)	2 660(12)	−69(11)
C(6)	−410(21)	2 779(14)	−1 068(11)
C(7)	−1 577(20)	3 714(14)	−1 441(10)
C(8)	−2 371(19)	4 495(14)	−824(9)
C(9)	−1 963(16)	4 415(11)	197(9)
N(10)	−2 774(13)	5 184(9)	798(7)
C(11)	−2 361(15)	5 037(10)	1 749(8)
C(12)	−3 247(17)	5 898(11)	2 431(9)
C(21)	−4 289(21)	9 381(13)	3 437(11)
C(22)	−5 300(16)	9 377(11)	2 402(10)
N(23)	−4 634(15)	8 626(9)	1 780(8)
C(24)	−5 392(17)	8 606(11)	833(9)
C(25)	−4 702(22)	7 838(12)	142(11)
C(26)	−5 455(22)	7 849(13)	−826(11)
C(27)	−6 868(22)	8 684(14)	−1 137(11)
C(28)	−7 536(19)	9 456(13)	−484(11)
C(29)	−6 839(17)	9 432(11)	514(10)
N(30)	−7 527(14)	10 177(9)	1 165(9)
C(31)	−6 767(18)	10 165(11)	2 093(11)
C(32)	−7 559(20)	11 066(12)	2 768(11)

Table 4. Distances (Å) and angles (°) for complex (7); primes and double primes refer to equivalent positions: $-x, 1 - y, 1 - z$ and $-1 - x, 1 - y, 1 - z$, respectively

Te−I(1)	2.886(2)	Te−I(2″)	4.245(2)
Te−I(2)	2.911(2)		
Te−I(1′)	3.761(2)		
Te−I(3)	3.788(2)		
Te−C(1)	2.136(11)	I(3)−C(21)	2.161(25)
Te−C(12)	2.140(12)	I(4)−C(32)	2.190(25)
C(1)−C(2)	1.51(2)	C(21)−C(22)	1.52(2)
C(2)−N(3)	1.28(2)	C(22)−N(23)	1.31(2)
C(2)−C(11)	1.42(2)	C(22)−C(31)	1.41(2)
N(3)−C(4)	1.39(2)	N(23)−C(24)	1.35(2)
C(4)−C(5)	1.40(2)	C(24)−C(25)	1.39(2)
C(4)−C(9)	1.41(2)	C(24)−C(29)	1.43(2)
C(5)−C(6)	1.37(2)	C(25)−C(26)	1.37(2)
C(6)−C(7)	1.41(2)	C(26)−C(27)	1.41(2)
C(7)−C(8)	1.37(2)	C(27)−C(28)	1.35(2)
C(8)−C(9)	1.40(2)	C(28)−C(29)	1.40(2)
C(9)−N(10)	1.35(2)	C(29)−N(30)	1.34(2)
N(10)−C(11)	1.32(2)	N(30)−C(31)	1.32(2)
C(11)−C(12)	1.51(2)	C(31)−C(32)	1.50(2)

I(1)−Te−I(2)	176.5(1)	I(2)−Te−C(12)	87.6(4)
I(1)−Te−I(1′)	95.7(1)	I(1′)−Te−I(3)	125.4(1)
I(1)−Te−I(3)	80.5(1)	I(1′)−Te−C(1)	71.9(4)
I(1)−Te−C(1)	90.3(4)	I(1′)−Te−C(12)	157.7(4)
I(1)−Te−C(12)	89.3(4)	I(3)−Te−C(1)	160.9(4)
I(2)−Te−I(1′)	86.6(1)	I(3)−Te−C(12)	76.8(4)
I(2)−Te−I(3)	100.3(1)	C(1)−Te−C(12)	86.4(4)
I(2)−Te−C(1)	87.9(4)		
Te−C(1)−C(2)	107(1)	I(3)−C(21)−C(22)	112(2)
C(1)−C(2)−N(3)	118(2)	C(21)−C(22)−N(23)	115(2)
C(1)−C(2)−C(11)	119(2)	C(21)−C(22)−C(31)	124(2)
N(3)−C(2)−C(11)	123(2)	N(23)−C(22)−C(31)	121(2)
C(2)−N(3)−C(4)	117(2)	C(22)−N(23)−C(24)	119(2)
N(3)−C(4)−C(5)	119(2)	N(23)−C(24)−C(25)	121(2)
N(3)−C(4)−C(9)	120(2)	N(23)−C(24)−C(29)	120(2)
C(5)−C(4)−C(9)	121(2)	C(25)−C(24)−C(29)	119(2)
C(4)−C(5)−C(6)	119(2)	C(24)−C(25)−C(26)	120(2)
C(5)−C(6)−C(7)	120(2)	C(25)−C(26)−C(27)	120(2)
C(6)−C(7)−C(8)	121(2)	C(26)−C(27)−C(28)	121(2)
C(7)−C(8)−C(9)	120(2)	C(27)−C(28)−C(29)	120(2)
C(8)−C(9)−N(10)	120(2)	C(28)−C(29)−N(30)	120(2)
C(8)−C(9)−C(4)	118(2)	C(28)−C(29)−C(24)	119(2)
N(10)−C(9)−C(4)	122(2)	N(30)−C(29)−C(24)	120(2)
C(9)−N(10)−C(11)	116(2)	C(29)−N(30)−C(31)	118(2)
N(10)−C(11)−C(12)	117(2)	N(30)−C(31)−C(32)	115(2)
N(10)−C(11)−C(2)	122(2)	N(30)−C(31)−C(22)	121(2)
C(12)−C(11)−C(2)	121(2)	C(32)−C(31)−C(22)	124(2)
C(11)−C(12)−Te	106(1)	C(31)−C(32)−I(4)	111(2)

ω/2θ scan mode with graphite-monochromated Mo-K_α radiation. The scan range (ω°) was calculated from (1.10 + 0.35 tan θ) and the scan speed varied from 1.1 to 3.5° min^{-1} depending on the intensity. Backgrounds were measured at each end of the scan. 4 291 Reflections were scanned in the range $2 < \theta < 25°$. Two standard reflections measured every 2 h showed a slight decrease in intensity (*ca.* 10%) and appropriate scaling factors were applied.

Lorentz, polarisation, and analytical[5] absorption corrections (transmission factor range 0.312—0.817) were applied, and 2 998 structure amplitudes [$F > 7\sigma(F)$] were considered observed and used in the structure analysis.

Crystal data. $C_{20}H_{16}I_4N_4Te$, M = 947.59, Triclinic, a = a = 7.667(2), b = 11.826(4) c = 13.739(4) Å, α = 93.26(3), β = 98.37(2), γ = 83.29(2)°, U = 1 223.1 Å^3, Z = 2, D_c = 2.57 g cm^{-3}, $F(000)$ = 856, μ(Mo-K_α) = 5.88 mm^{-1}, λ = 0.710 69 Å, space group $P1$ or $P\bar{1}$; $P\bar{1}$ established as a result of the analysis.

The positions of the Te and I atoms were determined by a combination of direct methods and Patterson and Fourier syntheses and those of the remaining non-hydrogen atoms from subsequent Fourier-difference maps. The structure was refined by least squares using anisotropic thermal parameters for the heavier atoms. Hydrogen atoms were placed in calculated positions 'riding' on their respective carbon atoms. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.001F^2]$, and refinement converged to R = 0.059.

Complex neutral-atom scattering factors were employed.[6] Computations were carried out on the University of Birmingham DEC 20 and 1906 A computers and on the CDC 7600 at the University of Manchester Regional Computer Centre with the MULTAN[7] and SHELX[8] programs.

Results and Discussion

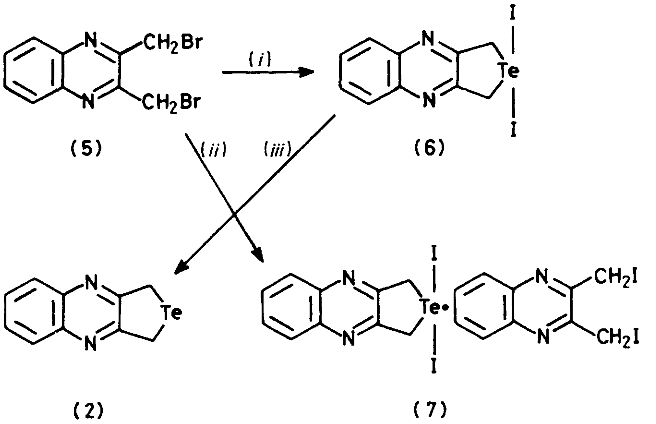
Table 1 combines preparative and analytical data. N.m.r., i.r., and u.v. spectral data are given in Table 2. Fractional atomic co-ordinates are given in Table 3 and important distances and bond angles in Table 4. Deviations of atoms (Å) from the mean planes are given in Table 5.

The reaction of 2,3-bis(bromomethyl)quinoxaline, (5) (Scheme 1), with powdered tellurium and sodium iodide gives a violet compound to which, on the basis of elemental analysis (Table 1), ^{1}H n.m.r. data (Table 2) and mass spectroscopic data (see below), structure (6) is reasonably assigned.

The ^{1}H n.m.r. spectrum of (5) has been studied[9] and shows resonances at δ 4.92 (s, 4 H, CH_2) and at 7.46—8.08 (m, 4 H, aromatic). The fact that the methylene protons of (6) [δ 4.74, J(TeH) = 31 Hz] are more shielded than those of (5) is in accord with simple expectation from electronegativity arguments as, indeed, is the further shielding seen for the methylene protons of (2) (Scheme 1, Table 2). The violet colour of (6) implies strong intermolecular interactions in the solid state and attempts are being made to define the nature of these interactions by X-ray crystallography. A mass spectral

Table 5. Deviations of atoms (Å) from mean planes. Atoms not used in defining the planes are marked with an asterisk. Estimated standard deviations are *ca.* 0.03 Å for C and N, 0.005 Å for Te and I

(*a*) Complexed organic residue							
C(1)	−0.02	C(2)	0.00	N(3)	0.03	C(4)	0.02
C(5)	−0.01	C(6)	−0.02	C(7)	0.00	C(8)	−0.01
C(9)	0.03	N(10)	0.00	C(11)	0.01	C(12)	−0.01
Te *	−0.19	I(1) *	2.68	I(2) *	−3.06		
(*b*) Free organic ligand							
C(21)	−0.10	C(22)	0.02	N(23)	0.02	C(24)	0.05
C(25)	0.02	C(26)	0.01	C(27)	−0.05	C(28)	−0.06
C(29)	0.01	N(30)	0.04	C(31)	0.03	C(32)	0.00
I(3) *	1.83	I(4) *	2.01				
(*c*) Equatorial plane of tellurium co-ordination octahedron							
Te	−0.05	I(1′)	−0.06	I(3)	0.08		
C(1)	0.18	C(2)	−0.15	I(1) *	2.81		
I(2) *	−2.93	I(2″) *	−1.02				



Scheme 1. (*i*) Te, NaI; (*ii*) Te, KI; (*iii*) N_2H_4

study of (6) was in good agreement with the proposed structure and the main fragmentation pathways are gathered into Scheme 2. It will be more convenient to discuss this later since the Scheme relates equally to complex (2). The observation of fragments TeI_2^+ and I_2^+ is significant.

Reduction of (6) with hydrazine hydrate affords (2). Elemental analysis, ^1H n.m.r. and mass spectroscopy all suggest the structure given in Scheme 1. The methylene protons show coupling to ^{125}Te confirming that the TeC linkage has remained intact. With the obvious exception of the iodine-containing fragments the mass spectrum of (2) is superimposable on that of (6). Many of the proposed fragmentations are supported by the observation of metastable ions at appropriate values of *m*/*e*. An interesting fragment at *m*/*e* 142 may arise from the parent ion (*m*/*e* = 286) by loss of H_2CTe, however no metastable transition is observed to support this suggestion.

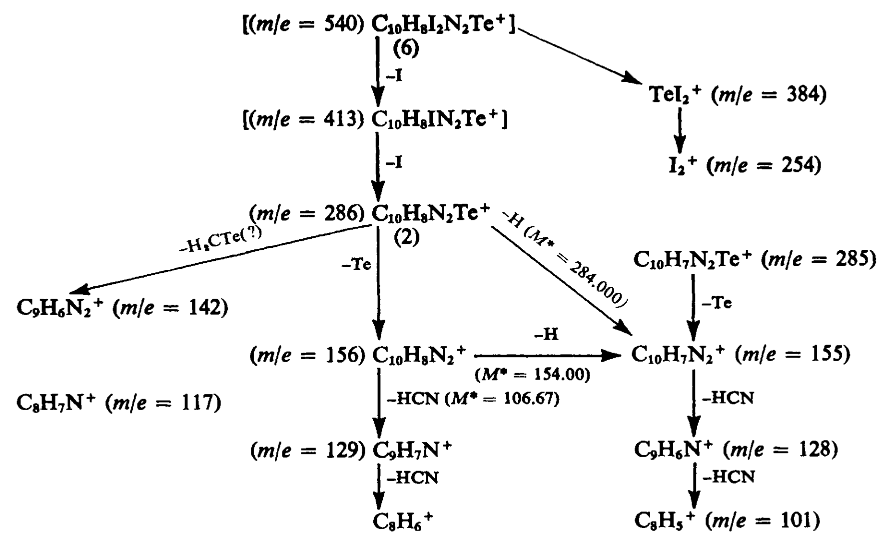
When (5) is reacted for a shorter time with tellurium powder and *potassium* iodide a yellow compound (7) rather than the violet product (6) is obtained. Repeated crystallization failed to alter the elemental analysis and the material was accepted as pure. Examination of i.r. and ^1H n.m.r. spectra revealed that (6) is almost certainly present in (7) together with another species, the ^1H n.m.r. spectrum of which is similar to, but not identical with, the spectrum of (5). This being the case it was noted that the elemental analysis and the integration of the n.m.r. spectrum supported the formulation as a 1 : 1 adduct of (6) with 2,3-bis(iodomethyl)quinoxaline. The mass spectrum contained an ion at *m*/*e* = 410 ($C_{10}H_8N_2I_2$). Confirmation of this formulation and definition of the intermolecular contacts were sought from *X*-ray crystallography (see later).

Reaction of (2) with 7,7,8,8-tetracyanoquinodimethane (tcnq) gave a black material (8) which proved to be a 1 : 1 complex, $C_{10}H_8N_2Te{\cdot}tcnq$. The u.v. spectrum (Table 2) clearly showed the presence of $C_{10}H_8N_2Te$ (2) in dichloromethane solution, the extra band at 394 nm being attributed to tcnq + $tcnq^{\cdot -}$.

A u.v. study of the compounds (Table 2) reveals that bands in the ranges 237—248 and 315—337 nm are characteristic of the quinoxaline nucleus. It would follow that the band at 270 (6) or 266 nm (7) must be due to the presence of Te–I bonds. A slight reduction in the frequency of ν(TeC) is noted on reduction of Te^{IV} [in (6)] to Te^{II} [in (2)]. The position of ν(CN) in the complex of (2) with tcnq [(8), Table 2] correlates both with the presence of tcnq [ν(CN) = 2 228 cm^{-1}] and with $tcnq^{\cdot -}$ [ν(CN) = 2 178 cm^{-1}].[10] The value of ν(TeC) at 505 cm^{-1} suggests a more positive tellurium atom [*cf.* 500 cm^{-1} for (2) (Te^{II}) and 514 cm^{-1} for (6) (Te^{IV})]. The properties of (8) will be more rationally presented as part of a more general survey of the donor properties of derivatives of telluracyclopentanes.

In view of the reported synthesis [11] of 2,3-dihydrotelluroquinolines by heating 2-chloro-3-(2′-chloroethyl)quinoline with an ethanolic solution of sodium hydrogentelluride ($NaBH_4$ + Te), it was decided to attempt the direct synthesis of (2) from the treatment of (5) with NaHTe ($NaBH_4$ + Te). The colourless product was identified as 2,3-dimethylquinoxaline (9) from the melting point [8] and n.m.r. spectrum (Table 2).

Crystal and Molecular Structure of (7).—The structure consists of discrete molecules of (6) and free 2,3-bis(iodomethyl)quinoxaline. Two molecules of (6) and two molecules of the di-iodide are however linked by relatively weak Te · · · I interactions into centrosymmetric dimers. These interactions are oriented *trans* to the Te–C bonds [Te–I(1′) = 3.761(2) and Te–I(3) = 3.788(2) Å] (see Figure for atom numbering). The atom I(1′) is linked to the centrosymmetrically related Te′ atom by a strong bond [Te′–I(1′) = 2.886(2) Å] thus forming the dimer. The Te–I(3) interaction serves to link in the organic di-iodide.



Scheme 2. Mass spectra of compounds (6) and (2) (Scheme 1) based on ^{130}Te, ^{127}I, ^{12}C, ^{14}N, and ^{1}H. Species given in square brackets were not observed. M^* denotes metastable species

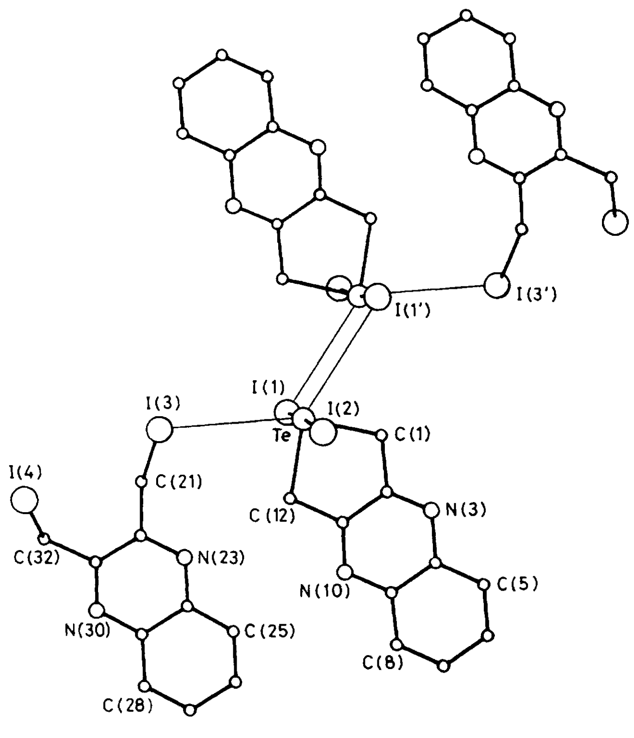


Figure. The structure of the dimer showing the atom-numbering scheme

The co-ordination about tellerium is approximately octahedral with two strongly bound iodine atoms, I(1) and I(2), in the axial positions, normal to the ring system of the heterocycle and the weakly linked I(1′) and I(3) in the equatorial plane (Table 5). Quite large angular deviations from ideal octahedral values, however, occur, in particular in the equatorial plane, the angle I(1′)–Te–I(3) is enlarged to 125.4(1)° with a concomitant decrease of the I(1′)–Te–C(1) and I(3)–Te–C(12) angles to 71.9(4) and 76.8(4)°, respectively.

The Te–C bond lengths [both 2.14(1) Å] are in excellent agreement with previous results [11–14] and with the sum of single bond covalent radii, 2.14 Å.[15] The axial Te–I bond lengths [2.886(2) and 2.911(2) Å] fall into the range *ca.* 2.95 ± 0.2 Å,[14] generally considered to be characteristic of covalent bonding, although somewhat longer than the sum of the covalent radii of Te and I, 2.70 Å.[15] The equatorial Te–I bonds, on the other hand, have lengths characteristic of secondary bonding,[16] *ca.* 3.8 ± 0.2 Å,[14] generally *trans* to Te–C bonds. Similar octahedral co-ordination occurs in α-dimethyltellurium di-iodide,[12] 1,3-dihydro-2,2-di-iodo-2λ^4-telluraindene [13] and in the adduct $Me_2TeI_2{\cdot}I_2$.[17]

The next closest Te–I interaction involves a centrosymmetrically related iodine atom translated one cell length along *x*, Te $\cdots$ I(2″) = 4.245(2) Å, which is close to the van der Waals distance, 4.35 Å.[15] If this interaction is significant, I(2″) would link the dimers into chains along *x*. The atom I(2″) is situated *ca.* 1 Å from the equatorial plane of the Te octahedron (Table 5) in the gap left by the large I(1′)–Te–I(3) angle (Figure). The angles I(2″)–Te–I(1′,3) are 70.4(1) and 57.2(1), respectively. Weak interactions clustered around the tellurium lone pair of electrons in the equatorial plane appear to be common in organotellurium(IV) derivatives.[18]

The shortest I $\cdots$ I distance is 3.864(2) Å, between I(2″) and I(3), which is considerably less than the sum of the van der Waals radii, 4.30 Å,[15] but greater than distances which would be considered to indicate a bonding interaction.[17,19] The packing in the crystal is characterised by parallel stacking of quinoxaline residues. There are however no abnormally short contact distances.

Bond lengths and angles in the organic moieties are unexceptional. The tellurium bound residue is planar to within ±0.03 Å, with the Te atom displaced 0.19 Å from the plane in the direction of I(2). The carbon framework of the free ligand is somewhat more distorted from planarity, with deviations of up to 0.10 Å occurring (Table 5). The two aromatic rings of the quinoxaline residue are each planar to within ±0.02 Å but the two rings are twisted relative to each other making a dihedral angle of *ca.* 2.25°.

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