Monatshefte für Chemie 129, 121–127 (1998)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Molecular Complexes of some N-Aryldithiocarbamates with π-Electron Acceptors

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Summary. Solid 1:1 CT complexes formed between some S-alkyl-N-aryldithiocarbamates and π-electron acceptors (2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*), tetracyanoethylene (*TCNE*), chloranil (*CHL*)) are synthesized and characterized. Spectral characteristics and stability of the complexes are investigated and discussed in terms of donor molecular structure, π-acceptor electron affinity, and solvent polarity. It is deduced that the complexes are mainly of the n-π type where the ground state wave function can be described primarily by the non-bonding structure. Ionization potentials of the donors are estimated from the CT transition energies of their complexes.

Keywords. Molecular complexes; N-Aryldithiocarbamates; Solvent effects; Spectroscopy.

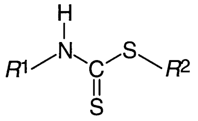
Komplexe einiger N-Aryldithiocarbamate mit π-Elektronenakzeptoren

Zusammenfassung. *Charge-transfer*-Komplexe aus S-Alkyl-N-aryldithiocarbamaten und π-Elektronenakzeptoren (2,3-Dichlor-5,6-dicyano-1,4-benzochinon (*DDQ*), Tetracyanoethylen (*TCNE*) und Chloranil (*CHL*); stöchiometrisches Verhältnis: 1:1) wurden hergestellt und charakterisiert. Die spektroskopischen Eigenschaften und die Stabilitäten der Verbindungen wurden untersucht und werden im Zusammenhang mit Parametern wie Struktur, π-Elektronenakzeptor-affinität und Lösungsmittelpolarität diskutiert. Es zeigt sich, daß die Komplexe hauptsächlich dem n-π-Typ angehören, in dem die Wellenfunktion des Grundzustands vorwiegend durch eine nichtbindende Struktur beschrieben werden kann. Die Ionisationspotentiale der Donatoren werden aus den *charge-transfer*-Übergangsenergien ihrer Komplexe abgeschätzt.

Introduction

Molecular complexation and structural recognition are key processes in biological systems. For instance, enzyme catalysis, drug action, and ion transfer through lipophilic membrances all involve complexation between two or more distinct molecules [1]. Sulfur donors are well known for their anticancer, antiviral, and antifungal activities as well as for their widespread industrial applications in the vulcanization of rubber [2, 3]. Charge-transfer complexes of thiourea, thiocarbonyl, and some related sulfur compounds with iodine (σ-acceptor) have received much attention in the literature [4–11]. Generally, it has been deduced that the formed complexes are of the n-σ type in which the sulfur atom is the donor site.

However, a similar study of such compounds with π-acceptors is lacking in the literature. Since the dithiocarbamate functionality is known to exhibit many biochemical features [2], it would be of interest to carry out a detailed study on the CT complexes of some S-alkyl-N-aryldithiocarbamates with π-acceptors like tetracyanoethylene (*TCNE*), chloranil (*CHL*), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*). The study involves synthesis and characterization of the solid CT complexes. The effects of donor molecular structure, the acceptor electron affinity, and the polarity of the solvent on the stability of the formed CT complexes were examined and are discussed. The general formula of the subjected dithiocarbamates is given below.



1: R^1=phenyl, R^2=CH_3 (S-methyl-N-phenyl-dithiocarbamate)
2: R^1=*p*-tolyl, R^2=CH_3 (S-methyl-N-(*p*-tolyl)-dithiocarbamate)
3: R^1=*p*-anisyl, R^2=CH_3 (S-methyl-N-(*p*-anisyl)-dithiocarbamate)
4: R^1=phenyl, R^2=C_2H_5 (S-ethyl-N-phenyl-dithiocarbamate)

Results and Discussion

Spectroscopic characteristics and formation constants

The electronic spectra of the CT complexes of **1**–**4** with *DDQ*, *TCNE*, and *CHL* in CH_2Cl_2 are given in Table 1. In all cases, a new band appeared in the 400–650 nm region which is not displayed by any component alone. Typical results at 10°C are shown in Fig. 1, representing the spectra for a series of dichloromethane solutions containing a varying excess of donor **3** (concentration: 0.01–$0.08\,\mathrm{mol \cdot dm^{-3}}$) and a fixed small concentration of acceptor (*TCNE*, $2 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}}$) using the solvent as a blank. Similar absorption spectra were observed for CT complexes

Table 1. Spectroscopic characteristics, formation constants (K_{CT}), molar extinction coefficients (ε_{CT}), and enthalpy changes (ΔH) for CT complexes of S-alkyl-N-aryldithiocarbamates **1**–**4** with π – electron acceptors in CH_2Cl_2 at various temperatures

	λ_{max} (nm)	E_{max} (eV)	IP (eV)	K_{CT} ($\mathrm{dm^3 \cdot mol^{-1}}$), °C				ε_{CT} ($\mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$)	$-\Delta H$ ($\mathrm{kcal \cdot mol^{-1}}$)
				10	15	20	25		
1-*TCNE*	508	2.442	8.46	6.41±0.38	6.05±0.35	5.62±0.19	5.19±0.17	346.17±19.7	2.37±0.14
2-*TCNE*	510	2.432	8.45	7.32±0.34	6.86±0.36	6.25±0.22	5.69±0.19	392.80±37.3	2.84±0.19
3-*TCNE*	514	2.413	8.42	8.53±0.57	7.87±0.23	7.20±0.25	6.38±0.19	362.96±18.9	3.22±0.24
3-*CHL*	465	2.668	8.29	4.26±0.29	3.98±0.15	3.71±0.16	3.42±0.17	239.88±15.7	2.44±0.09
3-*DDQ*	555	2.235	8.50						
4-*TCNE*	510	2.432	8.45	7.25±0.18	6.67±0.22	6.19±0.21	5.65±0.17	358.15±15.8	2.76±0.09

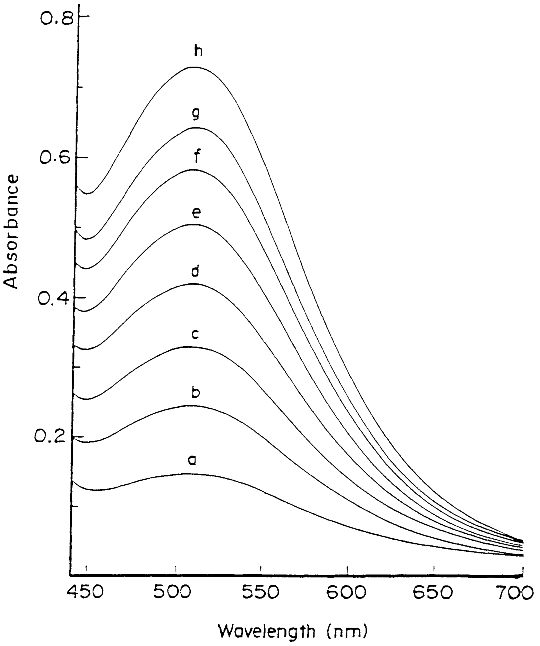


Fig. 1. Electronic absorption spectra of the CT complex of **3** with *TCNE* in CH_2Cl_2 ($2 \times 10^{-3}\,mol \cdot dm^{-3}$) at 10°C; [**3**] = 1, 2, 3, 4, 5, 6, 7 and 8 × $10^{-2}\,mol \cdot dm^{-3}$ for a, b, c, d, e, f, g and h respectively

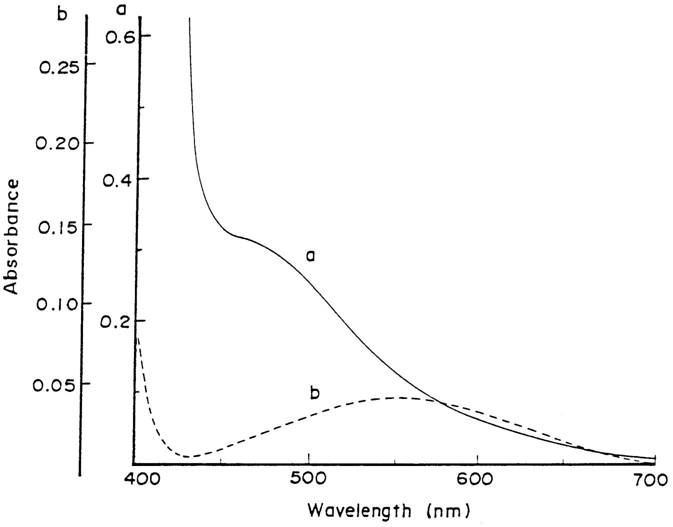


Fig. 2. Electronic absorption spectra of the CT complex of donor **3** with *CHL* and *DDQ* in CH_2Cl_2 at 10°C; a: *CHL*-**3** [CHL] = $4 \times 10^{-3}\,mol \cdot dm^{-3}$; [**3**] = $12 \times 10^{-2}\,mol \cdot dm^{-3}$; b: *DDQ*-**3**, [*DDQ*] = $2 \times 10^{-4}\,mol \cdot dm^{-3}$, [**3**] = $1 \times 10^{-3}\,mol \cdot dm^{-3}$

with *DDQ* and *CHL* (cf. Fig. 2). The new electronic absorption band can be assigned to a single intermolecular CT transition.

The formation constants (K_{CT}) and molar extinction coefficients (ε_{CT}) of the complexes in CH_2Cl_2 were determined spectrophotometrically in the temperature range of 10–25°C using both the *Benesi-Hildebrand* and the *Scott* equations [12, 13] under the condition $[D] \gg [A]$. All calculations were carried out by applying a linear least-squares method. The mean K_{CT} and ε_{CT} values are listed in Table 1. Generally, the relatively low K_{CT} values suggest that the formed complexes are of the weak type, *i.e.* that the ground state wave function has predominantly a nonbonding structure. The results listed in Table 1 clearly reveal that the stabilities of the complexes of donors **1**–**3** with the same π-acceptor (*TCNE*) are of the order **3** > **2** > **1**. This behaviour could be ascribed to the expected low electron donating ability of the sulfur thiocarbonyl group in the same sequence. Moreover, the high K_{CT} value of CT complexes, with **4** compared to those with **1** can be attributed to the expected high inductive effect of the ethyl group relative to that of the methyl moiety. From the observed dependence of the stability of the complexes on the donor molecular structure, it seems reasonable to conclude that they are of the n-π type, the sulfur thiocarbonyl group being responsible for the charge-transfer transition. With respect to the π-acceptor, the greater stability of **3**-*TCNE* compared to **3**-*CHL* is in accordance with the higher electron affinity of *TCNE* relative to *CHL*.

It is worth mentioning that the spectrophotometric determination of K_{CT} values for the CT complexes of donors **1**–**4** with *DDQ* could not be performed owing to the rapid precipitation of the complex.

The mean values of K_{CT} at various temperatures were utilized to estimate the enthalpy change (ΔH) for the CT complex formation applying *van't Hoff* plots. The results obtained are given in Table 1. It can be seen that the ΔH values of CT complexes of *TCNE* obey the order **3** > **2** > **4** > **1** which is in accordance with their stability constants.

Ionization potential of the donors

The ionization potential of the HOMO (n) on the donors **1**–**4** was estimated from the CT energies of their complexes with *TCNE*, *CHL*, and *DDQ* by adopting the empirical equations reported by *Aloisi* and *Pignataro* [14]. The values obtained are listed in Table 1. However, their experimental IP values are not available in the literature due to the lack of photoelectron data for these compounds. The values obtained (8.29–8.50 eV) can be compared with those reported previously for 1,3-diethylthiourea and 1,3-dibenzylthiourea (8.32 and 8.36 eV, respectively; Refs. [9, 15]. Furthermore, the IP values of donor **3** obtained from the CT energy of its CT complexes with the three π-acceptor are nearly the same (cf. Table 1). This suggests that the highest filled donor orbital involved in the CT interaction is the same for all applied π-acceptors.

Effect of solvent

The complexes of donor **3** with *TCNE* were investigated in different solvents of various polarities ($CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$) at various temperatures. Spectroscopic characteristics and the obtained K_{CT} values are given in Table 2. It is evident that the K_{CT} value decreases as the dielectric constant of the solvent increases ($CHCl_3$ ($D = 4.806$) $\rightarrow$ CH_2Cl_2 ($D = 9.08$) $\rightarrow$ $C_2H_4Cl_2$ ($D = 10.65$)). This trend can be attributed to the expected high stabilization of the free donor and acceptor due to the weak n-π type characteristics of the complex. This interpretation can be substantiated by the observed blue shift in the λ_{max} values of both donor **3** and π-acceptor *TCNE* as the solvent polarity is increased (λ_{max} (**3**): 295, 290, 286 nm;

Table 2. λ_{max}, E_{CT}, K_{CT}, ε_{CT}, and ΔH values for the CT complexes of donor **3** with *TCNE* in various solvents at different temperature

Solvent	Dielectric Constant (D)	λ_{max} (nm)	E_{CT} (eV)	K_{CT} ($dm^3 \cdot mol^{-1}$), °C				ε_{CT} ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)	$-\Delta H$ ($kcal \cdot mol^{-1}$)
				10	15	20	25		
$CHCl_3$	4.806	516	2.404	9.91±0.21	8.77±0.31	7.84±0.39	6.93±0.35	2677.8±185.0	3.97±0.07
CH_2Cl_2	9.08	514	2.413	7.32±0.39	6.86±0.35	6.25±0.22	5.69±0.18	392.8±37.0	2.84±0.19
$C_2H_4Cl_2$	10.65	507	2.447	2.11±0.04	1.98±0.06	1.83±0.20	1.69±0.02	752.4±79.3	2.46±0.10

λ_{max} (*TCNE*): 272, 268, 265 nm; solvents: $CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$). A similar behaviour has been reported previously for the effect of solvent on the stability of weak CT complexes [16, 17].

Characterization of the solid CT complexes

The results of chemical analysis (C, H, N, S, Cl) of the solid CT complexes (Table 3) clearly indicate the formation of 1:1 complexes in each case. A comparison of the IR spectra of the complexes with those of both free donors **1**–**4** and free π-acceptors *DDQ*, *TCNE*, and *CHL* reveals that they are generally close to a superposition of the IR spectra for the two components. For example, the characteristic bands of donors **1**–**4** such as ν_{N-H}, δ_{N-H}, ν_{C-N}, and $\nu_{C=S}$ which appear at 3200–3150, 1505–1480, 1310–1280 and 1030–1020 cm^{-1}, respectively, are found at about the same frequencies in the IR spectra of their CT complexes. Moreover, the vibration frequencies of C≡N for *DDQ* and *TCNE* (observed at 2240 and at 2260, 2230 cm^{-1}, respectively) are slightly shifted to lower frequencies in the corresponding IR spectra of their complexes with donors **2** and **3**, whereas they appear virtually at the same frequencies upon complex formation with donors **1** and **4**. Additionally, the bands of free *DDQ* ($\nu_{C=O}$: 1670 cm^{-1}, $\nu_{C=C}$: 1555 cm^{-1}, ν_{C-Cl}: 802, 720 cm^{-1}) as well as those of free *CHL* ($\nu_{C=O}$: 1690, 1680 cm^{-1}, $\nu_{C=C}$: 1570 cm^{-1}, ν_{C-Cl}: 750, 710 cm^{-1}) appear almost at the same positions in the IR spectra of their CT complexes. This behaviour can be considered as convincing evidence for their nonbonding structure [17, 18] and is in accordance with the results derived above.

Experimental

Materials and solutions

The electron donors **1**–**4** (S-methyl-N-phenyl-dithiocarbamate, S-methyl-N-(p-tolyl)-dithiocarbamate, S-methyl-N-(p-anisyl)-dithiocarbamate, and S-ethyl-N-phenyldithiocarbamate) were prepared according to literature procedures [19]. The ammonium salts of the donors were prepared by dropwise addition of the calculated amount of carbon disulfide in ethanol to the respective amine in an ice-cold mixture of ethanol and concentrated aqueous ammonia (0.1 mol each) with constant stirring. The temperature of the mixture was maintained between 0 and 5°C. The ammonium salts which precipitated were filtered off and washed with ethanol. A cold aqueous solution of each ammonium salt (0.1 mol) was treated dropwise with ethanolic methyl or ethyl iodide (0.1 mol) with vigorous stirring. The precipitate formed was filtered off, washed with water, and recrystallized from a water-ethanol mixture. The purity of the prepared compounds was checked by elemental analysis and thin layer chromatography.

The π-electron acceptors (tetracyanoethylene (*TCNE*), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*), and chloranil (*CHL*); Aldrich or Merck reagent grade) were recrystallized from chlorobenzene, dry methylene chloride, and dry benzene, respectively. Solvents were of spectral grade (BDH). Stock solutions of donors or acceptors were freshly prepared in a dry and deoxygenated solvent prior use in order to avoid any contamination.

Synthesis of the solid CT complexes

Equimolar amounts of donors (**1–4**) and π-acceptors (*DDQ*, *TCNE*, *CHL*) were dissolved separately at room temperature in a minimum volume of dry methylene chloride. The two solutions were mixed, and the resulting solution was left standing overnight at room temperature. The solid compound which separated was collected, filtered off, washed several times with diethyl ether and dried. The analytical data of the synthesized complexes (C, H, N, S, Cl) along with some of their physical properties are given in Table 3. Attempts to prepare the solid CT complexes of donors **1** and **4** with *CHL* failed. The elemental analyses of the complexes were carried out at the microanalytical laboratory, Assiut University, Assiut, Egypt.

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 with an accuracy of ± 0.02°C. IR

Table 3. Microanalytical data, colors, and melting points (d: decomposition)

	Color	m.p. (°C)	% calculated (found)				
			C	H	N	S	Cl
1-*DDQ*	dark brown	300(d)	46.83 (46.58)	2.21 (2.45)	10.24 (10.43)	15.63 (15.47)	17.28 (17.09)
1-*TCNE*	deep brown	70	53.99 (53.82)	2.91 (3.05)	22.48 (22.24)	20.58 (20.39)	
2-*DDQ*	pale brown	290(d)	48.12 (48.21)	2.61 (2.72)	9.90 (9.72)	15.11 (15.26)	16.71 (16.57)
2-*TCNE*	brown	93	55.36 (55.57)	3.41 (3.32)	21.52 (21.28)	19.71 (19.53)	
2-*CHL*	deep grey	95(d)	40.65 (40.37)	2.51 (2.42)	3.16 (3.35)	14.47 (14.16)	32.00 (31.84)
3-*DDQ*	brown	250(d)	46.37 (46.18)	2.52 (2.38)	9.54 (9.41)	14.56 (14.39)	16.10 (16.33)
3-*TCNE*	deep brown	125(d)	52.77 (52.58)	3.25 (3.36)	20.51 (20.39)	18.78 (18.61)	
3-*CHL*	deep brown	121(d)	39.23 (39.04)	2.41 (2.21)	3.05 (2.90)	13.96 (13.78)	30.88 (30.68)
4-*DDQ*	buff	300(d)	48.06 (48.18)	2.61 (2.78)	9.90 (9.68)	15.10 (15.27)	16.73 (16.87)
4-*TCNE*	dark brown	75	55.31 (55.09)	3.40 (3.23)	21.52 (21.44)	19.70 (19.63)	

spectra were measured using a Shimadzu 470 IR spectrophotometer (KBr discs, 4000–400 cm^{-1}). Computations were performed on a Copam 88S PC Computer with the aid of a BASIC program based on an unweighted linear least-squares fit.

References

[1] Uiterwijk JWHM, Harkema S, Feil D (1978) J Chem Soc Perkin Trans II, 72

[2] Theron GD, Ludwing RA (1962) The Dithiocarbamates and Related Compounds. Elsevier, Amsterdam, p 224

[3] Jorgensen CK (1983) Inorganic complexes. Academic Press, London, p 131

[4] Lang RP (1962) J Am Chem Soc **84**: 811

[5] Niedzielski RJ, Drago RS, Middaugh RL (1964) J Am Chem Soc **86**: 1694

[6] Bhasker KR, Gosavi RK, Rao CNR (1966) J Chem Soc Faraday Trans **62**: 29

[7] Bhasker KR, Bhat SN, Murthy ASN, Rao CNR (1966) J Chem Soc Faraday Trans **62**: 788

[8] Lang RP (1968) J Phys Chem **72**: 2129

[9] Abd El-Mottaleb MSA, El-Arrash AM, Abu-Ali MM (1978) Z Phys Chem (Leipzig) **259**: 1083

[10] Seal BK, Banerjee B, Mukherjee DC (1986) Ind J Chem **25A**: 799; (1986) **25A**: 942

[11] De Faria DLA, Goncalves NS, Santos PS (1989) Spectrochim Acta **45A**: 643

[12] Benesi HA, Hildebrand JH (1949) J Am Chem Soc **71**: 2703

[13] Scott RL (1956) Recl Trav Chim Pays-Bas **75**: 787

[14] Aloisi GG, Pignataro S (1973) J Chem Soc Faraday Trans **69**: 534

[15] Seal BK, Banerjee B, Mukherjee DC (1986) Ind J Chem **25A**(9): 799

[16] Dorval-Burnotte C, Zeeger-Huyskens T (1975) Ann Soc Chim Belg **89**: 559

[17] Hamed MMA, Mohamed MB, Mahmoud MR (1994) Bull Chem Soc Jpn **67**(8): 2006

[18] Kainer H, Otting W (1955) Chem Ber 1921

[19] Hadjikostas CC, Katsoulos GA, Shakhater SK (1987) Inorg Chim Acta **133**: 129

Received July 15, 1997. Accepted August 13, 1997