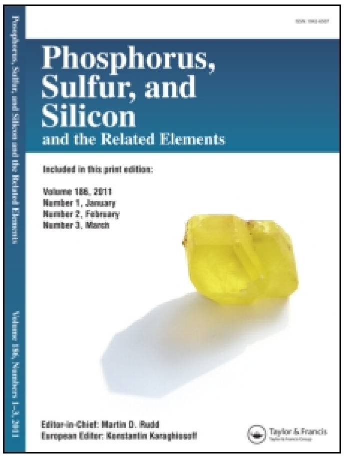

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHARGE-TRANSFER COMPLEXES OF SOME HETEROARYLTHIOUREA DERIVATIVES WITH π-ACCEPTORS

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To cite this Article Hamed, M. M. A. , Salman, H. M. A. , Abd-alla, E. M. and Mahmoud, M. R.(1993) 'CHARGE-TRANSFER COMPLEXES OF SOME HETEROARYLTHIOUREA DERIVATIVES WITH π-ACCEPTORS', Phosphorus, Sulfur, and Silicon and the Related Elements, 80: 1, 127 — 134

To link to this Article: DOI: 10.1080/10426509308036886

URL: http://dx.doi.org/10.1080/10426509308036886

Phosphorus, Sulfur, and Silicon, 1993, Vol. 80, pp. 127–134
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CHARGE-TRANSFER COMPLEXES OF SOME HETEROARYLTHIOUREA DERIVATIVES WITH π-ACCEPTORS

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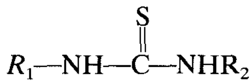
(Received October 15, 1992; in final form March 4, 1993)

Spectral characteristics and thermodynamic properties of charge-transfer molecular complexes of some heteroarylthioureas with π-acceptors DDQ, TCNE and CHL are investigated and discussed. It is deduced that the formed CT complexes are of n-π kind. Moreover, 1:1 solid CT complexes are synthesized and characterized.

Key words: Charge-transfer complexes; solvent effects; stability; solid CT complex; hetroarylthioureas.

INTRODUCTION

Due to the wide applications of thiourea derivatives in many important fields (biological, pharmaceutical and industrial)[1] CT complexes of such compounds with I_2 as σ-acceptor receive much attention in the literature.[2–9] It was concluded that the formed complexes are of the n-σ type with the site of the n-donor action at the sulfur atom. Very limited information is available in the literature concerning the interaction of such compounds with π-acceptors.[10] Continuing our interest in the investigation of CT molecular complexes of thiourea derivatives and related sulfur compounds with π-electron acceptors,[11,12] this article describes a systematic study on CT complexes of some heteroarylthiourea derivatives. The study involves synthesis and characterization of the solid CT complexes. Donor molecular structure and solvent effects on stability and spectral characteristics of the CT complexes are investigated and discussed. The general molecular formula of the donors is



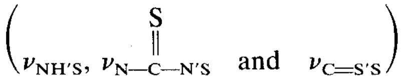
$$R_1\text{—NH—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—NHR}_2$$

R_1 = 2-pyridyl; R_2 = CH_3; 1-methyl-3-(2-pyridyl)thiourea (I)
R_1 = 2-pyridyl; R_2 = Ph; 1-phenyl-3-(2-pyridyl)thiourea (II)
R_1 = 2-pyrimidyl; R_2 = Ph; 1-phenyl-3-(2-pyrimidyl)thiourea (III).

RESULTS AND DISCUSSION

Chemical Analysis and Infrared Spectra

Chemical analysis data reported in Table I clearly indicates the formation of 1:1 CT complexes. Comparison of the selected IR spectral bands of the donors I–III as well as those of the acceptors (DDQ and TCNE) with the corresponding ones appearing in the IR spectra of the isolated complexes reveals that, the IR bands of the donors I–III



$$\left(\nu_{\mathrm{NH's}},\ \nu_{\mathrm{N-\overset{\overset{S}{\|}}{C}-N's}} \text{ and } \nu_{\mathrm{C=S's}}\right)$$

which appeared at 3150–3300, 1345–1350 and 1005–1090 cm^{-1}, are shifted to lower frequencies on complex formation. The observed large shift in $\nu_{C=S}$ to lower frequencies (60–70 cm^{-1}) suggests that the sulfur thiocarbonyl is the donor site. Moreover, the $\nu_{C\equiv N}$ of the acceptors DDQ and TCNE (at 2237 and 2260, 2225 cm^{-1}, respectively), $\nu_{C=0}$ and ν_{C-Cl} of DDQ which appeared at 1678 and 802

TABLE I
Microanalysis data, color and melting points for the solid CT complexes of donors I–III with the π-acceptors TCNE and DDQ

Complex	Color	M.P °C	% Calc. (Found) C	H	N	S	Cl
I-TCNE	brown	180d	52.84 (52.90)	3.07 (3.09)	33.21 (33.35)	10.86 (10.70)	-
II-TCNE	reddish brown	140d	60.46 (60.53)	3.10 (3.12)	27.44 (27.50)	8.97 (8.85)	-
III-TCNE	brown	150	56.94 (56.98)	2.81 (2.88)	31.27 (31.35)	8.94 (8.81)	-
I-DDQ	yellow	155d	45.66 (45.70)	2.30 (2.33)	17.76 (17.80)	8.13 (8.20)	17.98 (17.87)
II-DDQ	yellow	210d	52.61 (52.71)	2.43 (2.47)	15.35 (15.40)	7.03 (7.10)	15.54 (15.60)
III-DDQ	yellow	230d	49.87 (49.83)	2.20 (2.25)	18.38 (18.43)	7.01 (7.08)	15.51 (15.58)

d = decomposed.

cm^{-1}, respectively, are shifted also to lower frequencies (appeared at 2230–2210, 1630–1615 and 770–760 cm^{-1} for $\nu_{C\equiv N}$, $\nu_{C=O}$ and ν_{C-Cl}, respectively). This behaviour is in accordance with charge migration from donor to acceptor.

Electronic Spectral Characteristics

The recorded electronic spectra of the studied heteroarylthioureas-TCNE complexes in CH_2Cl_2 display one broad absorption band in the wavelength range 400–700 nm (λ_{max} = 540, 540 and 525 nm, respectively) where neither the donor nor the acceptor separately absorbed in this region (Figure 1, Table II). The electronic spectra of II-CHL CT complex solution displays one broad CT band with λ_{max} at 510 nm. On the other hand, the obtained electronic spectra of the CT complex solution of donor II with DDQ shows a group of absorption bands at 448sh, 472, 516 and 587 nm (cf. Figure 2). Such absorption bands are characteristic of the absorption of the radical anion DDQ^-.[13-16] One can deduce that the DDQ-II CT complex exists predominantly in an ionic form (D^+, A^-) i.e., it is of strong nature

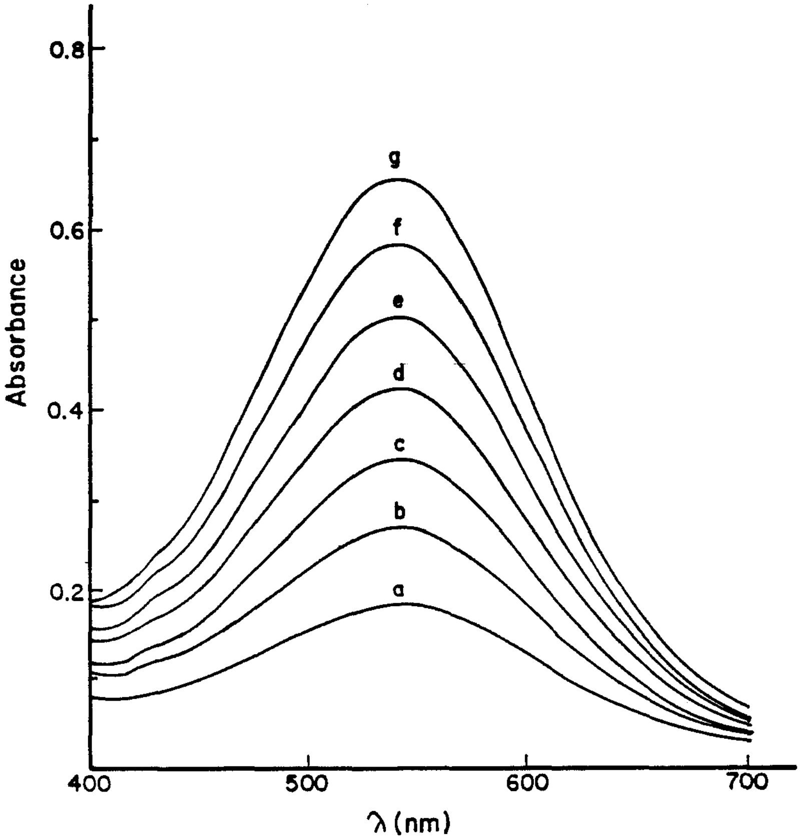


FIGURE 1 Electronic absorption spectra of the CT complex solutions of donor II with TCNE in CH_2Cl_2 at 20°C. [II] = 0.01 mol dm^{-3}; [TCNE] = 0.004, 0.006, 0.008, 0.01, 0.12, 0.14 and 0.16 mol dm^{-3} for a, b, c, d, e, f and g, respectively.

TABLE II

Spectral characteristics, formation constants (K_{CT}) and thermodynamic parameters values for the CT complexes of heteroarylthioureas with π-acceptors at different temperatures in CH_2Cl_2 as well as the ionization potential of the donors

Complex	λ_{max} nm	E_{CT} eV	i.p eV	$K_{CT}(dm^3mol^{-1})$, °C 10	15	20	25	$\varepsilon_{CT}(dm^3mol^{-1}cm^{-1})$ 10°C	$-\Delta H$ K cal mol^{-1}	$(\frac{b}{a})^2$
I-TCNE	540	2.286	8.27	18.9±3.5	14.55±2.15	12.83±1.35	8.28±2.59	492.00±87.00	8.70±1.47	0.165
II-TCNE	540	2.286	8.27	12.45±1.44	10.69±1.07	9.32±0.90	7.63±1.65	443.00±55.00	5.38±0.36	0.102
III-TCNE	525	3.352	8.35	10.71±2.14	7.14±1.95	5.10±0.94	3.31±0.74	329.00±37.00	12.93±0.48	0.239
II-CHL	510	2.421	8.00	-	-	-	-	-	-	-

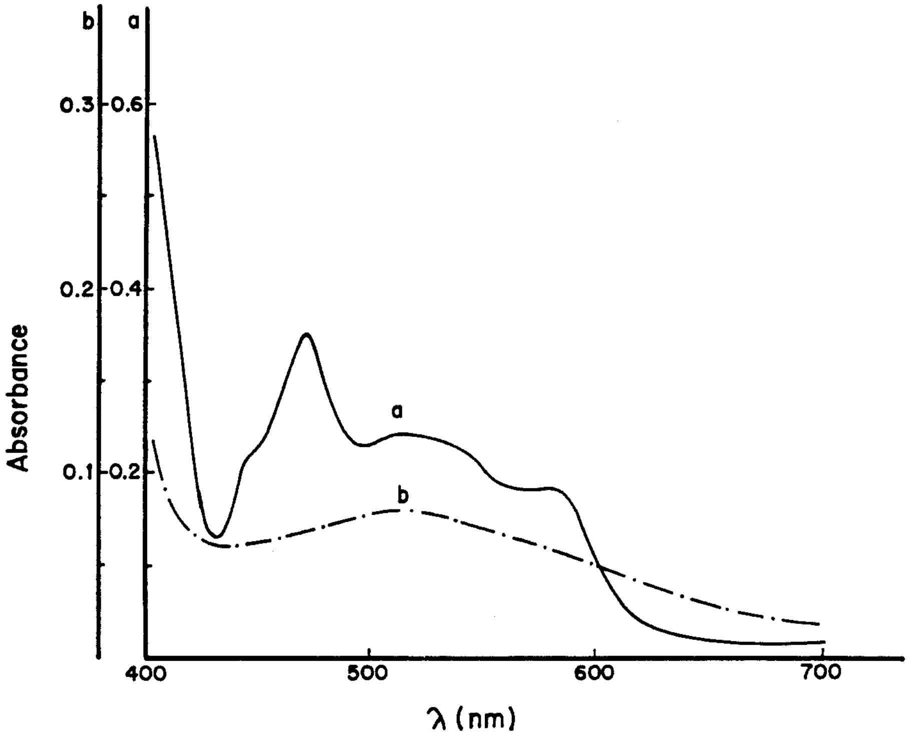


FIGURE 2 Electronic absorption spectra of the CT complex solutions of donor II with DDQ and CHL in CH_2Cl_2 at 20°C. a) DDQ-II CT complex, [DDQ] = [II] = 1×10^{-3} mol dm^{-3}; b) CHL-II CT complex, [CHL] = 4×10^{-3} mol dm^{-3}, [II] = 5×10^{-4} mol dm^{-3}.

while the complexes with TCNE and CHL are mainly of the nonbonded type (D—A).

Ionization Potential of the Donors

The ionization potential of the HOMO (*n*) on the donors I–III was estimated from CT energies of their complexes with TCNE or CHL by adopting the empirical equations reported by Aloisi and Pignataro[17] and the values obtained are listed in Table II. The values obtained (8.0–8.35 eV) can be compared with those for tetramethylthiourea and thiourea (8.12 and 8.50 eV, respectively) determined before by electron impact mass spectrometric technique.[5,18]

Thermodynamic Properties

Formation constant values (K_{CT}) of the CT complexes of donors I–III with TCNE in temperature range 10–25°C were determined spectrophotometrically in CH_2Cl_2 making use of the Scott Equation.[19] All calculations were carried out by using a linear least squares method. The obtained K_{CT} and ε_{CT} values are listed in Table II. The stability of the formed CT complex of donors I–III with TCNE is of the order: I (R_1 = 2-pyridyl, R_2 = CH_3) > II (R_1 = 2-pyridyl, R_2 = Ph) > III (R_1

= 2-pyrimidyl, R_2 = Ph). This behaviour could be ascribed to the expected low donor character of the sulfur thiocarbonyl group in the same sequence. The high donor character of donor I (R_2 = CH_3) compared to that of donor II (R_2 = Ph) could be attributed to the relatively high inductive effect of its methyl group. The observed high donor ability of donor II compared to that of donor III could be ascribed to the expected high electron withdrawing power of the pyrimidine moiety of compound III relative to that of the pyridine of compound II. This results from the fact that the pyrimidine is considered to be a much weaker base (pK_a = 1.31) than pyridine (pK_a = 5.20).[20] Generally, the observed dependence of CT complex stability on donor molecular structure substantiates the above described conclusion that the sulfur thiocarbonyl group is the donor site responsible for such charge transfer transition.

It is worth noting that no reliable K_{CT} values are obtained for CHL-II complex owing to the expected weak character of such a complex. This is due to the low electron affinity of CHL compared to that of DDQ or TCNE.

The enthalpy changes (ΔH) connected with the formation of the studied CT complexes were obtained from Van't Hoff equation plots and are listed in Table II.

According to Mulliken,[21,22] the ratio between the coefficient of the dative bond wave function ($\psi_{D^+-A^-}$) to the nonbonded wave function (ψ_{D-A}), $(b/a)^2$ was evaluated and recorded in Table II. The results obtained indicate that the magnitude of the interaction between heteroarylthiourea derivatives and TCNE is high.

Effect of Solvent

To study the effect of solvent on the stability of the formed heteroarylthioureas I–III CT complexes, the complex of donor I with TCNE has been investigated in different solvents of various polarities ($C_2H_4Cl_2$, CH_2Cl_2 and $CHCl_3$) at 10°C. The determined K_{CT} values along with the spectral characteristics of this complex in the different solvent used are presented in Table III.

TABLE III
Spectral characteristics, formation constants (K_{CT}) for the CT complex of donor I with TCNE at 10°C in various solvents as well as the ionization potential of donor I

Solvent	Dielectric constant (D)	λ_{max} nm	E_{CT} eV	i.p eV	K_{CT} ($dm^3 mol^{-1}$)	ε_{CT} ($dm^3 mol^{-1} cm^{-1}$)
$C_2H_4Cl_2$	10.65	542	2.278	8.25	15.42 ± 2.70	678.00 ± 188.00
CH_2Cl_2	9.08	540	2.286	8.27	18.90 ± 3.50	492.00 ± 87.00
$CHCl_3$	4.80	535	2.308	8.29	23.82 ± 3.87	683.00 ± 190.00

Careful examination of this Table reveals that the formation constant value of the CT molecular complex decreases as dielectric constant of the solvent is increased along the direction $CHCl_3 \rightarrow CH_2Cl_2 \rightarrow C_2H_2Cl_2$. This behaviour can be interpreted in the following way: the formed CT complex is a strong n-π type i.e., there is a high contribution of the dative structure wave function $\psi_{D^+-A^-}$ to the wave function of the CT ground state. Thus increasing the dielectric constant of medium will result in dissociation of the dative structure $D^+ - A^-$ into the corresponding radical ions (D^+, A^-) owing to the expected high dipole-dipole or dipole-induced dipole interaction in the same direction i.e. low K_{CT} value.

EXPERIMENTAL

Preparation of heteroarylthiourea derivatives. The electron donors I–III were prepared by the reaction of methylisothiocyanate and phenylisothiocyanate with 2-aminopyridine and 2-aminopyrimidine in presence of pyridine as a solvent. The reaction mixture was refluxed for 30 minutes and cooled. The precipitate formed was filtered off and recrystallized from ethanol. The purity of the compounds was checked by elemental analysis and thin layer chromatography.

I ($C_7H_9N_3S$) Calc'd.: C 50.26, H 5.43, N 25.14, S 19.18. Found: C 50.20, H 5.40, N 25.20, S 19.20; m.p. 145°C.

II ($C_{12}H_{11}N_3S$) Calc'd.: C 62.84, H 4.84, N 18.34, S 13.99. Found: C 62.70, H 4.80, N 18.40, S 13.90; m.p. 171°C.

III ($C_{11}H_{10}N_4S$) Calc'd.: C 57.35, H 4.38, N 24.34, S 13.93. Found: C 57.30, H 4.40, N 24.40, S 13.80; m.p. 198–200°C.

Electron π-acceptors. The electron acceptors; tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) "Chloranil" (Aldrich) were recrystallized from chlorobenzene, dry methylene chloride and dry benzene respectively.

Solvents were of spectral grade (BDH). Stock solutions of donors or acceptors were prepared in the proper deoxygenated solvent where they were freshly prepared prior use in order to avoid any contamination.

Synthesis of the solid CT complexes. Equimolar amounts of donors (I, II and III) and π-acceptors (DDQ and TCNE) were dissolved separately at room temperature in a minimum volume of dry methylene chloride. The two solutions were mixed and the resulting mixture was left at room temperature for 4 hours. The solid CT complexes which separated out were recrystallized from absolute ethanol. The analytical data of the prepared complexes (C, N, S and Cl) and some of their physical properties are listed in Table I.

Several attempts were made to prepare the CT complexes of donors I–III with CHL but all failed.

Physical measurements and computations. Electronic spectra were recorded with a CECIL CE 599 spectrophotometer using 1 cm matched silica cells. Temperature control was achieved using an ultrathermostat of accuracy ±0.02°C. IR spectra were performed on Shimadzu 408 IR spectrophotometer as KBr discs (4000–650 cm^{-1}). Computations were performed on a copam 88S PC computer with aid of a BASIC program based on an unweighted linear least-squares fits.

REFERENCES

1. F. Duus, in D. N. Jones (ed.) "Comprehensive Organic Chemistry," Pergamon Press, Oxford, Vol. 3, p. 452 (1979).
2. R. P. Lang, *J. Am. Chem. Soc.*, **84,** 811 (1962).
3. D. L. A. De Faria, N. S. Goncalves and Santos, *Spectrochim. Acta*, **45A,** 643 (1989).
4. B. K. Seal, B. Banerjee and D. C. Mukherjee, *Indian J. Chem.*, **25A,** 799 (1986); **25A,** 942 (1986).
5. K. R. Bhasker, R. K. Gosavi and C. N. R. Rao, *J. Chem. Soc., Faraday Trans.*, **62,** 29 (1966).
6. M. S. A. Abd El-Mottaleb, A. M. El-Arrash and M. M. Abu-Ali, *Z. Phys. Chem. (Leipzig)*, **259,** 1083 (1978).
7. R. P. Lang, *J. Phys. Chem.*, **72,** 2129 (1968).

8. R. J. Niedzielski, R. S. Drago and R. L. Middaugh, *J. Am. Chem. Soc.*, **86,** 1694 (1964).
9. K. R. Bhasker, S. N. Bhat, A. S. N. Murthy and C. N. R. Rao, *J. Chem. Soc., Faraday Trans.*, **62,** 788 (1966).
10. V. R. Misra, D. C. Tewari and P. N. Tripathi, *Electrochim. Acta*, **29,** 1335 (1984).
11. H. M. A. Salman, S. A. El-Gyar, M. M. A. Hamed and M. A. El-Gahami, *Canadian J. Appl. Spectroscopy*, **37,** 137 (1992).
12. M. M. A. Hamed, H. M. A. Salman and S. A. El-Gyar, *Phosphorus, Sulfur and Silicon*, **71,** 185 (1992).
13. Y. Iida, *Bull. Chem. Soc. Jpn.*, **44,** 2615 (1971).
14. Y. Iida and Y. Matsunga, *Bull. Chem. Soc. Jpn.*, **40,** 231 (1967).
15. J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. C. Anderson and A. J. Epstein, *J. Am. Chem. Soc.*, **108,** 4459 (1986).
16. M. R. Mahmoud, H. M. A. Salman and A. A. Ahmed, *Canadian J. Appl. Spectroscopy* (1992) in press.
17. G. G. Aloisi and S. Pignataro, *J. Chem. Soc., Faraday Trans.*, **69,** 534 (1973).
18. M. Baldwin, A. Maccoll, A. Kirkien-Konasiewicz and B. Saville, *Chem. Ind.*, (London) 286 (1966).
19. R. L. Scott, *Rec. Trav. Chim. Pays-Bas*, **75,** 787 (1956).
20. D. J. Brown, in A. Katritzky (ed.) "Comprehensive Heterocyclic Chemistry," Pergamon Press, Oxford, Vol. 3, p. 60 (1984).
21. R. S. Mulliken, *J. Phys. Chem.*, **56,** 801 (1952); *Rec. Trav. Chim. Pays-Bas*, **75,** 845 (1956); *J. Chem. Phys.*, **61,** 20 (1964).
22. R. S. Mulliken and W. P. Person, *Annu. Rev. Phys. Chem.*, **13,** 107 (1962); *J. Am. Chem. Soc.*, **91,** 3409 (1969).