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Charge transfer complexes: synthesis of 3,5-naphtho-1-telluracyclohexane, a new electron donor

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Abstract

The reaction of 1,8-bis(bromomethyl)naphthalene with tellurium powder and sodium iodide gives the orange 3,5-naphtho-1-telluracyclohexane-1,1-diiodide which on reduction gives 3,5-naphtho-1-telluracyclohexane. Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with elemental tellurium and sodium iodide gives the yellow 1,2,4,5-bis(diiodotelluracyclopentano)bezene, which upon reduction affords a highly insoluble material. 3,5-Naphtho-1-selenahexane has been prepared in excellent yield by treating sodium selenide with 1,8-bis(bromomethyl)napthalene. Charge-transfer complexes of the telluride and of telluracyclohexane and telluracyclopentane are reported.

Introduction

The charge-transfer complexes of selenium and tellurium donors represent a promising new subject of research [1]. We have recently described the charge-transfer (CT) complexes of a series of tellurium donors [2,3]; in particular we observed that for the complex of 3,4-benzo-1-telluracyclopentane (I) with 7,7,8,8-tetracyanoquinodimethane (TCNQ) there is significant charge-transfer and that telluraxanthene (II) does not give a complex. Electrochemical oxidation of I to a rare oxidation state of Te^{III} was observed [4].

^{125}Te Mössbauer studies suggested that the electron density was removed from *p*-orbital of tellurium in forming the I-TCNQ complex and that the interaction was not of the π–π type, a proposal made for phenoxatellurine III-TCNQ complex [5]. In view of these interesting observations we decided to find out whether other molecules containing telluracyclopentane and telluracyclohexane rings would show similar effects. As part of our studies of CT, we now report the synthesis of the hitherto unknown heterocyclic compounds 1,1-diiodo-3,5-naphtho-1-telluracy-

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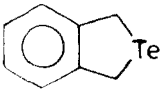

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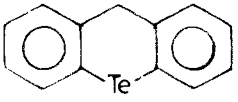

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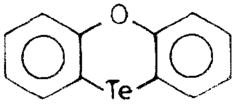

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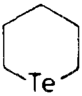

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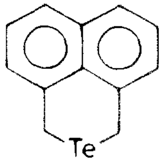

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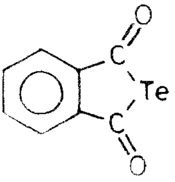

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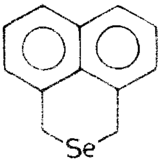

(VIII)

clohexane and 1,2,4,5-bis(diiodotelluracyclopentano)benzene. CT complexes of the new donor (VI) as well as of some related donors (IV, V) with TCNQ, have been studied.

Experimental

Synthesis. 1,8-Bis(bromomethyl)naphthalene, 1,2,4,5-tetrakis(bromomethyl)benzene and TCNQ were obtained from Aldrich. Tellurium and selenium powder were obtained from Fluka. 1-Telluracyclopentane [6], 1-telluracyclohexane [7] and tellurophthalic anhydride [8] were by published methods. 3,5-Naphtho-1-selenahexane was prepared by a modified method in excellent yields [9a].

1,1-Diiodo-3,5-naphthotelluracyclohexane. A mixture of 1,8-bis(bromomethyl)naphthalene (1.0 g, 0.0032 mol), powdered tellurium (0.4 g, 0.0032 mol) and potassium iodide (2.1 g, 0.012 mol) in 2-methoxyethanol (50 ml) was stirred under gentle reflux for 2 h, during which some precipitation occurred. Water (100 ml) was added to complete the precipitation, and the precipitate was then filtered off, washed with water then acetone, and air dried. It was recrystallised from 2-methoxyethanol to give orange crystals, m.p. 220–222° C.

3,5-Naphtho-1-telluracyclohexane. To a suspension of 1,1-diiodo-3,5-naphthotelluracyclopentane (0.62 g) in ethanol (40 ml) and water (10 ml) was added dropwise a solution of hydrazine hydrate (0.24 g) in ethanol (10 ml). The mixture was warmed gently until all the solid has dissolved, was then poured into water (100 ml). After extraction with ether the ethereal layer was separated and dried over anhydrous sodium sulphate, and the solvent then removed on a rotary evaporator. The yellowish powder was dissoluted in ether containing charcoal, and the filtered solution then evaporated to give yellow needles, m.p. 102–104° C.

1,2,4,5-Bis(diiodotelluracyclopentano)benzene. This compound was made by treating 1,2,4,5-tetrakis(bromomethyl)benzene (1.0 g, 2.2 mmol) with elemental tellurium (0.566 g, 4.4 mmol) under the conditions described for 1,1-diiodo-3,5-naphtho-1-telluracyclohexane. Recrystallisation from 2-methoxyethanol afforded a deep yellow powder, m.p. 217–218 ° C (d).

Attempted synthesis of 1,2,4,5-bis(telluracyclopentano)benzene. Reduction of 1,2,4,5-bis(diiodotelluracyclopentano)benzene with hydrazine hydrate gave a greenish yellow powder, m.p. 205 ° C. Attempted direct synthesis of this compound by reaction of sodium telluride [10] with 1,2,4,5-tetrakis(bromomethyl)benzene either in one phase or under two phase conditions [8] also gave the greenish yellow powder.

3,5-Naphtho-1-selenocyclohexane. To a well-stirred suspension of selenium (0.12 g, 1.59 mmol) in water was added sodium borohydride (0.12 g, 1.59 mmol) in water (25 ml) at room temperature. The selenium was consumed within 10 min. 1,8-Bis(bromomethyl)naphthalene (0.5 g, 1.59 mmol) in toluene (25 ml) was then added through a dropping funnel. After addition of the phase-transfer catalyst, tetrabutylammonium hydrogensulphate (0.1 g), the temperature was raised to 60 ° C and kept at 60 ° C for 8 h. The organic layer was separated, washed with 5% aqueous sodium carbonate, then evaporated in vacuo to give an orange product. Recrystallisation from petroleum ether (40–60 ° C) yielded orange crystals, m.p. 82 ° C (lit. [9a] 83.5–84.5 ° C).

Charge-transfer complexes. All the complexes were synthesised by an essentially similar procedure, and only one typical procedure is described.

Telluracyclopentane-TCNQ. To a warm solution of telluracyclopentane (0.20 g, 1.1 mmol) in acetonitrile (20 ml) was added a warm solution of TCNQ (0.2 g, 1.1 mmol) in acetonitrile (20 ml). The resulting solution was stirred and refluxed for 1 h, then evaporated in vacuo to leave a dark violet powder, which was washed with petroleum ether (40–60 ° C) and dried, m.p. 161–162 ° C.

Physical measurements. Analysis for C and H was by the Analytical Services Section, RSIC, Lucknow. Infrared spectra were recorded for KBr discs with a Perkin–Elmer 681 instrument. The mass spectrum was determined at 70 eV with Varian MAT 1125 instrument. The UV/visible spectra in solution were recorded with a Shimadzu UV 260 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL FX 100 instrument with TMS as internal standard. ESR data were obtained with a Varian E-112 spectrometer (X band) with TCNE as g marker ($g = 2.00277$).

Results and discussion

The novel heterocycle (VI) was conveniently synthesised by reduction of the readily accessible diiodide X (Scheme 1). A study of ring inversion of this compound together with O, S and Se analogues has recently appeared [9b], but no synthetic details were given. The diiodide XI was also synthesised in goods yield, but it attempted reduction to give X, gave only an intractable solid, which was insoluble in the majority of common solvents and could not be purified. Attempted direct synthesis by the reaction of Na_2Te with 1,2,4,5-tetrakis(bromomethyl)benzene (XIII) yielded the same product, probably a polymer.

The new heterocycles obtained were satisfactorily characterised by elemental analysis, UV/visible, IR and NMR spectra. The data are summarised in Table 1, 2. In particular, the mass spectrum study of XI was in good agreement with the proposed structure, and the main fragmentation pathways are shown in Scheme 2.

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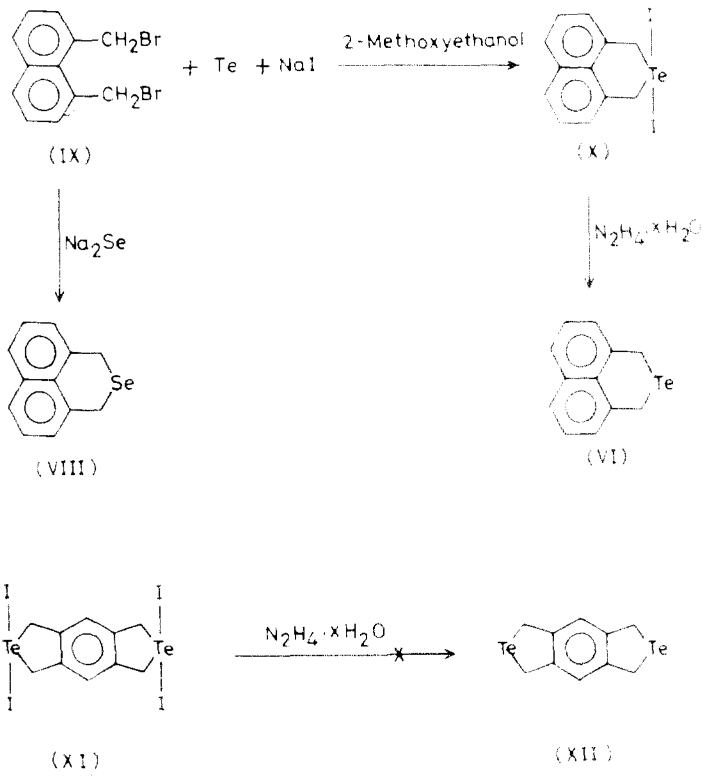
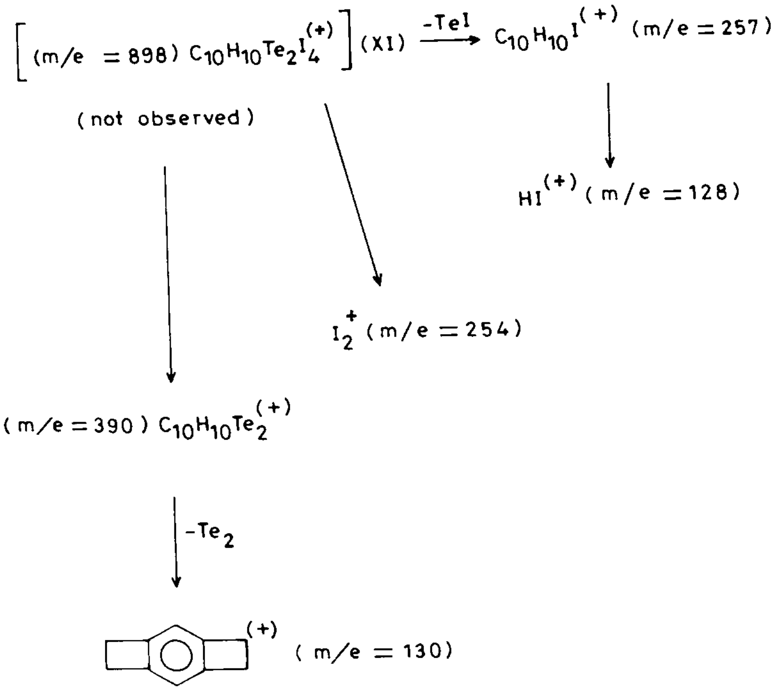


Scheme 1

Table 1

Analytical data

Compound	Colour	M.p. (°C)	Yield (%)	Analyses (Found (calcd.)(%))	
				C	H
X	orange	220–222 (d)	58	26.1 (26.9)	2.25 (1.88)
VI	yellow	102–104	46	50.6 (51.1)	3.88 (3.58)
VI·TCNQ	black	158 (d)	100	59.5 (59.3)	2.38 (2.90)
XI	yellow	217–219 (d)	80	15.1 (14.5)	1.23 (1.12)
IV·TCNQ	dark violet	161	88	49.1 (48.8)	3.09 (3.10)
V·TCNQ	dark brown	160	90	50.4 (50.8)	3.73 (3.49)
VII	orange	82 (Lit. [9a] 83.5–84.5)	68	61.2 (61.8)	4.14 (4.32)



Scheme 2

Table 2

Spectroscopic data

Compound	UV-VIS spectra (λ_{max}, nm)	IR (cm^{-1}) [c]	^1H NMR (δ ppm vs. TMS), J (Hz))	ESR g factor
X	398, 317, 230 [a]	470 (ν(Te–C))	5.0 (CH_2, s, 4H), 7.6–8.2 (aromatic, m, 8H) [d]	–
VI	315, 236 [a]	450 (ν(Te–C))	4.45 (CH_2, s, 4H, J(TeH) 26), 7.2–7.8 (aromatic, m, 8H) [e]	–
VI·TCNQ	655, 629, 315 [b]	2205s (ν(C≡N))	–	2.00
XI	337, 269 [a]	517m (ν(Te–C))	4.6 (CH_2, s, 4H), 7.4 (aromatic, s, 2H) [d]	–
IV·TCNQ	648 [b]	2170vs, 2200w (ν(C≡N))	–	2.00
V·TCNQ	623 [b]	2160vs, 2200w (ν(C≡N))	–	2.00
VII	300, 232 [a]	–	4.52 (CH_2, s, 4H), 7.2–7.8 (aromatic, m, 8H) [e]	–
XIII	334, 211 [a]	–	4.8 (CH_2, s, 4H) 7.6 (aromatic, 2H) [d]	–
IX	304, 233 [a]	–	5.6 (CH_2, s, 4H), 7.5–8.2 (aromatic, m, 8H) [e]	–

[a] CH_2Cl_2. [b] CH_3CN. [c] KBr. [d] DMSO-d_6. [e] $CDCl_3$.

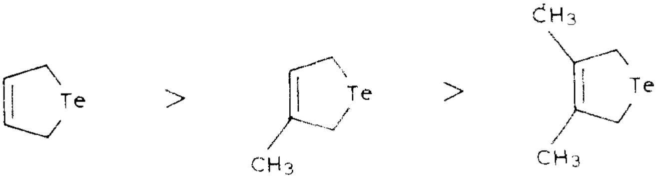
No molecular ion was observed in the 70 eV spectrum. The observation of $(C_{10}H_{10}Te_2)^+$ cluster ion as a major tellurium-containing fragment is significant.

In contrast to compound VI, its selenium analogue, VIII was found to be best prepared (in excellent yields) by using phase transfer catalysis techniques.

Charge-transfer complexes. The reaction of the organotellurium (Te^{II}) donors with TCNQ in acetonitrile solution afforded 1/1 complexes. No complex was isolated from VII.

The UV-VIS spectra for the 1/1 complexes show a new band in the region 623–655 nm in acetonitrile. This absorption is ascribed to the charge-transfer (HOMO-LUMO transition) complexes, since neither the donors nor the π-acceptor separately absorb in this region.

A quantitative measure of the degree of CT can be obtained from either diffuse X-ray measurements [11] or vibrational spectra [12], and we recently suggested the use of ^{125}Te Mössbauer spectroscopy [2]. For our complexes we used vibrational spectroscopy, focusing on the nitrile stretching mode of the TCNQ anion [12]. All the complexes show the $\nu(C\equiv N)$ stretching vibration in the region 2160–2205, typical of $TCNQ^{\cdot-}$ (cf. Li^+ $TCNQ^{\cdot-}$ 2160 and 2205, $TCNQ^0$ 2230 cm^{-1}), suggesting significant radical-ion character in all these complexes. In particular telluracyclopentane and telluracyclohexane complexes are probably ionic in the ground state, i.e. $(C_4H_8Te)^{\cdot+}(TCNQ)^{\cdot-}$. Owing to the presence of a unit charge on each TCNQ, semiconducting behaviour can be expected for the present complexes. The fact that anomalously high electron donor effects were also observed for III and IV, unambiguously supports the hypothesis that localised p-electrons on tellurium take part in coordination with π-acceptors and not with the delocalised π-orbitals of the heterocycle [2]. This suggestion is further supported by interesting observations of McWhinnie et al. [13], who found that the order of donor strength in CT complexes of 2,5-dihydrotellurophene and the 3-methyl and 3,4-dimethyl derivatives towards TCNQ is:



This is not surprising in view of the fact that species in which a hetero-atom is not directly linked with the π-system usually act as p-donors towards σ- and π-acceptors [14].

The poor electron-donating properties of VIII are probably due to electron-withdrawing properties of the carbonyl groups.

ESR measurements on the solid complexes gave a sharp signal which was superimposable on the signal of the standard (g value 2.0027), indicating that the spins seem to be observable only on the TCNQ. In no case was the signal due to the radical cation observed.

Acknowledgements

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