Donor–Acceptor Complexes of Organotellurium Compounds. Physical Studies: Tellurium-125 Mössbauer Spectroscopy for the Measure of Charge Transfer. Crystal and Molecular Structure of the Complex Dibenzotellurophene–7,7,8,8-Tetracyano-*p*-quinodimethane †

Harkesh B. Singh and William R. McWhinnie *
Chemistry Department, University of Aston in Birmingham, Birmingham B4 7ET
Ronald F. Ziolo
Xerox Corporation, Webster Research Center, Webster, New York, 14580, U.S.A.
Colin H. W. Jones
Department of Chemistry, Simon Fraser University, Burnaby, B.C., V5A 156, Canada

A range of organotellurium(II) compounds, together with two selenium compounds are used as donors to form donor–acceptor complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq). Generally, the stoicheiometry is 1 : 1 but two ditellurides provide an exception in giving R_2Te_2·2tcnq (R = Ph or C_6H_4OEt-*p*). The complexes are electrical insulators although the conductivities vary over several orders of magnitude. The two ditelluride complexes show evidence of semiconducting properties. E.s.r. and i.r. data are discussed and it is concluded that in most cases the degree of charge transfer is small. Exceptions to the rule appear to be the tcnq complex of 1,3-dihydro-2-telluraindene and Ph_2Te_2·2tcnq which do involve significant charge transfer as assessed from a ^{125}Te Mössbauer study. A method of assessing the degree of charge transfer for donor–acceptor complexes of organotellurium compounds using Mössbauer spectroscopy is given. The crystal and molecular structure of the tcnq complex of dibenzotellurophene has been determined and molecular parameters compared with the known structures of the component molecules. The structural data confirm conclusions from i.r. and Mössbauer studies that, in this instance, the degree of charge transfer is very small. A novel feature of the structure is that in addition to intermolecular interactions within the mixed stacks, there are significant Te · · · N interactions between stacks. As a consequence, two different orientations of tcnq occur in the complex.

Charge-transfer complexes have played an important role in the development of molecular conductors [1] (' organic metals ') typified by the complex of tetrathiafulvalene (ttf) [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole] with 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq). To date, the most successful synthetic strategies for the production of a truely metallic organic solid may be described as variations on the ttf theme. In particular interesting properties are produced by substitution of selenium for sulphur in ttf [2] and recently the materials (tmtsf)$_2$X {where tmtsf = tetramethyltetraselenafulvalene [4,5-dimethyl-2-(4′,5′-dimethyl-1′,3′-diselenol-2′-ylidene)-1,3-diselenole] and $X^- = PF_6^-$, AsF_6^-, or ClO_4^-} have been shown to be superconducting at 1.4 K under enhanced pressure or under ambient pressure in the case of the perchlorate.[3,4]

The logical sequence of this approach has now led to the recent reports of derivatives of the tetratellurafulvalene ring system [5,6] and Wudl and Aharon-Shalom [6] have reported preliminary results on the tcnq complex of hexamethylenetetratellurafulvalene [5,6-dihydro-4*H*-2-(5′,6′-dihydro-4′*H*-1′,3′-ditellurapentalen-2′-ylidene)-1,3-ditellurapentalene].

An alternative approach in which tellurium chemistry has become more important is the synthesis of donors with the spin-bearing chalcogen on the periphery of the molecule. The tcnq complex of naphtho[1,8-*cd*]-1,2-ditellurole has an encouragingly high compacted-disc conductivity [7] and more recently Sandman *et al.*[8] have reported the synthesis of a range of related compounds, *e.g.* 5,6 : 11,12-bis(epiditelluro)-naphthacene. A view is held that, tellurium, being both larger and more electropositive than sulphur and selenium, may enhance both intermolecular and interchain interactions.

The literature is sparse in its reference to charge-transfer complexes of even simple organotellurium compounds although the work of Zingaro and co-workers [9] with phenoxatellurin (dibenzo[*b*,*e*]-1-oxa-4-tellurine) and tcnq is a notable exception. Wudl [10] has commented that no structural studies of single crystals of tellurium-containing donor–acceptor complexes are available. Doubtless this situation will not long remain and in this paper we contribute structural data on one such complex. We also report on the synthesis of charge-transfer complexes of a range of organotellurium compounds with, mainly, tcnq and also chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone).[11] Physical studies of the new compounds are reported and we particularly draw attention to the potential use of ^{125}Te Mössbauer spectroscopy as an investigative tool for the compounds.

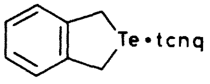
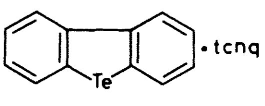
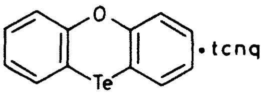
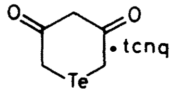
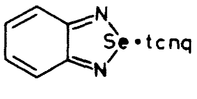
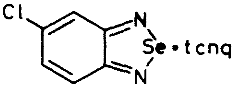
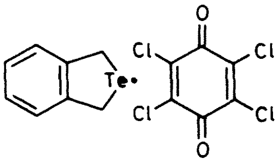
Experimental

Synthesis of Charge-transfer Complexes.—7,7,8,8-Tetracyano-*p*-quinodimethane (tcnq) was either obtained from Aldrich or synthesised by the literature method.[12] Chloranil was obtained from Koch-light. Organotellurium donors were synthesized following the indicated literature methods: dibenzotellurophene (dbt),[13] 1,3-dihydro-2-telluraindene,[14] phenoxytellurin,[15] 1-telluracyclohexane-3,5-dione,[16] diphenyl telluride,[17] diphenyl ditelluride,[18] bis(*p*-ethoxyphenyl) ditelluride,[19] bis(*p*-ethoxyphenyl) telluride,[20] and 9,10-dihydro-9-telluranthracene.[21] Two organoselenium donors were also

---

† Dibenzo[*b*,*d*]tellurole–7,7,8,8-tetracyano-*p*-quinodinethane (1/1). *Supplementary data available* (No. SUP 23903, 29 pp.): experimental details of intensity measurements, solution and refinement, structure factors, thermal parameters, H-atom co-ordinates, root-mean-square amplitudes of thermal vibration, least-squares planes, C–H distances, torsion angles, stereoscopic packing diagram. See Instructions for Authors, *J. Chem, Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical data for donor–acceptor complexes of organotellurium and organoselenium compounds

Compound	Colour	M.p. (°C)	Te(%) Found (calc.)	Compound	Colour	M.p. (°C)	Te(%) Found (calc.)	C(%) Found (calc.)	H(%) Found (calc.)	N(%) Found (calc.)
 (1)	Greenish brown	170	29.1 (29.3)	Ph_2Te_2·2tcnq	Black	>250	31.4 (31.2)	—	—	—
 (2)	Deep violet	200 (decomp.)	25.5 (26.4)	(p-$EtOC_6H_4)_2Te$·tcnq	Black	200 (decomp.)	21.8 (22.2)	—	—	—
 (3)	Black	250	24.8 (25.5)	(p-$EtOC_6H_4)_2Te_2$·2tcnq	Purple	150 (decomp.)	28.6 (28.2)	52.6 (53.1)	2.90 (2.90)	11.9 (12.4)
 (4)	Greenish brown	160 (decomp.)	28.8 (29.7)	 (6)	Violet	180	—	54.9 (55.8)	2.20 (2.10)	21.0 (21.7)
Ph_2Te·tcnq	Violet	210 (decomp.)	26.2 (26.3)	 (7)	Green	162	—	50.4 (51.3)	1.50 (1.65)	19.7 (19.9)
 (5)	Violet	168	28.0 (26.7)							

considered, namely 2,1,3-benzoselenadiazole and the 5-chloro-derivative.

All complexes were synthesized by essentially similar methods and the following experiments are typical of those carried out.

(a) *Complex of tcnq with* 2,1,3-*benzoselenadiazole* (' *piaselenole* ').[22] To a solution of 2,1,3-benzoselenadiazole (0.37 g, 2 mmol) in boiling acetonitrile (20 cm^3) was added tcnq (0.4 g, 2 mmol) in hot acetonitrile (20 cm^3). The reaction mixture was stirred and refluxed for 1 h after which time the volume was reduced to 10 cm^3. On cooling to room temperature the complex $C_6H_4N_2Se$·tcnq was obtained.

(b) *Complex of tcnq with bis*(*p-ethoxyphenyl*) *ditelluride*. In a dinitrogen-filled dry box, the ditelluride (0.50 g, 2 mmol) and tcnq (0.41 g, 2 mmol) were mixed in a flask to which acetonitrile (100 cm^3) was added. The mixture was heated to reflux for 1 h after which time the volume was reduced to 50 cm^3. On cooling the solution to room temperature crystals of the complex (p-$EtOC_6H_4)_2Te_2$·2tcnq were obtained.

(c) *Attempt to react* 9,10-*dihydro*-9-*telluranthracene with tcnq*. 9,10-Dihydro-9-telluranthracene and tcnq were refluxed in equimolar proportions in acetonitrile over 4 h. Cooling the solution affected a mixture of the starting materials. Variation of quantities, time of reflux, and volume of solvent failed to give a complex.

Table 1 reports the complexes synthesised, together with analytical data which were obtained *via* the Analytical Services Section, Department of Chemistry, University of Aston (C, H, and N) and volumetrically [23] (Te).

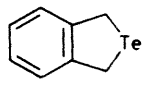
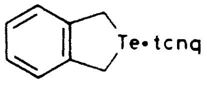
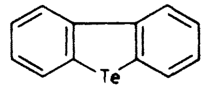
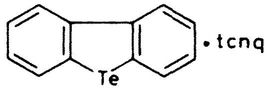
Physical Measurements.—Conductivity measurements. Samples were ground in an agate mortar and compressed into discs of diameter 13 mm and thickness 0.6—0.8 mm. Silver paste was painted on each side of the pellet to function as electrodes. Gold wires were attached by silver paste and the conductance measured by the two-probe method, or in some cases, the four-probe method. Facilities were available to monitor conductance in the range 40 to −190 °C. For the complex of dibenzotellurophene with tcnq one measurement was made by the four-probe method on a single crystal.

Attempts were also made to measure the conductance of acetonitrile solutions of some of the complexes using a standard bridge.

Infrared measurements were made for Nujol mulls with a Perkin-Elmer 599 instrument. E.s.r. spectra at room temperature were obtained at X-band frequency with a JEOL PE-1X spectrometer. Calibration was with a standard manganese(II) sample diluted with magnesium oxide.

Mössbauer measurements. These were obtained as previously reported [24] using a ^{125}Sb–Cu source. Both source and absorber were at 4 K. Data are given in Table 2 while other relevant physical data are gathered into Tables 3 and 4.

Table 2. Some ^{125}Te Mössbauer data for organotellurium complexes with tcnq

Complex	δ(Sb–Cu)/mm s^{-1}	δ(I–Cu)/mm s^{-1} [δ(Sb–Cu) + 0.15]	Δ/mm s^{-1}	$\Lambda_{exp.}$/mm s^{-1}
	0.07 ± 0.11	0.22	10.24 ± 0.24	5.8 ± 0.4
 (1)	0.31 ± 0.11	0.46	8.72 ± 0.22	6.5 ± 0.3
		0.14 ± 0.08	9.30 + 0.2	5.8
 (2)	0.07 ± 0.10	0.22	9.16 ± 0.21	5.4 ± 0.3
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$		0.28 ± 0.08	10.6 ± 0.1	6.4
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2\cdot2$tcnq	0.18 ± 0.12	0.33	10.50 ± 0.3	5.6 ± 0.4
Ph_2Te_2		0.37 ± 0.08	10.70 ± 0.1	6.1
$Ph_2Te_2\cdot2$tcnq	0.21 ± 0.21	0.36	9.70 ± 0.3	5.9 ± 0.6
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}$		0.24	11.13	
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}\cdot$tcnq	0.04 ± 0.13	0.19	10.9 ± 0.3	5.8 ± 0.4
(5) *		0.32 ± 0.08	10.4 ± 0.1	6.3

* For structure of (5) see Table 1.

Table 3. Infrared and e.s.r. data for tcnq complexes with organotellurium and organoselenium donors

Complex [a]	ν(CN)/cm^{-1}	*g* Factor (±0.003)
(1)	2 183	2.004
	2 112	2.001 [b]
(2)	2 220	2.001
(3)	2 186	1.999
	2 148	
(4)	2 208	
	2 160	
$Ph_2Te\cdot$tcnq	2 228	2.001
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}\cdot$tcnq	2 236	1.996
$Ph_2Te_2\cdot2$tcnq	2 228	2.003
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2\cdot2$tcnq	2 226	2.002
(6)	2 225	2.002
(7)	2 232	1.999

[a] For structures of complexes (1)—(4), (6), and (7) see Table 1. [b] In CH_3CN.

Table 4. Compressed-disc conductivity data (together with some solution data)

	Conductivity	
Compound [b]	Compressed disc (Ω^{-1} cm^{-1})	Solution [a] (Ω^{-1} cm^2 mol^{-1})
(6)	$>10^{-14}$	15
(1)	$>10^{-14}$	
(2)	10^{-7} [c]	12
$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2\cdot2$tcnq	1.8×10^{-8} (293 K)	
	3.6×10^{-9} (77 K)	
$Ph_2Te_2\cdot2$tcnq	2.6×10^{-8} (293 K)	
	4×10^{-9} (77 K)	

[a] Acetonitrile solution. [b] For structures of complexes (1), (2), and (6) see Table 1. [c] Single-crystal measurement.

*Crystal and Molecular Structure of Dibenzotellurophene–7,7,8,8-Tetracyano-*p*-quinodimethane.—Crystal data.* $C_{12}H_8Te\cdot C_{12}H_4N_4$, M = 484.0, monoclinic, space group $P2_1/n$, a = 14.849(5), b = 8.172(2), c = 16.275(4) Å, β = 92.05(3)°, U = 1 974 Å^3 at 23 °C, Z = 4, D_c = 1.63 g cm^{-3}, $F(000)$ = 944, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 15.8 cm^{-1}. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement, using the setting angles of 25 reflections in the range $4 < \theta < 11°$.

Data were collected on an Enraf-Nonius CAD4 automatic diffractometer with a crystal measuring 0.10 × 0.12 × 0.20 mm. The structure determination was performed by the crystallography staff of the Molecular Structure Corporation, College Station, Texas. A total of 4 987 reflections were collected for $2\theta < 55.0°$, of which 4 514 were unique and not systematically absent. The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement (310 variables) produced agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.041$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o]^{\frac{1}{2}} = 0.046$ using 2 295 reflections with $F_o^2 > 3.0\sigma(F_o^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o)^2$. Scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_c;[26] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Waber.[27] The final positional parameters are given in Table 5.

Table 5. Atomic co-ordinates with standard deviations in parentheses

Atom	*x*	*y*	*z*
Te	0.242 54(3)	—0.173 28(6)	0.094 82(3)
N(1)	0.420 5(5)	0.721 9(9)	0.244 8(4)
N(2)	0.385 5(4)	1.028 1(8)	0.463 4(4)
N(3)	−0.063 9(5)	0.559 2(9)	0.216 5(4)
N(4)	−0.096 2(5)	0.984 2(8)	0.370 1(4)
C(1)	0.229 8(4)	−0.087 9(8)	−0.025 7(4)
C(2)	0.198 1(4)	−0.178 6(8)	−0.093 9(4)
C(3)	0.194 8(5)	−0.102 8(10)	−0.170 0(4)
C(4)	0.223 7(5)	0.056 8(10)	−0.177 6(4)
C(5)	0.253 9(4)	0.145 7(9)	−0.110 9(4)
C(6)	0.258 0(4)	0.073 8(8)	−0.033 2(4)
C(7)	0.290 0(4)	0.154 2(8)	0.041 8(4)
C(8)	0.319 1(4)	0.316 4(8)	0.045 9(4)
C(9)	0.348 1(5)	0.384 2(8)	0.120 8(5)
C(10)	0.347 6(5)	0.292 7(9)	0.191 0(4)
C(11)	0.320 4(4)	0.130 7(9)	0.188 8(4)
C(12)	0.289 4(4)	0.062 6(8)	0.114 2(4)
C(13)	0.472 0(4)	0.644 7(7)	0.538 2(4)
C(14)	0.495 8(4)	0.477 2(8)	0.415 6(4)
C(15)	0.466 3(4)	0.629 2(7)	0.449 7(4)
C(16)	0.434 0(4)	0.753 8(8)	0.401 6(4)
C(17)	0.426 6(5)	0.735 8(8)	0.314 0(4)
C(18)	0.406 4(4)	0.907 2(8)	0.4351(4)
C(19)	−0.006 0(4)	0.421 8(9)	0.424 0(4)
C(20)	−0.021 2(4)	0.664 4(8)	0.510 2(4)
C(21)	−0.028 6(4)	0.591 1(8)	0.429 7(4)
C(22)	−0.055 5(4)	0.679 4(9)	0.362 1(4)
C(23)	−0.060 3(5)	0.610 6(10)	0.280 6(4)
C(24)	−0.078 1(5)	0.851 5(9)	0.366 5(4)

Discussion

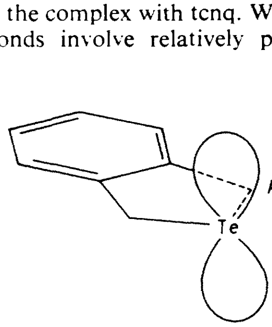
Generally, the reaction of organotellurium(II) compounds with tcnq in acetonitrile solution afforded complexes of 1 : 1 stoicheiometry. Exceptions were the two ditellurides considered, where the stoicheiometry was $R_2Te_2{\cdot}2tcnq$ (R = Ph or C_6H_4OEt-*p*) and 9,10-dihydro-9-telluranthracene, $C_{13}H_{10}Te$, which failed to give a complex. The conductivity of compacted discs was investigated and the data (Table 4) fall into two categories. Some complexes are clearly insulators; of most interest in the light of further discussion is the insulating nature of the complex of tcnq with 1,3-dihydro-2-telluraindene. The second group has conductivities some six- or seven-orders of magnitude greater. The two ditellurides give 1 : 2 complexes which show semiconducting behaviour (increase in resistivity on lowering the temperature). The complex of dibenzotellurophene gives a single-crystal conductivity of 10^{-7} Ω^{-1} cm^{-1}; this is significantly lower than the value of 0.8×10^{-4} Ω^{-1} cm^{-1} reported by Engler.[28] It is also of interest to note that the 2,1,3-benzoselenadiazole complex, $C_6H_4N_2$-Se·tcnq, initially voilet, turned green after 20 h *in vacuo* prior to spluttering on silver contacts. The conductivity reported (Table 4) is for the green modification. Solution conductivities were monitored for two complexes. Low conductivities in acetonitrile solution were observed which showed little concentration dependence.

Solid-state e.s.r. data in general show a single line which cannot be annealed out of the samples by heating and cooling. The *g* factor is, within the errors, the same for each sample and is very close to the free-electron value suggesting that the signal arises from unpaired electron density on tcnq. In no case was it possible to see a resonance from a tellurium centred radical. This was not surprising since even when reasonable evidence exists for the electrochemical formation of a radical cation such as that procured from phenoxatellurin, no e.s.r. signal was detected.[29] The authors attribute the failure to observe signals to the rapid formation of a dimer which, in turn, interacts with a neutral phenoxatellurin molecule to give a complex cation which may be isolated as the perchlorate. E.s.r. data have been obtained for anion radicals formed by electrochemical reduction of nitro-substituted phenoxatellurins,[30] however it is not surprising that unpaired spin density was largely associated with the nitro-groups. These remarks are of particular significance for the complex of tcnq with 1,3-dihydro-2-telluraindene which other data (see below) suggest to be ionic. Even for this compound no tellurium centred resonance is observed. This may be a consequence of the increasingly large spin–orbit coupling constant as the series S, Se, Te is traversed.[31] Thus in a series of radicals derived from a series of perinaphthalene-1,8-dichalcogenides, no spectrum was obtained from the ditelluride. Also, despite failure to observe signals from radical cations of phenoxatellurin, the selenium analogue does give a broad e.s.r. spectrum from which ^{77}Se hyperfine splitting is just discernible.[32] An alternative explanation could be that the 1,3-dihydro-2-telluraindene complex contains cation dimers with a singlet ground state.

Some i.r. data are given in Table 3. It was recently suggested that the degree of charge transfer in organic conductors could be monitored by examination of ν(CN) for tcnq.[33] The method is applicable only to conducting materials, however the compounds in Table 3 do fall into two categories: (*a*) those which show ν(CN) around 2 230 cm^{-1} (the value for neutral tcnq) and (*b*) the complexes of 1,3-dihydro-2-telluraindene and phenoxatellurin which show one ν(CN) around 2 180 cm^{-1}, a value similar to that observed for the salts Na^+tcnq^- and K^+tcnq^-. Only one compound fails to fit into these categories, namely the complex of 1-telluracyclohexane-3,5-dione. A simplistic conclusion would be that in the majority of cases there is very little charge transfer, but that in two cases essentially ionic compounds may have been formed.

It seemed possible that ^{125}Te Mössbauer spectroscopy would be a suitable method to probe the electronic structures of the complexes more deeply. An interesting set of data were obtained (Table 2) from which it is seen that two organotellurium compounds have significantly modified Mössbauer parameters in the presence of tcnq, namely Ph_2Te_2 and 1,3-dihydro-2-telluraindene. We synthesised a further complex of the latter donor with 2,3,5,6-tetrachloro-*p*-benzoquinone (' chloranil ') but this material gave, within the errors, values of δ and Δ indistinguishable from those of the telluride.

We have previously suggested that Mössbauer spectroscopy may be usefully used to set up a scale of Lewis acidity relative to a standard organotellurium base, $(p\text{-}EtOC_6H_4)_2Te$.[34] Withdrawal of *p*-electron density would lead to a reduction of Δ, hence the change in Δ could be correlated with the co-ordinate bond strength. An extension of this argument is applicable here. We have developed the argument for 1,3-dihydro-2-telluraindene (I). We assume that electron density will be removed from p_z in forming the complex with tcnq. We further assume that the Te–C bonds involve relatively pure tellurium *p*



(I)

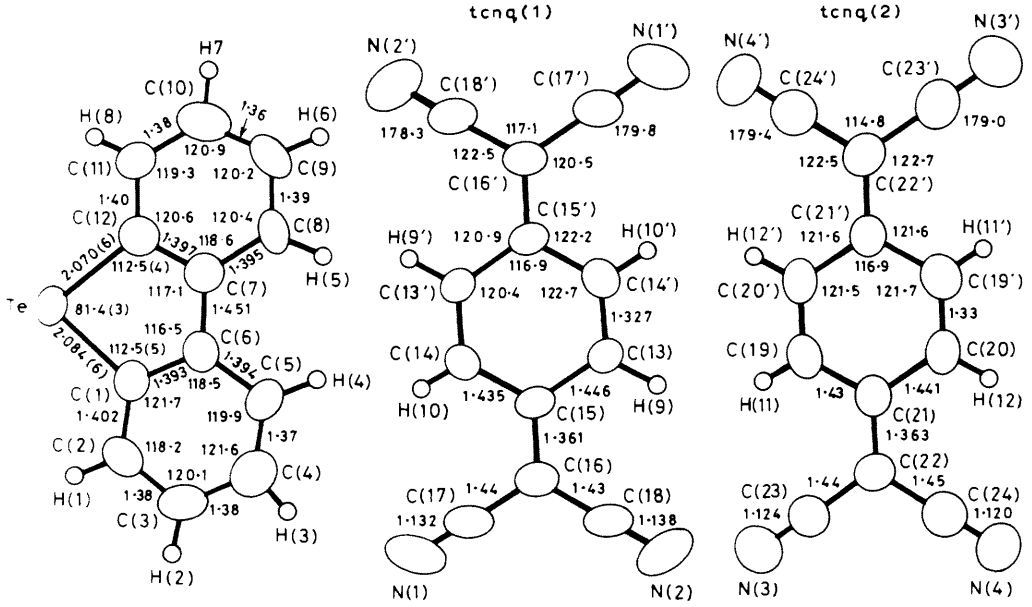


Figure 1. Perspective views of dbt and tcnq with atom-labelling schemes, interatomic distances (Å), and angles (°). The estimated standard deviations are 0.008—0.01 Å for the C–C distances and 0.5—0.9° for the C–C–C angles

orbitals. Some justification for these assumptions is available. The ionisation potential of (I) was measured by mass spectrometry using the extrapolated voltage-difference method [35] and a value of 6.55 eV (1 eV = 9.65 kJ mol^{-1}) obtained; a figure which certainly implies ionisation from a $\pi(p)$-type orbital. Furthermore the significant increase in δ (Table 2) is consistent with deshielding of the s electrons by removal of p-electron density.

Estimates of ionisation potentials made for other tellurium(II) compounds include 9,10-dihydro-9-telluranthracene (10.25 eV), diphenyl telluride (8.85 eV), and phenoxatellurin (8.75 eV). The latter figure illustrates the problem of mass-spectroscopically deduced values often being greater than those obtained from other methods since a value of 7.61 eV has been obtained for phenoxatellurin by photoelectron spectroscopy.

The assumption of relatively pure tellurium p-orbital involvement in the Te–C bonds of (I) has some indirect support from the crystal structure of the di-iodide of (I) [36] in which at 86° the C–Te–C angle is close to the ideal 90°. Similar C–Te–C angles are observed for a series of telluronium salts derived from (I).[37]

Given the above assumptions, equation (i) follows,[24] where

$$\Delta/12 = U_z - U_c \qquad \text{(i)}$$

Δ is the ^{125}Te Mössbauer quadrupole splitting (mm s^{-1}), U_z the occupancy of the p_z orbital (2.00 for the free telluride), and U_c the occupancy of the p_x and p_y orbitals (calculated to be 1.14). If electron density is withdrawn from p_z, the occupancy of p_x and p_y should change as tellurium becomes more positive, thus giving equation (ii) for the complex, where σ is the new

$$\Delta(\text{complex})/12 = \sigma - [a_0 + A(2 - \sigma)] \qquad \text{(ii)}$$

occupancy of p_z, a_0 = 1.14, and A is a positive constant reflecting the increased occupancy of p_x and p_y which is assumed to be proportional to the electron withdrawal from p_z,[38] *i.e.* $(2 - \sigma)$, thus giving equation (iii). Hence, for a series of

$$\Delta(\text{complex})/12 = \sigma(A + 1) - (a_0 + 2A) \qquad \text{(iii)}$$

complexes of (I) (or indeed for any given organotellurium donor) with a range of acceptors, Δ(complex) is linearly related to σ, or $(2 - \sigma)$ the quantity of charge transferred. This should then be a useful addition to other methods for the estimation of the degree of charge transfer. There is one proviso in using the method, namely that all measurements are made at 4 K and should strictly be compared with other physical measurements at the same temperature.

It would appear that there is a negligible transfer of charge from the tellurium p_z orbital of (I) in its complex with chloranil, thus the variation of Δ with acceptor is illustrated. The Mössbauer data for the two complexes and the normal value of Δ for (I) make it improbable that the interaction of (I) with the acceptors is of the π–π type, a proposal that has more reasonably been made for the tcnq complex of phenoxatellurin.[9]

In an effort to produce a derivative of (I) in which $(2 - \sigma)$ was unambiguously equal to unity (and hence to evaluate A), attempts have been made to oxidise electrochemically the telluride. To date very small yields of materials such as $(C_8H_8Te)PF_6$ have been obtained, more work is required on the synthesis and the compounds will be the subject of a future paper. In the meantime it is suggested that $(C_8H_8Te)\cdot$tcnq is appreciably ionic.

The only other complex in which significant charge transfer is present is that of diphenyl ditelluride with tcnq. Given that some tetratellurafulvalene compounds are now available [5,6] it will be interesting to see the variation of ^{125}Te Mössbauer parameters with acceptor as more complexes become available for study.

*Crystal and Molecular Structure of Dibenzotellurophene–7,7,8,8-Tetracyano-*p*-quinodimethane.*—The structure of dbt·tcnq consists of quasi-hexagonal packed mixed stacks of alternating donor and acceptor molecules parallel to the *a* axis. A stereoscopic packing diagram appears in SUP No. 23903. A perspective view of the dbt·tcnq components together with the atom-labelling scheme, distances, and angles is given in Figure 1. The dbt and tcnq molecules are nearly

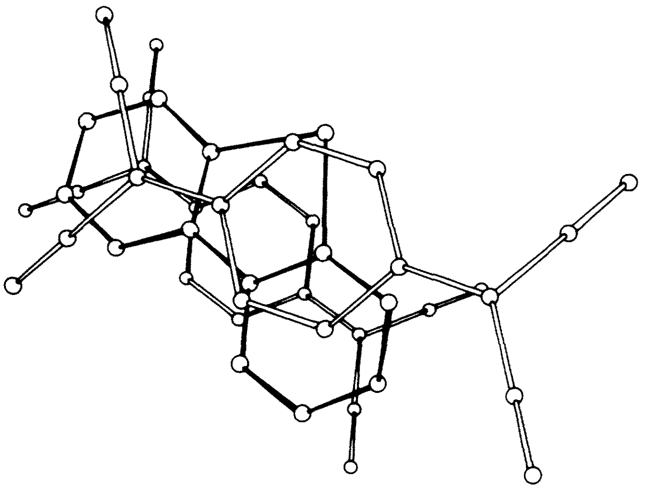


Figure 2. Overlap diagram of dbt·tcnq

planar and are dimensionally identical * to the uncomplexed dbt [39] and tcnq [40] molecules, consistent with a found charge of zero for the tcnq molecule [41] in the present structure. This is also consistent with conclusions from i.r. and Mössbauer data.

Of particular interest in the structure is the relative arrangement of the dbt and tcnq components. Since the tcnq molecules are located on the centres of symmetry of space group $P2_1/n$, the two unique halves of tcnq occur in different molecules. In the present structure, this situation gives rise to different orientations of tcnq above and below the tellurium donor as illustrated in Figure 2. In one case [tcnq(2), background and containing N(3)], the ring-external bond type of overlap is observed similar to that found in (1 : 1) tcnq complexes of carbazole [42] and dibenzothiophene (dibenzo-[*b,d*]thiole).[43] In the present case the long axis of tcnq(2) is rotated approximately 4° with respect to that of the donor with the molecules slightly displaced along the axes. The mean interplanar spacing between the least-squares planes of the donor and acceptor is 3.45 Å with the acceptor atom donor-plane distances ranging from 3.165 to 3.736 Å. The dihedral angle between the planes is 3.5°. In the second orientation [tcnq(1), foreground and containing N(1)], the long axis of the acceptor is rotated approximately 24° with respect to that of the donor to give a donor–acceptor arrangement similar to that observed in the tcnq complex of 1,10-phenanthroline.[44] In this case, the arrangement of dbt and tcnq(1) is skewed to an even greater extent than in the case of tcnq(2). The dihedral angle between the planes is 5.7° with a consequently slightly larger mean interplanar spacing of 3.51 Å (range 3.259—3.769 Å). Semi-empirical calculations [45] suggest that the orientation in the tcnq complex of 1,10-phenanthroline is close to the one most favourable for charge-transfer interactions. In the present structure, both orientations lead to only weak charge-transfer interaction as noted above, consistent with the relatively large separations between the planes of adjacently stacked molecules. The two-mode orientation of tcnq in dbt·tcnq is a unique feature of the complex.

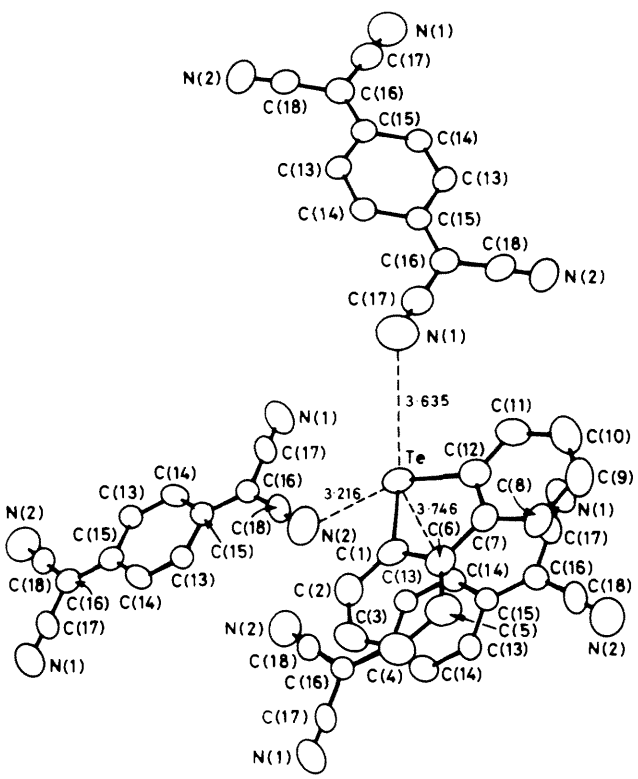


Figure 3. Co-ordination geometry and contacts (Å) about tellurium in dbt·tcnq

The co-ordination geometry about Te and the relative orientation of the tcnq molecules involving close contacts to tellurium is illustrated in Figure 3. The most significant intermolecular interaction occurs between stacks through the short Te · · · N(2) (0.5 – *x*, –1.5 + *y*, 0.5 – *z*) contact at 3.216(6) Å. This value is approximately 0.4—0.5 Å shorter than the van der Waals distance,[46,47] and is comparable to the short Te · · · N secondary bonding interactions in $Ph_3Te(SCN)$ [48] and $Ph_3Te(NCO)$.[49] Other contacts between Te and tcnq at or near the van der Waals distances involve again only tcnq(1) and are the interstack Te · · · N(1) (*x*, –1 + *y*, *z*) contact at 3.635(7) Å and the intrastack Te–C(14) (0.5 – *x*, –0.5 + *y*, 0.5 – *z*) contact at 3.746(6) Å. Although Te^{II} is typically square planar,[50] the long Te · · · N(1) distance and the N(2) · · · Te–C angles [86.79, C(1); 160.73°, C(12)] suggest a distorted geometry for Te in the present structure with N(2) 0.85 Å out of the least-squares plane of the dbt molecule. All other intermolecular distances involving Te and tcnq (non-hydrogen atoms) are greater than 3.8 Å. All intermolecular C–C distances less than 3.5 Å (van der Waals distance, 3.4 Å) [47] are between dbt and tcnq in the stack. These distances (all 0.5 – *x*, –0.5 – *y*, 0.5 – *z*) are C(10)–C(22) 3.36(1), C(8)–C(20) 3.402(9), C(9)–C(24) 3.43(1), C(2)–C(14′) 3.432(9), C(8)–C(18) 3.455(9), C(6)–C(13) 3.463(8), C(3)–C(14′) 3.47(1), and C(12)–C(19) 3.492(9) Å. The only intermolecular C–N distance less than 3.4 Å is N(3)–C(17) (0.5 – *x*, –0.5 + *y*, 0.5 – *z*) at 3.39(1) Å.† Thus, interactions appear to occur between adjacent molecules within the stacks as well as between molecules in

---

* The root-mean-square (r.m.s.) discrepancy between the complexed and uncomplexed molecules, in both cases, is 0.01 Å or approximately one e.s.d. No respective bond length differs by more than 3 e.s.d.s and the maximum difference for any bond angle is less than 2 e.s.d.s, the r.m.s. discrepancy being less than 1°. The r.m.s. deviations for the non-hydrogen atoms from their their respective dbt, tcnq(1), or tcnq(2) least-squares planes are 0.011, 0.016, and 0.017 Å respectively. These values are close to the e.s.d.s of the C-atom positions.

† All of the intermolecular C–H and N–H distances are greater than 2.9 Å except N(1)–H(11) [0.5 – *x*, 0.5 + *y*, 0.5 – *z*] at 2.75(7) Å, N(2)–H(1) (0.5 – *x*, – 0.5 + *y*, 0.5 – *z*) at 2.68(8) Å, and N(4)–H(4,5) [– 0.5 + *x*, 1.5 – *y*, 0.5 + *z*] at 2.9(1) and 2.7(1) Å, respectively. There are no close H–H contacts; the shortest is H(2)–H(3) [0.5 – *x*, – 0.5 + *y*, –0.5 – *z*] at 2.8(1) Å.

different stacks. It is the latter feature which further distinguishes the structure from those of other mixed-stack equimolar donor–acceptor complexes where the only significant intermolecular interactions occur between molecules within a stack.

Since charge-transfer interactions are weak in dbt·tcnq, the Te ··· N(2) secondary bonding and packing considerations appear to be the major factors influencing the orientation of tcnq(1). In the absence of this interaction, the ring-external bond orientation [tcnq(2)] is observed, presumably, for the reasons suggested by Wright and Ahmad[43] in their discussion of the structure of the tcnq complex of dibenzothiophene. In the latter complex where there are two independent tcnq molecules, secondary bonding is absent and only one mode to overlap is observed. Thus, it appears that the size and coordination requirements of the chalcogen atom play an important role in determining the crystal structures and packing arrangements of these complexes. A similar conclusion was reached by Wright and Ahmad[43] in their study of the tcnq complexes of dibenzothiophene and dibenzofuran. The structure of the analogous selenium complex has not been reported.

Acknowledgements

One of us (H. B. S.) thanks the Government of India for a study scholarship. We are grateful to Dr. R. W. Fane (Department of Physics, University of Aston in Birmingham) for providing facilities for compressed-disc conductivity measurements, also to Dr. A. J. Epstein (Xerox Corporation) for the single-crystal measurement on dbt·tcnq.

References

1 J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79.
2 E. M. Engler, B. A. Scott, S. Etemad, T. Penney, and V. V. Patel, *J. Am. Chem. Soc.*, 1977, **99**, 5909.
3 D. Jerome, A. Mazand, M. Ribault, and M. Bechgaard, *J. Phys. Lett.*, 1980, **41**, L-95.
4 K. Bechgaard, K. Carneiro, F. B. Rasmussen, H. Olsen, C. S. Jacobsen, H. J. Pederson, and J. C. Scott, *J. Am. Chem. Soc.*, 1981, **103**, 2440.
5 K. Lestrup, D. Talham, A. Bloch, T. Poehler, and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 1982, 336.
6 F. Wudl and E. Aharon-Shalom, *J. Am. Chem. Soc.*, 1982, **104**, 1154.
7 D. Dauplaise, J. Meinwald, J. C. Scott, H. Temkin, and J. Clardy, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 382; J. Meinwald, D. Dauplaise, F. Wudl, and J. J. Hauser, *J. Am. Chem. Soc.*, 1977, **99**, 255.
8 D. J. Sandman, J. C. Stark, and B. M. Foxman, *Organometallics*, 1982, **1**, 739.
9 D. P. Rainville, R. A. Zingaro, and J. P. Ferraris, *Can. J. Chem.*, 1980, **58**, 1133.
10 F. Wudl, 'The Physics and Chemistry of Low Dimensional Solids,' ed. L. Alcacer, D. Reidel Publishing Co., New York, 1980, pp. 265—279.
11 J. B. Torrance, J. J. Mayerle, V. Y. Lee, R. Bozio, and C. Pecile, *Solid State Commun.*, 1981, **38**, 1165.
12 L. R. Melby, R. J. Harder, W. R. Hartler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
13 J. D. McCullough, *Inorg. Chem.*, 1975, **14**, 2885.
14 R. F. Ziolo and W. H. H. Gunther, *J. Organomet. Chem.*, 1978, **146**, 254.
15 H. D. K. Drew, *J. Chem. Soc.*, 1926, 223.
16 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1920, 1462.
17 W. R. McWhinnie and M. G. Patel, *J. Chem. Soc., Dalton Trans.*, 1972, 199.
18 W. H. H. Gunther, J. Nepywoda, and J. Y. C. Chu, *Organomet. Chem.*, 1974, **74**, 79.
19 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, 2307.
20 M. G. Patel, Ph.D. Thesis, University of Aston, Birmingham, 1972.
21 W. Lohner and K. Praefcke, *J. Organomet. Chem.*, 1981, **205**, 167.
22 L. S. Efros and Z. V. Todres-Selektor, *J. Gen. Chem. (USSR)*, 1957, **27**, 1064.
23 F. H. Kruse, R. W. Sanftner, and J. F. Suttle, *Anal. Chem.*, 1953, **25**, 500.
24 C. H. W. Jones, R. Schultz, W. R. McWhinnie, and N. S. Dance, *Can. J. Chem.*, 1976, **54**, 3234.
25 D. T. Cromer and J. T. Waber, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. **4**, Table 2.2B.
26 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.
27 Ref. 25, Table 2.3.1.
28 E. M. Engler, Proc. 3rd Int. Symp. on Organic Selenium and Tellurium Compounds, eds. D. Cagniant and A. Kirsch, University of Metz, France, 1979, p. 357.
29 G. Cauquis and M. Maurey-Mey, *Bull. Soc. Chim. Fr.*, 1973, **291**.
30 A. Gioaba, V. Em. Sahini, and E. Volanschi, *J. Chem. Soc., Perkin Trans. 2*, 1977, 529.
31 H. Bock, G. Brahler, D. Dauplaise, and J. Meinwald, *Chem. Ber.*, 1981, **114**, 2622.
32 B. Lamotte and G. Berthier, *J. Chem. Phys.*, 1966, **63**, 369; H. F. Chiu and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1973, **258**.
33 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.
34 I. Davies, W. R. McWhinnie, N. S. Dance, and C. H. W. Jones, *Inorg. Chim. Acta*, 1978, **29**, L203.
35 J. W. Warren, *Nature (London)*, 1950, **165**, 810.
36 C. Knobler and R. F. Ziolo, *J. Organomet. Chem.*, 1979, **178**, 423.
37 R. H. Jones and T. A. Hamor, *J. Organomet. Chem.*, 1982, **234**, 299.
38 Yu-Nian Hsieh, G. V. Rubenacker, C. P. Cheng, and T. L. Brown, *J. Am. Chem. Soc.*, 1977, **99**, 1384.
39 J. D. McCullough, *Inorg. Chem.*, 1975, **14**, 2539.
40 R. E. Sorg, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 932.
41 F. H. Herbstein, in 'Perspectives in Structural Chemistry,' eds. J. D. Duiritz and J. A. Ibers, John Wiley and Sons, New York, 1971, vol. 4, p. 355.
42 H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2675.
43 J. D. Wright and Z. A. Ahmad, *Acta Crystallogr., Sect. B*, 1981, **37**, 1848.
44 I. Goldberg and U. Schmueli, *Acta Crystallogr., Sect. B*, 1977, **33**, 2189.
45 I. Goldberg, *Theor. Chim. Acta*, 1975, **40**, 271.
46 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
47 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.
48 J.-S. Lee, D. D. Titus, and R. F. Ziolo, *Inorg. Chem.*, 1977, **16**, 2487.
49 D. D. Titus, J.-S. Lee, and R. F. Ziolo, *J. Organomet. Chem.*, 1976, **120**, 381.
50 S. Husebye, Proc. 4th Int. Conf. on the Organic Chemistry of Selenium and Tellurium, University of Aston, 1983.

Received 11th March 1983; *Paper* 3/385