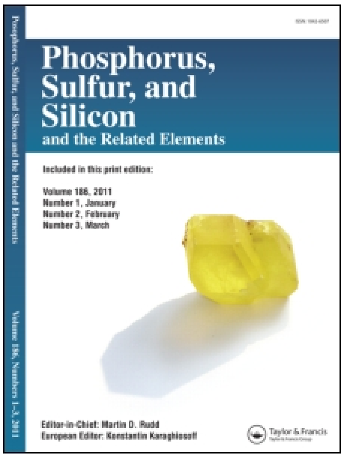

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MOLECULAR INTERACTIONS BETWEEN SUBSTITUTED 3-AMINOMETHYLBENZIMIDAZOLE-2-THIOLS AND TETRACYANOETHYLENE

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MOLECULAR INTERACTIONS BETWEEN SUBSTITUTED 3-AMINOMETHYLBENZIMIDAZOLE-2-THIOLS AND TETRACYANOETHYLENE

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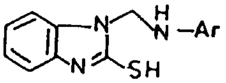
The charge-transfer (CT) complexes of substituted 3-aminomethylbenzimidazole-2-thiols 1a–h as donors with tetracyanoethylene (TCNE) as π-acceptors were studied spectrophotometrically. The stability constants of the complexes were affected by substituents and solvent polarities as well as the thermodynamic properties likewise ΔG, ΔH and ΔS.

Key words: Arylaminomethylbenzimidazolethiols, TCNE, CT-complexation, thermodynamic properties.

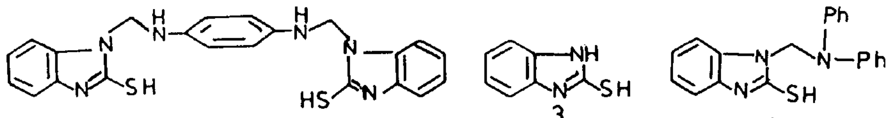
In our recent publications, we have described the interaction of TCNE with 1,2,4-triazole-3-thiols[1]; 1,2,4-triazino[5,6-b]indole-3-thione[2] and S-methyldithiocarbazate,[3] as a biologically active sulfur compound. Due to the physiological activity and further applications of 2-mercaptobenzimidazole as a fungicide, a bactericide and a wood preservative[4,5] efforts have continued towards the interaction of TCNE with 2-mercaptobenzazoles[6] and benzimidazol-2-ylmethanethiols.[7]

With this background we became interested in the chemical interactions between TCNE and mercaptobenzimidazole derivatives.



1

a, Ar=C_6H_5
b, Ar=C_6H_4-CH_3-o
c, Ar=C_6H_4-CH_3-m
d, Ar=C_6H_4-CH_3-p
e, Ar=C_6H_4-OCH_3-p
f, Ar=C_6H_4-Cl-o
g, Ar=C_6H_4-Cl-m
h, Ar=C_6H_4-Cl-p
i, Ar=$C_{10}H_7$



2 3 4

FIGURE 1

TABLE I

Physical and analytical data of substituted-3-aminomethylbenzimidazole-2-thiols 1a–i, 2, and 4

Compound*	m.p	Yield	Mol. Formula	Analysis % Found(Calcd)				
	°C	%	(M.Wt)	C	H	N	S	Cl
1a	170-72	71	$C_{14}H_{13}N_3S$	65.71	5.24	16.29	12.64	
			(255.343)	(65.85	5.13	16.46	12.56)	
1b	151-53	77	$C_{15}H_{15}N_3S$	66.69	5.55	15.76	12.06	
			(269.370)					
1c	133-35	68	$C_{15}H_{15}N_3S$	66.93	5.44	15.49	11.86	
			(269.370)					
1d	128-30	73	$C_{15}H_{15}N_3S$	66.77	5.68	15.71	12.11	
			(269.370)	(66.88	5.61	15.60	11.90)	
1e	188-90	84	$C_{15}H_{15}N_3OS$	62.94	5.44	14.59	11.41	
			(285.369)	(63.13	5.30	14.72	11.24)	
1f	163-65	63	$C_{14}H_{12}N_3ClS$	58.19	4.29	14.36	10.84	12.38
			(289.788)					
1g	143-45	66	$C_{14}H_{12}N_3ClS$	57.97	4.11	14.63	11.26	12.07
			(289.788)					
1h	119-21	69	$C_{14}H_{12}N_3ClS$	57.82	4.24	14.69	11.17	12.42
			(289.788)	(58.03	4.17	14.50	11.07	12.23)
1i	211-13	89	$C_{18}H_{15}N_3S$	71.03	5.11	13.99	10.31	
	(dec.)		(305.403)	(70.79	4.95	13.76	10.50)	
2	228-30	91	$C_{22}H_{20}N_6S_2$	61.33	4.95	19.67	14.59	
			(432.572)	(61.09	4.66	19.43	14.83)	
4	164-66	59	$C_{20}H_{17}N_3S$	72.65	5.29	12.44	9.81	
			(331.440)	(72.48	5.17	12.68	9.67)	

*All compounds are colourless except 1i has a gray colour and 2 has white colour. Also, all compounds recrystallized from ethanol except 1i and 2 recrystallized from DMF/ethanol.

The aim of this paper is to study the interaction between TCNE as electron acceptor and substituted 3-aminomethylbenzimidazole-2-thiols 1a–i and 2 as electron donors at different temperatures by electronic absorption to:

—Determine the site and type of interaction in 1a–i and 2.

—Discuss the effect of SH attached to imidazole ring and the aryl-NH groups on the basicity of the donors.

—Investigate the effect of π-electron clouds of phenyl as well as naphthyl groups on the electron releasing properties of substituted 3-aminomethylbenzimidazole-2-thiols 1a–i.

—The impact of attachment of two aminomethylbenzimidazolyl-2-thiols groups to the benzene ring on the course of reaction, which may proceed with TCNE.

TABLE II

The ¹H-NMR, IR and MS spectral data of compounds 1a–i, 2 and 4

Compound	¹H-NMR(δ,TMS)*	IR(KBr,cm^{-1})	MS m/z(rel. intensity %)
1a	5.25(s,br,1H)SH; 5.60 (s,2H)CH$_2$, 6.75-7.30 (m,10H)Ar-H,NH.	3420,3340(NH); 3060(Ar-CH) 2960(Ali-CH); 1610(Ar-C=C).	150(100); 104(66); 77(46); 65(39).
1b	2.15(s,3H)CH$_3$; 5.30 (s,br,1H)SH; 5.70(s, 2H)CH$_2$; 6.68-7.25(m, 9H)Ar-H, NH.	3425,3335(NH); 3060(Ar-CH); 2970,2915(Ali-CH); 1620, 1590(Ar-C=C).	150(100); 119(71); 118(61); 91(48); 65(22).
1c	2.18(s,3H)CH$_3$; 5.18 (s,br,1H)SH; 5.67(s, 2H)CH$_2$; 6.65-7.32(m,9H) Ar-H, NH.	3440,3325(NH); 3085(Ar-CH) 2980,2910(Ali-CH); 1610, 1580(Ar-C=C).	
1d	2.21(s,3H)CH$_3$; 5.25(s, br,1H)SH; 5.65(s,2H)CH$_2$ CH$_2$; 6.68-7.28(m,9H) Ar-H, NH.	3430,3322(NH); 3080(Ar-CH), 2978,2910(Ali-CH); 1615, 1600(Ar-C=C).	
1e	3.86(s,3H)OCH$_3$; 5.24 (s,br,1H)SH, 5,62(s, 2H)CH$_2$; 6.65-7.25(m, 9H)Ar-H, NH.	3420,3320(NH); 3070(Ar-CH); 2960,2940,2840(Ali-CH); 1590(Ar-C=C).	150(100), 135(59); 134(56); 107(49); 76(55).
1f	5.32(s,br,1H)SH; 5.72 (s,2H)CH$_2$; 6.91-7.42 (m,9H)Ar-H, NH.	3420,3340(NH), 3080(Ar-CH); 2960(Ali-CH); 1610(Ar-C=C).	
1g	5.27(s,br,1H)SH; 5.70 (s,2H)CH$_2$; 6.88-7.39 (m,9H)Ar-H, NH.	3425,3330(NH), 3075(Ar-CH); 2970(Ali-CH); 1610(Ar-C=C).	

TABLE II (*Continued*)

compound	^{1}H-NMR(δ,TMS)*	IR(KBr, cm^{-1})	MS m/z(rel. intensity %)
1h	5.30(s,br,1H)SH; 5.66 (s,2H)CH$_2$; 6.90-7.44 (m,9H)Ar-H, NH.	3446,3340(NH); 3060(Ar-CH); 2950(Ali-CH); 1610,1600 (Ar-C=C).	150(100); 138/140(77); 110 (63); 75(41).
1i	5.34(s,br,1H)SH; 5.73 (s,2H)CH$_2$; 6.77-7.56 (m,12H)Ar-H, NH.	3445-3360(NH); 2990,2980 (Ali-CH); 1610,1575 (Ar-C=C).	153(69); 150(100); 126(44); 65(33).
2	Insoluble in DMSO-d$_6$ or deuterated solvents.	3420,3380(NH); 2950(Ali-CH) 1620, 1580(Ar-C=C).	150(100); 132(82); 120(57); 104(22); 92(32); 73(81); 65(66).
4	5.28(s,br,1H)SH, 5.79 (s,2H)CH$_2$; 6.76-7.51 (m,14H)Ar-H.	3103(Ar-CH);2939(Ali-CH) 1588(Ar-C=C).	

*The solvent of ^{1}H-NMR is CDCl$_3$, except 1i in DMSO-d$_6$.

Mixing dichloromethane solution of the donors 1a–h and TCNE results in formation of a colored solution characterized by an intense electronic absorption in the visible region (595–657 nm), that is attributed to neither component of the complex alone, but to a new molecular species. Such spectra do not exhibit any noticeable variations in intensity with time.

Application of Job's method[8] for continuous variation for 1a–h/TCNE CT-complexes indicates a 1:1 stoichiometric ratio.

The association constants K_{ct} of the CT-complexes examined were determined at six different temperatures (Table III) in dichloromethane using Benesi-Hildebrand's equation.[9]

To study the structural factors which are responsible for complex formation and determine the complexation center in the CT-complexes of donors 1a–i and 2 with TCNE, a comparison including the CT-complex of 2-mercaptobenzimidazole 3 with TCNE[6] was needed. Table III contains the spectrophotometric values of CT-complexes between 1a–h, 3 and TCNE. Accordingly the basic character decreases in the order: 1e > 1b–d > 1a > 1f–h > 3.

A careful examination of Table III reveals that, the spectrophotometric data are affected by variation of the substituents in the aryl group 1a–h (595–657 nm). These results confirm that, the aryl-NH group plays an important role in determining the basicity of substituted 3-aminomethylbenzimidazole-2-thiols 1a–h towards TCNE. It is interesting in this respect to note that, in case of CTC's of the methylated phenylaminomethylbenzimidazole-2-thiols 1b–d with TCNE, the base strength of these donors follow the order para > ortho > meta; while for the

TABLE III

Thermodynamic and spectrophotometric results of substituted-3-aminomethylbenzimidazole-2-thiols <u>1a–h</u> and <u>4</u> with TCNE complexes

Donor	λ_{max}	K_{ct}/1 mol^{-1}						ϵ_{max}	$-\Delta G$	$-\Delta H$	$-\Delta S$	i.p	E
	nm	10°C	15°C	20°C	25°C	30°C	35°C	1.mol^{-1}cm^{-1}	kcal.mol^{-1}	kcal.mol^{-1}	Cal.mol^{-1}K^{-1}	eV	eV
<u>1a</u>	621	7.762 $\pm4X10^{-4}$	6.998 $\pm3.3X10^{-4}$	6.222 $\pm3.2X10^{-4}$	5.689 $\pm4X10^{-4}$	5.129 $\pm3.6X10^{-4}$	4.624 $\pm5.8X10^{-4}$	286	1.025 $\pm3X10^{-3}$	3.648 $\pm2.7X10^{-3}$	8.802 $\pm1.9X10^{-3}$	7.867	1.997
<u>1b</u>	636	9.772 $\pm3.2X10^{-4}$	8.647 $\pm3.7X10^{-4}$	7.583 $\pm4.1X10^{-4}$	7.000 $\pm3.1X10^{-4}$	6.166 $\pm3.5X10^{-4}$	5.600 $\pm4.3X10^{-4}$	143	1.147 $\pm2.9X10^{-3}$	3.922 $\pm3.2X10^{-3}$	9.314 $\pm3.1X10^{-3}$	7.804	1.950
<u>1c</u>	628	8.511 $\pm2.9X10^{-4}$	7.500 $\pm2.7X10^{-4}$	6.536 $\pm2.5X10^{-4}$	6.033 $\pm2.7X10^{-4}$	5.495 $\pm3.3X10^{-4}$	4.954 $\pm4X10^{-4}$	154	1.059 $\pm1.8X10^{-3}$	3.762 $\pm2.4X10^{-3}$	9.070 $\pm3.2X10^{-3}$	7.837	1.975
<u>1d</u>	642	11.220 $\pm3.1X10^{-4}$	9.772 $\pm3.6X10^{-4}$	8.710 $\pm2.8X10^{-4}$	7.762 $\pm2.9X10^{-4}$	6.918 $\pm3.4X10^{-4}$	6.166 $\pm5X10^{-4}$	250	1.208 $\pm1.3X10^{-3}$	4.186 $\pm1.9X10^{-3}$	9.995 $\pm2.2X10^{-3}$	7.780	1.931
<u>1e</u>	657	13.183 $\pm4X10^{-4}$	11.482 $\pm4.6X10^{-4}$	9.772 $\pm4.2X10^{-4}$	8.590 $\pm5X10^{-4}$	—	---	313	1.268 $\pm3X10^{-3}$	5.004 $\pm3.6X10^{-3}$	12.539 $\pm3.2X10^{-3}$	7.721	1.887
<u>1f</u>	595	3.698 $\pm2X10^{-4}$	---	3.206 $\pm2.6X10^{-4}$	2.864 $\pm2.3X10^{-4}$	2.723 $\pm3.1X10^{-4}$	2.570 $\pm3.5X10^{-4}$	104	0.620 $\pm4X10^{-3}$	2.612 $\pm5X10^{-4}$	6.683 $\pm4.1X10^{-4}$	7.997	2.095
<u>1g</u>	602	4.519 $\pm1.9X10^{-4}$	4.121 $\pm2.4X10^{-4}$	3.715 $\pm1.8X10^{-4}$	3.388 $\pm2.3X10^{-4}$	3.126 $\pm3.2X10^{-4}$	2.851 $\pm3.4X10^{-4}$	91	0.719 $\pm3X10^{-3}$	3.256 $\pm2.3X10^{-3}$	8.512 $\pm4X10^{-4}$	7.928	2.043
<u>1h</u>	608	5.012 $\pm2.2X10^{-4}$	4.624 $\pm2.8X10^{-4}$	4.121 $\pm2.6X10^{-4}$	3.673 $\pm2.8X10^{-4}$	3.428 $\pm3.2X10^{-4}$	3.162 $\pm3.5X10^{-4}$	111	0.767 $\pm2.4X10^{-3}$	3.351 $\pm3X10^{-3}$	8.671 $\pm2.3X10^{-3}$	7.889	2.013
<u>3</u>*	592	---	---	9.023	----	----	----	200	---	---	---	7.997	2.095
<u>4</u>	570	--	---	3.167	----	---	---	222	---	---	---	8.105	2.175

*The data taken from Reference 6.

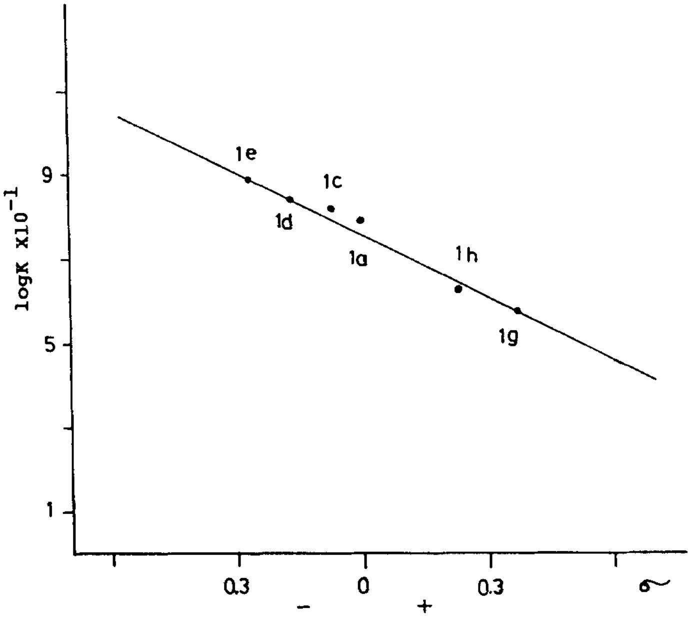


FIGURE 2 Hammet plot for complex formation between TCNE with some *m* and *p* substituted-3-aminomethylbenzimidazole-2-thiols.

chlorinated phenylaminomethylbenzimidazole-2-thiols 1f–h it follows the order para > meta > ortho. This trend is in agreement with the normal principles of the inductive and mesomeric effects of the nature of substituents.[10,11]

Plotting log K_{ct} for *m*, *p*-phenylaminomethylbenzimidazole-2-thiol derivatives 1a–h complexed with TCNE against Hammet's values[12] which are a good measure of the electronic inductive and mesomeric effects involved in the CT-complexation, gives a straight line with a slope $\rho = -0.687$ and correlation coefficient $r^* = 0.993$ (Figure 2).

The ionization potential values of the donors listed in Table III, were estimated from the energies of the CT-bands applying the well known empirical equation[12] $i.p = a \pm b\bar{\nu}_{ct}$. As seen in Table III, the i.p values of donors 1a–h vary regularly with the transition energies of the corresponding CT-complex.[12,13]

Substitution of the hydrogen atom of NH-attached to aryl group by phenyl group in 1a inhibits the electron releasing character of these donors (see Table III). From the above findings it is reasonable to conclude that the substituted 3-aminomethylbenzimidazole-2-thiol system can undergo three different types of transitions based on the presence of the three donating centers π-π^* (aryl group), n-π^* (N-atom) and n-π^* (S-atom).

Several attempts were made to dissolve 1i, and 2 in dichloromethane, dichloroethane, chloroform, and ethyl acetate, but all trials failed.

THERMODYNAMIC STUDIES

From the data given in Table III as ΔH values decreases, a corresponding decrease in ΔS was also observed. This simultaneous decrease in these thermodynamic

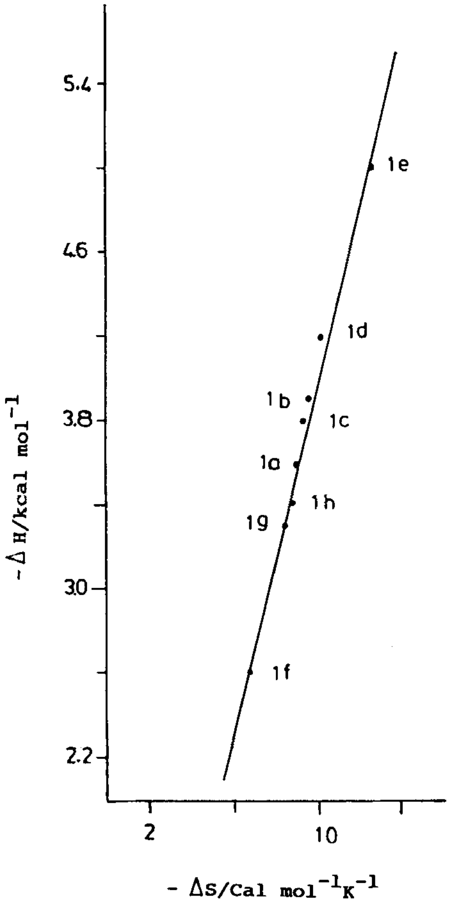


FIGURE 3 Relationships between enthalpies and entropies of formation for CT-complexes of a series of substituted-3-aminomethylbenzimidazole-2-thiols with TCNE.

parameters may serve as an indication of the physical restraints imposed upon the complex components as the strength of the interaction between them increase. The experimental results in Table III also show that the values of the thermodynamic properties are affected by variation of the substituents in the arylaminomethylbenzimidazole-thiol system.

A linear relationship between ΔH and ΔS (Figure 3) usually shown by series of related equilibria involving moderate changes in structures[13] is also indication of this behaviour; where the slope 415 K represents the so-called "isokinetic temperature."[14]

SOLVENT EFFECT

In order to investigate the effect of solvents on the CT-interaction between phenyl-3-aminomethylbenzimidazole-2-thiol 1a and TCNE, the electronic absorption spectra of the 1a-TCNE complex were investigated in different solvents having various

TABLE IV

Thermodynamic parameters of phenyl-3-aminomethylbenzimidazole-2-thiol <u>1a</u> with TCNE in different solvents

Solvent	λ_{max}	$K_{ct}/1\ mol^{-1}$						ε_{max}	$-\Delta G$	$-\Delta H$	$-\Delta S$	Dielectric
	nm	10°C	15°C	20°C	25°C	30°C	35°C	$1.mol^{-1}cm^{-1}$	$kcal\ mol^{-1}$	$kcal\ mol^{-1}$	$Cal.mol^{-1}K^{-1}$	constant
Dichloromethane	621	7.762 $\pm4X10^{-4}$	6.998 $\pm3.3X10^{-4}$	6.222 $\pm3.2X10^{-4}$	5.689 $\pm4X10^{-4}$	5.129 $\pm3.6X10^{-4}$	4.624 $\pm5.8X10^{-4}$	286	1.025 $\pm3X10^{-3}$	3.648 $\pm2.7X10^{-3}$	8.802 $\pm1.9X10^{-3}$	8.90
1,2-Dichloroethane	617	6.400 $\pm3.6X10^{-4}$	5.647 $\pm2.8X10^{-4}$	5.077 $\pm2X1o^{-4}$	4.667 $\pm2.9X10^{-4}$	4.226 $\pm3.2X10^{-4}$	3.981 $\pm4.4X10^{-4}$	167	0.908 $\pm3.1X10^{-3}$	3.239 $\pm2.5X10^{-3}$	7.823 $\pm3.6X10^{-3}$	10.65
Chloroform	628	8.735 $\pm4.3X10^{-4}$	7.993 $\pm3.7X10^{-4}$	7.266 $\pm3X10^{-4}$	6.309 $\pm4.1X10^{-4}$	5.623 $\pm3.9X10^{-4}$	5.070 $\pm4.6X10^{-4}$	206	1.086 $\pm3.6X10^{-3}$	3.938 $\pm3.3X10^{-3}$	9.570 $\pm2.4X10^{-3}$	4.80
Ethyl acetate	600	4.074 $\pm5X10^{-4}$	3.715 $\pm5.3X10^{-4}$	3.388 $\pm4.7X10^{-4}$	3.162 $\pm4.9X10^{-4}$	2.884 $\pm5.1X10^{-4}$	2.691 $\pm5.5X10^{-4}$	29	0.679 $\pm4.7X10^{-3}$	2.812 $\pm4.3X10^{-3}$	7.158 $\pm4.1X10^{-3}$	—

polarities. The different values of λ_{max} as well as K_{ct} in Table IV suggested that, the role of solvent interaction with TCNE cannot be neglected. The observed increase in K_{ct} values measured in chloroform suggests that, the complex is better solvated by chloroform than by other solvents. This can be ascribed to the presence of a certain competition between donor and solvent via formation of a hydrogen bond between the nitrogen-lone pair of the donor and the hydrogen atom of chloroform.

Since dichloromethane and 1,2-dichloroethane are of comparable polarity their effect on complex formation is similar. The chlorinated solvents were chosen since they are more suitable than any others such as ethyl acetate (see Table IV). It has been reported that, despite Franck-Condon constraints increasing polarity of the solvent will result in high stabilization of the excited state owing to an increased dipole-dipole or dipole-induced dipole interaction.[15-18]

EXPERIMENTAL

Melting points are uncorrected. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer equipped with a temperature regulated cell holder. Matched quartz (stoppered) cells of 1 cm path length were used. All scans covered the range 350–850 nm. IR spectra were recorded on Perkin-Elmer 983 spectrophotometer. ^{1}H-NMR spectra on Bruker WM 300 (300 MHz), and the chemical shifts were expressed as δ(ppm) with TMS as the internal standard. The MS spectra were recorded on MAT 311A (70 eV, EI mode, temp. of inlet system given). Elemental analysis were performed by microanalytical unit at Cairo and Duisburg Universities.

Preparation of aryl-3-aminomethylbenzimidazole-2-thiols 1a–h and 4

By adding 37% aqueous formaldehyde solution (2 ml) to a hot mixture of 2-mercaptobenzimidazole 3 (0.01 mol) and the appropriate amine (0.01 mol) in 20 ml absolute ethanol. The mixture was heated on a water bath for 10 min. and then set aside at room temperature over night. The reaction mixture was then chromatographed on thin layer plates using toluene/ethyl acetate (4:1) as eluent. Only one zone was well separated which contained compound 1a–h. The base line of TLC contained unreacted 2-mercaptobenzimidazole which was established from the comparison of its spectral data as well as melting point of those of an authentic sample (Aldrich) reagent.

Preparation of naphthyl-3-aminomethylbenzimidazole-2-thiol 1i and 1,4-bis(3-aminomethylbenzimidazole-2-thiol)benzene 2

By adding 37% aqueous formaldehyde solution (2 ml) to a hot mixture of 2-mercaptobenzimidazole 3 (0.01 mol) and α-naphthylamine (0.01 mol) or paraphenylenediamine (0.01 mol) in 20 ml absolute ethanol, gray crystals of 1i or white crystals of 2 had precipitated.

Analytical and physical data of 1a–i, 2 and 4 are recorded in Tables I and II.

Tetracyanoethylene (TCNE, Aldrich) was recrystallized from chloroform and sublimed. Dichloromethane, dichloroethane, chloroform and ethyl acetate were purified, dried and distilled before use by standard methods.[19]

UV/vis spectrophotometric measurements on the complexes of aryl-3-aminomethylbenzimidazole-2-thiols 1a–h and 4 with TCNE

For the determination of the stoichiometry by Job's method,[8] stock solutions (2×10^{-2} mol/l) of TCNE and donors 1a–h and 4 were prepared accurately.

Association constants (K_{ct}) values of the CT-complexes were determined using Benesi-Hildebrand's equation[9] for a 1:1 CT-complexes

$$\frac{[A]l}{d} = \frac{1}{K\varepsilon} \cdot \frac{1}{[D]} + \frac{1}{\varepsilon}$$

where [A] and [D] are the initial molar concentration of acceptor and donor respectively, l the length of the light path in cm, d is the optical density, ε is the apparent molar extinction coefficient and K is the association constant.

Donors 1a–h and 4 as well as TCNE concentrations ranged from 1×10^{-2} to 1×10^{-1} M (1 M = 1 mol dm^{-3}). Dichloromethane was used as a solvent for the study of all CT-complexes. The effect of temperature on the formation and stability of CT-complexes in dichloromethane was determined by increasing the temperature of all gradually from 10°C to 35°C (±0.5°C) and decreasing it from 35 to 10°C with the same sample, whenever the change of the intensity was not reversible, the donor-acceptor pair in question was not regarded as forming a stable CTC.

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