

## THE EFFECT OF TWO SUBSTITUENTS ON DIFFERENT ORGANOSELENIDES AND TELLURIDES TO FORM NEW CHARGE - TRANSFER COMPLEXES

Khalid Y. Abid \* and A.R. Tahir

\* Sana's University, Sana's - Republic of Yemen

\*\* Al-Tahtay University, Misratta -Libya.

تأثير مجموعتين معوضتين على بعض مركبات السلينيوم  
والتلوريوم العضوية لتكوين معقدات انتقال شحنات جديدة  
خالد يحيى عبد و عبد الرحيم طاهر

تم في هذا البحث تحضير العديد من مركبات السلينيوم والتلوريوم العضوية الجديدة ودُرس تأثير مجموعتين معوضتين هما methoxy - و nitro - على هذه المركبات عندما تكون معقدات جديدة لانتقال الشحنات مع مركبات عضوية تعمل كمستقبلات للإلكترون .

المعقدات الجديدة تم تأكيدها من خلال نتائج التحليل الكيمائية والفيزيائية وتبين أن هذه المعقدات قد تكونت عبر روابط كيميائية ضعيفة وأن تأثير المجموعتين المعوضتين كان محدوداً على مثل هذه المعقدات .

**Kew words :** Charge - transfer, Complexes, P-Benzoquinone, Methoxy group, Nitro group

### ABSTRACT

Different organotellurides and selenides were prepared as electron donors and reacted with p-Benzoquinone (p-BQ) and m-Dinitrobenzene (m-DNB) as electron acceptors.

The resulted molecules were considered as new charge transfer complexes. The physical and analytical data proved that this type of complexes were formed via very weak interaction.

## INTRODUCTION

During the last few years interest has grown in the study of intramolecular charge transfer (CT) interaction [1,2]. In fact interest in molecular charge transfer complexes, particularly those such as the strongly conducting black-polymorph of the complex of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) [3] and the complex tetramethyltetraselenafulvalene-tetracyanoquinodimethane (TMTSF-TCNQ) [4] which show superconductivity at low temperature continues to be strong. The use of trinitrobenzene as an electron acceptor with phenoxtellurine (as an electron donor) has encouraged the researchers to look for other electron acceptors for the same purpose [5].

We have recently developed an interest in the role of charge transfer (CT) complexes formed by more simple organic derivatives [6], particularly of selenium and tellureum as donors. The electron acceptors we have used in our study are p-Benzoquinone (p-BQ) and m-Dinitrobenzene (m-DNB).

It has been concluded [7], that the charge transfer interaction is possible in these weak donor - acceptor combinations but can scarcely be the main intermolecular force to govern a molecular arrangement in a crystal.

This paper is an extension of two previous pieces of work [6,8] in which we consider the effects of methoxy group (-MeO) and nitro group (-NO<sub>2</sub>) substituents on the properties of the CT complexes.

## EXPERIMENTAL

Chemicals and solvents :

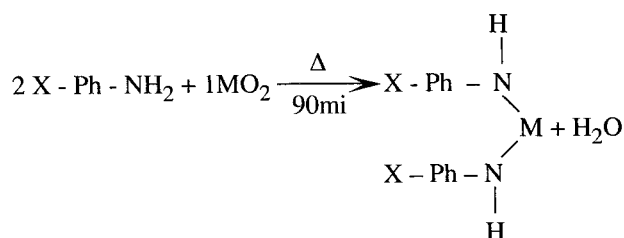
all starting materials and solvents were obtained from well known commercial sources such as Aldrich and BDH chemicals.

Synthesis of Organoselenium and -tellurium compounds:

Preparation of compound No. 1 (table - 1) :

Selenium dioxide (4.44g, 0.04mol) was dissolved in dist. water (25 cm<sup>3</sup>) and treated with Aniline (5.76g, 0.08mol) in

methanol (25cm<sup>3</sup>). The mixture was boiled for 90 minutes, it was allowed to cool. The residue was recrystallised from ethanol to form redish brown crystals (m.p. 95 - 96C). The typical equation for these preparations as follows :-



were : X = H, NO<sub>2</sub>, CH<sub>3</sub>O

M = Se, Te

Synthesis of Charge Transfer Complexes, a typical method is :

To a hot solution of the prepared donor (organoselenium or- tellurium) in acetonitrile solvent (25cm<sup>3</sup>) was added to the acceptor compound in the same solvent (25cm<sup>3</sup>) (2:1), The mixture was stirred and reflexed for 60 minutes, after which the voleme was reduced. On cooling to room temperature, small dark coloured crystals of the complex were deposited.

## Physical measurements

Infra-red spectra were recorded for KBr discs with a BIO - RADFTS - UOA. UV / VIS spectra were recorded for Acetone solutions in 1cm pathway quartz cells with a PU 8625 UV / VIS spectrophotometer / Phillips. Molar conductivity for the freshly new prepared complexes were measured with a PW 9526 digital conductivity meter/ Philips.

## Results and Disussion

The obtained correct analytical data (C%, H%, N%) analysis in Table - 1) agree with the suggested new prepared compounds and complexes. All the complexes were found to be stable in air for several months. The melting points for the Benzoquinone (BQ) complexes are higher than that of the m-Dinitrobenen (m-DNB) complexes. Similar observation been noted for BQ and

DNB complexes in previous studies [6,8].

It has been reported [9], that the introduction of electron- donating groups into the benzen ring will increase the  $\pi$ -basicity of the donors in general. This will lead to a red-shift in the CT absorption spectrum.

In our study we have used a donating group (-MeO) as well as a withdrawing group (-NO<sub>2</sub>) as substituents of the (-H) in every prepared compound (table 1) for the sake of comparison.

Usually the m-dinitrobenzen (m-DNB) appeared at  $\nu$  (1300 - 1375 and 1500 - 1575 cm<sup>-1</sup>), while the p-benzoquinone (p-BQ) appeared at  $\nu$  (1500, 1620 and 1680- 1850 cm<sup>-1</sup>). The infra - red spectra of the DNB complexes (No. 3,6,9,11,14 and 15) were virtually the superposition of the spectra of the individual components (table 2). Also there is no clear shift of  $\nu$  (CO) with the BQ complexes, despite all of the following considerations [8,10]:-

1. the organo tellurides usually offers CT complexes more clear than that of the organo selenides.
2. the ionisation potential of tellurium and selenium are quite low which ease the CT operation, and,
3. we found a clear splitting of the band 1540 cm<sup>-1</sup> in complex no.3 (as an example) (figure 1).

This implies an extremely weak CT interaction, and could be in line with results previously obtained for the 1,3-dihydro- 2- telluraindene- DNB complex [8,10].

The electronic absorption spectra for the CT complex were measured in acetonitrile solution. A typical; example of complex no. 8 is in figure 2.

In the present study, the obtained results (table 2) are

quite similar to that of previous studies on BQ and DNB complexes [6,8]. It has been assumed that, since all the BQ and DNB complexes absorb at the same region of visible spectrum the absorption must due to a certain transition. The transition is from the last occupied molecular orbital on the donor to the lowest empty molecular orbital on the acceptor (HOMO - LUMO) [6,8]. The idea, that this type of weak interaction is indeed sort of  $\pi - \pi$  charge transfer [11]. Recently, it has been suspected that since there is no hydrogen bond is possible between such molecules and  $\pi - \pi$  overlap is slight, so the arrangement of the molecules might be due to strong electrostatic interaction [7]. These judgments are in good agreement with the present obtained results (table 2).

It has been pointed out [12], that the molar conductivity for charge transfer complexes is an indication for the electronic current movement in a solution when these complexes is dissolved. The rate of the conduction in any solution depends on the concentration, valency and speed of the ions.

In our study we found low values for the molar conductivity (table 2) despite of the presence of Se and Te metals within the chemical structure of the electron donors. Sines all the prepared complexes have same valency (II) for Se and Te, this could indicate little concentration dependence and implies weak complexation. Random values has been observed for both BQ complexes (table 2), similar to that of analogue study [6].

Finally, from the obtained results (table 1,2) one can conclude that the addition of two different substituents (-OMe, - MO<sub>2</sub>) on the organo selenide and telluride donors has made no big difference on the formation of new charge transfer complexes.

The effect of two substituents

Table 1. Physical and analytical data for new compounds.

No.	Compound	Colour (M.P. °C)	Yield %	C% Calcd Found	H% Calcd Found	N% Calcd Found
	P-BQ	Red (115)	-	-	-	-
	m-DNB	Yellow (85)	-	-	-	-
1	$\begin{array}{c} \text{H} \\   \\ \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$	Reddish Brown (95-96)	87	45.1 54.7	4.2 4.6	11.2 10.6
2	$\begin{array}{c} \text{H} \\   \\ \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$ . BQ . DNB	Brown (150-152)	75	58.4 58.2	4.8 4.3	7.1 7.5
3		Brown (100-102)	85	49.6 50.1	4.3 3.9	13.6 13.0
4	$\begin{array}{c} \text{H} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{NO}_2 - \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$	Yellow (53-54)	70	40.1 40.8	3.3 2.8	16.1 15.9
5	$\begin{array}{c} \text{H} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{NO}_2 - \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$ . BQ . DNB	Dark brown (110-112)	65	46.8 47.3	5.0 4.6	11.5 12.2
6		Dark Yellow (82-84)	68	41.1 41.5	3.1 2.7	15.9 16.1
7	$\begin{array}{c} \text{H} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{MeO} - \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$	Violet (98-100)	78	51.0 52.2	5.3 5.0	8.2 8.7
8	$\begin{array}{c} \text{H} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{MeO} - \text{Ph} - \text{N} \quad \text{Se} \\   \\ \text{H} \end{array}$ . BQ . DNB	Dark Violet (93-94)	65	55.1 55.7	5.2 4.6	6.1 6.5
9		Violet (86-88)	75	48.2 48.9	3.8 4.0	11.9 11.4
10	$\begin{array}{c} \text{H} \\   \\ \text{Ph} - \text{N} \\ / \quad \backslash \\ \text{Ph} - \text{N} \quad \text{Te} \\   \\ \text{H} \end{array}$	Pale Yellow (190-192)	85	45.5 46.2	4.0 3.8	9.2 9.0

No.	Compound	Colour (M.P. ?)	Yield %	C% Calcd Found	H% Calcd Found	N% Calcd Found
11	$\begin{array}{c} \text{H} \\   \\ \text{Ph} - \text{N} \\   \\ \text{Ph} - \text{N} \\   \\ \text{H} \end{array} \text{Te} \cdot \text{DNB}$	Reddish Brown (74-76)	70	45.0 44.2	3.3 3.7	11.7 11.2
12	$\begin{array}{c} \text{H} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\   \\ \text{H} \end{array} \text{Te}$	Yellow (130-132)	80	36.2 35.5	2.5 2.9	14.1 13.8
13	$\begin{array}{c} \text{H} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\   \\ \text{NO}_2 - \text{Ph} - \text{N} \\   \\ \text{H} \end{array} \text{Te} \cdot \text{DNB}$	Greenish Yellow (74-76)	90	41.2 42.0	2.7 2.3	16.0 17.0
14	$\begin{array}{c} \text{H} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\   \\ \text{H} \end{array} \text{Te}$	Brownish Red (66-68)	80	45.2 46.1	4.3 3.9	7.5 7.1
15	$\begin{array}{c} \text{H} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\   \\ \text{MeO} - \text{Ph} - \text{N} \\   \\ \text{H} \end{array} \text{Te} \cdot \text{DNB}$	Brown (72-74)	75	44.4 44.1	3.3 3.5	10.4 10.6

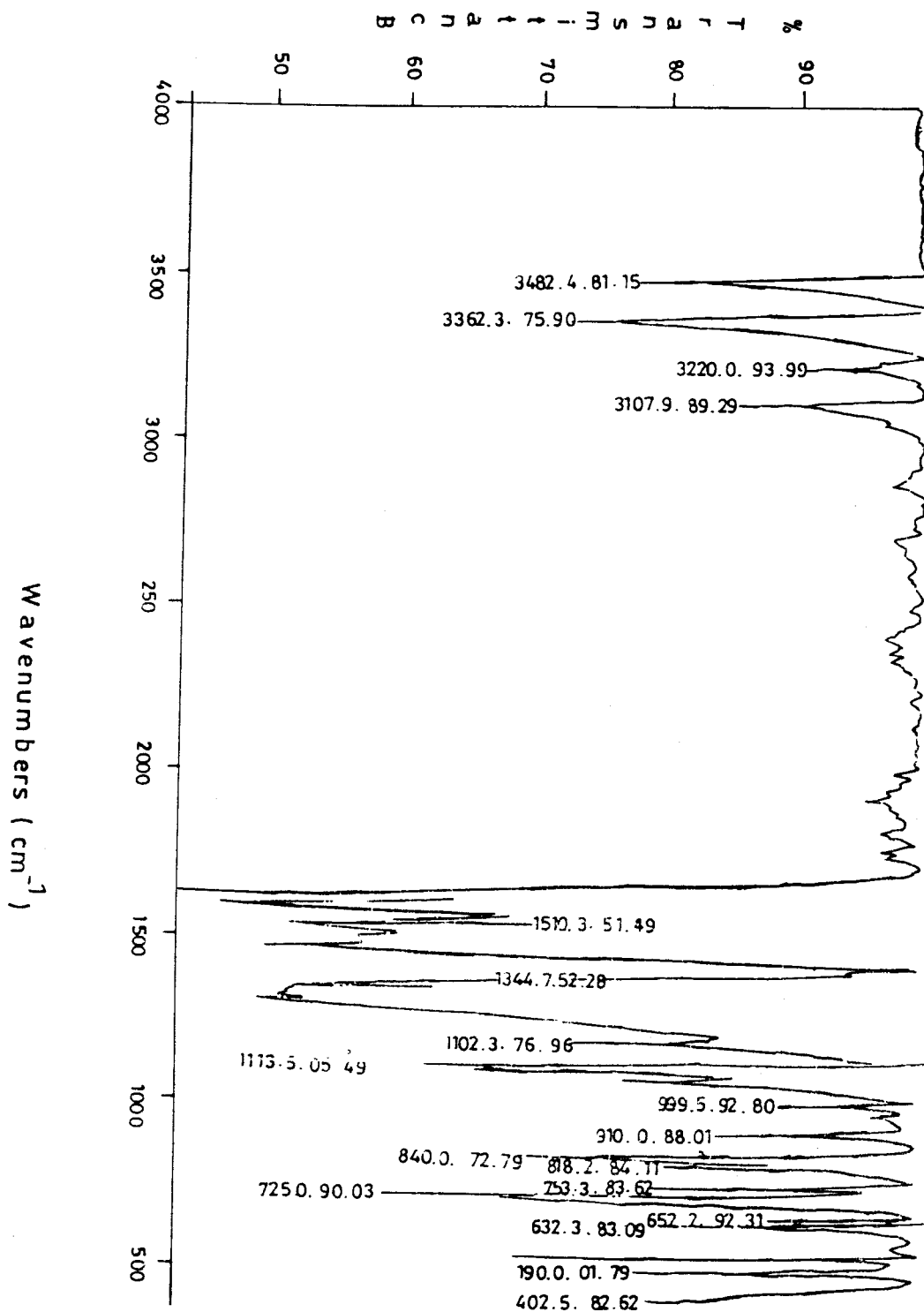
Table 2. Infra Red, Electronic Absorption and Molar Conductivity Data.

No.	$\nu$ (Cm <sup>-1</sup> )		UV-VIS $\lambda$ Max (nm)	Molar Conductivity $\Omega^{-1}$ CM <sup>2</sup> Mol <sup>-1</sup>
	(CO)	(C-NO)		
2	1602,1612,1767	1330,1540	550	30.3
3			558	71.2
5	1634	1300,1505,1590	510	11.18
6			590	7.31
8	1631	1347,1537	595,610	56.7
9			570	16.0
11		1348,1528,1539	405	41.7
12				8.4
14		1319,1363,1371,1587	595	15.2
15		1301,1349,1512,1538	398	80.2

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Figure - 1 : IR spectrum of complex No. 3



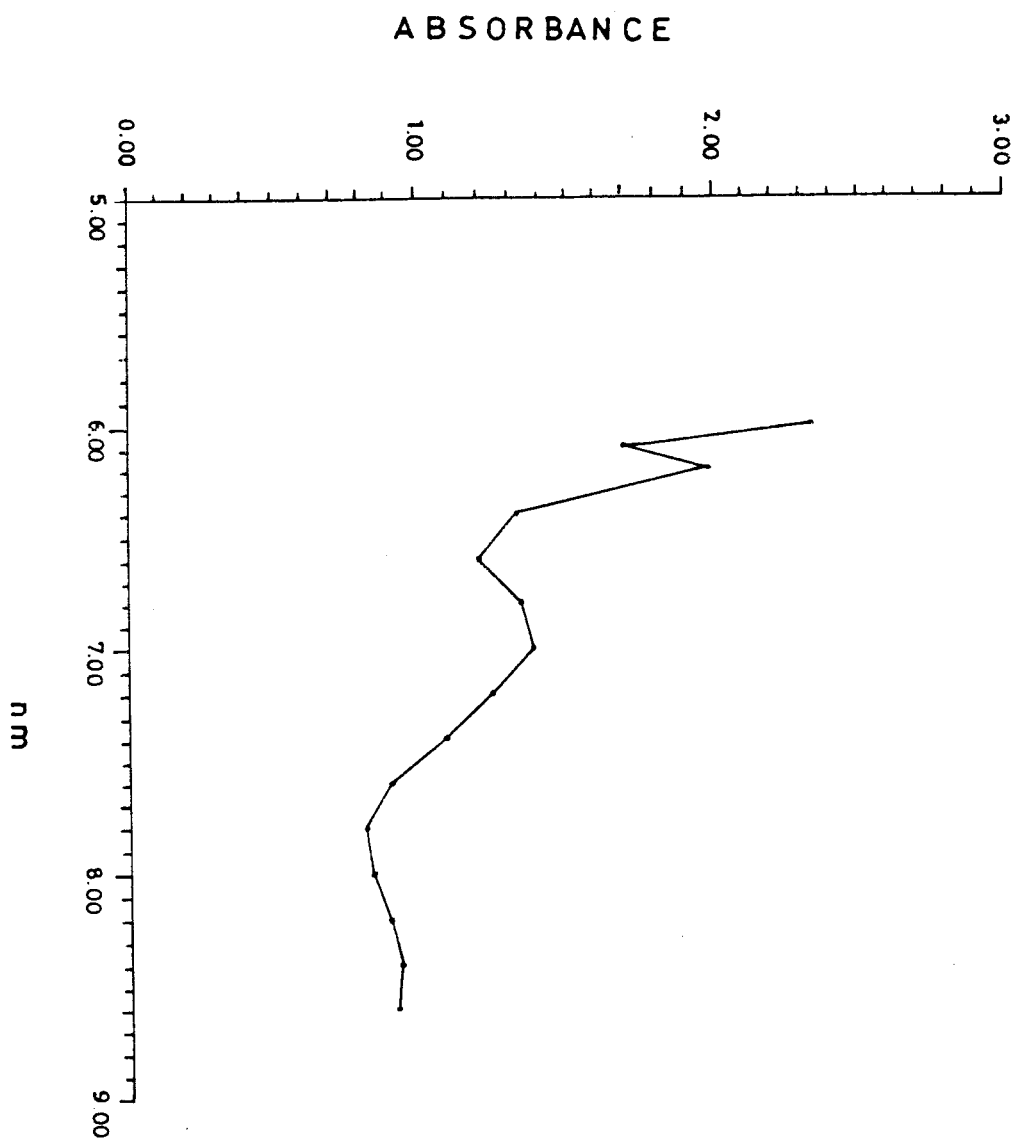


Figure - 2 : E. A spectrum of complex No. 8