Results and discussion

The charge-transfer complexes of the cyclic tellurides (1-4) and thione (7) were synthesised by mixing boiling solutions of the donor and acceptor in 1:1 stoichiometry using acetonitrile as the solvent. The complexes were dark red to brown crystalline solids. The results of elemental analysis (Table 1) authenticated the 1:1 stoichiometries of the complexes. The complexes have also been characterised by IR, UV-Visible and ESR spectroscopic techniques. The data are presented in Table 2. It has been suggested that the degree of charge transfer (C-T) in donor-acceptor complexes could be monitored by examination of $\nu(\text{C} = \text{O})$ and $\nu(\text{C} = \text{N})$ modes of TCNQ. The strong $\nu(\text{C} = \text{O})$ absorption of DDQ at 1680 cm$^{-1}$ was absent in the complexes, instead the characteristic absorption of phenoxy radical (1560-1565 cm$^{-1}$) appeared. The $\nu(\text{C} = \text{N})$ absorption of neutral DDQ (2222 cm$^{-1}$) was shifted slightly but the intensity was enhanced in the case of complexes with (2) and (3), whereas in other DDQ complexes band position was shifted considerably. All these observations clearly indicate that DDQ radical ion (DDQ$^-$) is formed and the complexes have considerable ionic character. The nitrile stretching frequency of the TCNQ complex, (7): TCNQ, was shifted to 2218 cm$^{-1}$ compared to 2230 cm$^{-1}$ in neutral TCNQ suggesting radical ion character of the complex.

The UV spectra of telluride-DDQ complexes in acetonitrile showed the presence of a new band in the region 395-470 nm which was originally absent in the reactants. This band can be interpreted in terms of charge-transfer (HOMO $\rightarrow$ LUMO) transition. Similar type of bands have been observed by Brandon et al. in the electronic spectra of $\text{M}^+$-DDQ$^-$ complex ($\text{M}^+ = \text{metallicinium}$). This suggests a radical-ion character of the complex. The TCNQ complex of (7) showed a new band at 398 nm which has been attributed to TCNQ $^+$+ TCNQ$^-$ complex. McWhinnie et al. have also observed a similar type of band in the C-T complex of TCNQ with 1,3-dihydrotellurolo[3,4-$h$]-quinoxaline. The other bands observed in C-T complexes of (7) with TCNQ are due to thione (7).

Sharp single signals were observed in the ESR spectra of the complexes. The signals were superimposable with marker signal suggesting that the signals were due to unpaired electron on DDQ and TCNQ. It is worth noting that (5) and (6) did not react with DDQ and TCNQ.
Table 1—Analytical data for donor-acceptor complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P. ('C)</th>
<th>Found (Calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>(1):DDQ</td>
<td>Dark red</td>
<td>107-110</td>
<td>35.00 (35.09)</td>
</tr>
<tr>
<td>(2):DDQ</td>
<td>Dark red</td>
<td>90-92</td>
<td>36.14 (36.76)</td>
</tr>
<tr>
<td>(3):DDQ</td>
<td>Brown</td>
<td>105</td>
<td>41.12 (41.86)</td>
</tr>
<tr>
<td>(4):DDQ</td>
<td>Brown</td>
<td>179(d)</td>
<td>46.34 (47.20)</td>
</tr>
<tr>
<td>(7):TCNQ</td>
<td>Brown</td>
<td>220(d)</td>
<td>57.92 (58.46)</td>
</tr>
</tbody>
</table>

Experimental

IR spectra were recorded in KBr on a Perkin Elmer 681 instrument. Electronic spectra were recorded in acetonitrile on a Shimadzu UV-260 spectrophotometer. ESR spectra were recorded on a Varian E-112 ESR spectrometer using TCNE (tetracyanoethylene) as the g-marker (g = 2.00277) at room temperature. The syntheses of donors 1-telluracyclohexane, 1-telluracycloptane, 3,4-benzo-1-telluracycloptane, 3,5-naphtho-1-telluracyclohexane, 3,5-naphtho-1-selenacyclohexane and 4,5-{1,8-bis(thiomethyl)naphthalene}-1,3-dithiole-2-thione were reported elsewhere. DDQ and TCNQ were obtained from Aldrich.

All the complexes were synthesised by essentially similar methods; a typical synthesis is described below:

Synthesis of 3,5-naphtho-1-telluracyclohexane-DDQ complex

A warm acetonitrile solution (10 ml) of 3.5-naphtho-1-telluracyclohexane (30 mg, 0.10 mmol) was added to a warm acetonitrile solution of a DDQ (24 mg, 0.10 mmol). The reaction mixture was refluxed for 1h after which the volume was reduced. On cooling to room temperature the complex was obtained. The dark brown solid was filtered, washed with acetonitrile and dried.

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