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Spectroscopic and structure investigation of the molecular complexes of tris(2-aminoethyl)amine with π-acceptors

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ABSTRACT

The intermolecular charge transfer CT-complexes of tris(2-aminoethyl)amine (TREN) with different π-acceptors such as picric acid (PIC), o-chloranil (CHL) and tetracyanoquinolines (TCNQ) were investigated in both solid and liquid phase. Spectroscopic techniques, such as FT-IR, ^{1}H NMR, ^{13}C NMR, and UV–vis, were used to characterize the molecular complexes. Spectral data, for example, formation constants, molar extinction coefficient, standard free energy, and ionization potentials for the complexes were calculated for the 1:1 molecular CT-complexes. Exploring the single crystal of TREN/PIC, grown by slow evaporation technique from methanol solution at room temperature, shows that CT-complex stabilized by two noncovalent interactions, namely, hydrogen bond and dipole–dipole interactions. In addition, the structure of tris(2-aminoethyl)amine and CHL and TCNQ complexes were investigated by DFT calculations at B3LYP/6-311++G(d,p) level of theory.

1. Introduction

Compounds that involve charge-transfer (CT) process are ubiquitous in both biological systems [1] and optoelectronic devices [2]. For example, the CT interactions are responsible for stabilizing the organic molecules that intercalate between DNA bases, which can be used for cancer therapy [3]. In addition, CT process plays a key role in biological energy conversion in particular photosystems I and II (PSI and PSII) [4,5]. On the other hand, CT complexes are widely used in material science applications such as fabrication of layer-by-layer films [6], preparation of supramolecular crystals [7], and supra-amphiphiles [8]. The driving forces for the CT complex formation have always been intriguing to the researchers.

Noncovalent interactions, in particular hydrogen bonding (HB), have been a cornerstone in the design of such molecular complexes, which was firstly introduced in 1970 by O. Hassel in his Nobel lecture. Noncovalent interactions, such as electrostatic (ion–ion, ion–dipole, and dipole–dipole), π–π stacking interactions, cation–π interactions, van der Waals forces, hydrophobic interactions, and hydrogen bonding, play key role in the self assembly of supramolecular systems [9,10]. In particular, hydrogen bond (HB) attracts special interest due to the importance in crystal engineering, drug delivery, and eventually in biological systems [11–13]. In analogy to HB, halogen bonding was recently introduced to play important part in the assembly of supramolecular systems [14] as well as CT molecular complexes [15,16].

The stability of the CT complexes depends on the strength of the donor compounds, which based on different organic and inorganic molecules. For example, imidazoles [17], thiazoles [18], and pyrimidines [19] derivatives have been widely used to construct the scaffold of donors. Herein, we extended the CT donor skeleton with tris(2-aminoethyl)amine (TREN, Scheme 1), which has been widely used as scaffold for the synthesis of 3-fold symmetric tripodal ligands [20], and metal binding ligands for both transition metals [21–25] and main group elements [26]. In such complexes, noncovalent interactions reported to be the deriving forces, for example, HB was the main binding force in the synthesis of water-soluble chelators from TREN derivatives that show promising contrast agents in magnetic resonance imaging (MRI) applications [27,28]. In addition, HB plays the key role for the sulfonamide and amide derivatives of TREN to facilitate the phospholipid translocation across vesicle and erythrocyte membranes [29]. In this work, we are investigating the molecular CT-complex between tris(2-aminoethyl)amine (TREN) and different acceptors such as picric acid (PIC), *o*-chloranil (CHL), and tetracyanoquinodimethane (TCNQ), in order to study the role of noncovalent interactions in complex stabilization. Theoretical calculations (DFT) using B3LYP/6-311++G(d,p) level of theory were used to corroborate the experimental results.

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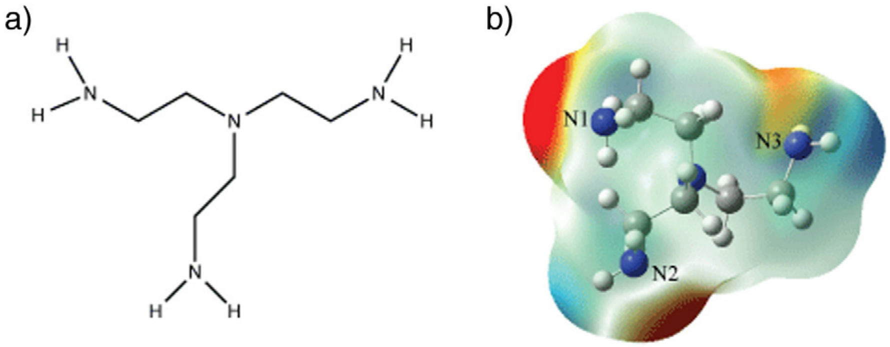

Scheme 1. a) Structure of tris(2-aminoethyl)amine (TREN), b) electrostatic potential map of TREN, B3LYP/6-311++G (d,p), the red to blue color spans −23.7 to +23.07 kcal/mol^{-1}.

2. Experimental

2.1. Materials and solutions

Tris(2-aminoethyl)amine (TREN) was supplied from Sigma-Aldrich (Germany) and used without further purification. All solvents were of spectral grade (BDH). The stock solutions of the donor (TREN) and acceptors (picric acid (PIC), 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL), and tetracyanoquinodimethane (TCNQ) were freshly prepared in a dry and deoxygenated solvent prior to use in order to avoid any contamination.

2.2. Instruments

Absorption spectra were scanned on a Shimadzu 2401PC spectrophotometer using 1 cm matched quartz cells. Temperature control was achieved using a Julabo F30 ultrathermostat with an accuracy of ±0.05 °C. Infrared spectral measurements (FT-IR) for the free donor and the CT-complex were recorded in KBR pellets using FT-IR Prestige-21 Shimadzu, in the range of 400–4000 cm^{-1}. The ^{1}HNMR spectra were recorded by 200 and 300 MHz Varian EM 390 spectrometer; chemical shifts are reported in ppm with TMS as an internal standard and are given in δ units.

Crystallographic data of the TREN-PIC were collected on a Smart CCD diffractometer of Bruker AXS using Mo Kα radiation. The crystal does not show significant intensity loss through data collection. Lorentz-Polarization corrections were performed by SAINT [30]. Absorption corrections were made by using SADABS [31]. The structure was solved by direct or Patterson methods using SHELXS-97 [32] to find the position of heavy atoms. Other non-hydrogen atoms were located by Fourier syn- theses and refined using SHELXS-97. The least-squares refinements were performed using all independent reflections by the full matrix on F2. All non-hydrogen atoms were refined anisotropically. X-ray diffraction study was carried out using XRD-6000 (SHIMADZU). The X-ray was detected using a fast counting detector based on silicon strip technology. The crystal structure and lattice parameter were analyzed by Bragg's law, 2dsinθ = nλ and particle size is calculated by Debye Scherer's formula, t = 0.9 λ/B cos θ [33,34].

2.3. Synthesis

A hot methanolic solution (25 mL) of each acceptor (3.0 mmol): PIC (69 mg), CHL (74 mg), or TCNQ (61 mg) was added to a solution of TREN (1.0 mmol, 149 L) in 10 mL of methanol. Transparent solutions was obtained in each case, which was kept standing for 5 days. A yellow, Brawn and black crystals were deposited for the CT complexes of TREN/PIC, TREN/CHL, and TREN/TCNQ, respectively, which were washed and re-crystallized from methanol.

CT complex of TREN/(PIC)$_3$: For $C_{24}H_{24}N_{13}O_{21}\cdot CH_3OH$ (862.57): calcd. C, 34.81; H, 3.27; N, 21.11; found C, 33.99; H, 3.06; N, 21.32. IR (KBr): (cm^{-1}): 3058 (br, C–H$_{Ar}$), 2944 (br, C–H$_{aliph}$), 2734 (w, NH_3^+), 1604, 1479 and 1427 (vs, skeletal C = C), 1540 (vs, NO_{2asy}), 1328 (vs, NO_{2sy}), 1260 ((vs, C–O), 1157 (m, C–NH$_{str}$), 916 (C–H$_{def}$), and 704 (N–H$_{wag}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.59 (s, 6 H, 3H-3$_{Ph}$, 3H-5$_{Ph}$), 7.56 (br.s, 3H, 3 O–H), 2.91 (br.s, 6H, 3NH$_2$), 2.61 [m, 12H, $N(CH_2CH_2NH_2)_3$]; ^{13}C NMR: δ 161.50 (3 C-1$_{Ph}$), 142.20 (3 C-2$_{Ph}$, 3 C-6$_{Ph}$), 124.60 (3 C-3$_{Ph}$, 3 C-5$_{Ph}$), 124.30 (3 C-4$_{Ph}$), 51.60 [$N(CH_2)_3-$], 36.40 ppm (3 –CH_2NH_2).

CT complex of TREN/(CHL)$_3$: Anal. For $C_{12}H_{18}N_4O_2Cl_4$ (392.11): calcd. C, 36.67; H, 4.63; N, 14.29; Found C, 35.85; H, 4.72; N, 13.98. IR (KBr): (cm^{-1}): 3211(br, N–H$_{str}$), 2944 (br, C–H$_{aliph}$), 1737, 1654 (m, C=O), 1005 (C–Cl). ^{1}H NMR (400 MHz, DMSO-d_6): 8.05–7.93 (m, 3 H, OH$^+$), 3.86 (br.s, 3 H, 3NH$^-$), 2.88 [m, 6 H, N–CH_2-]; 2.62 [m, 6 H, N–CH_2.

CT complex of TREN/(TCNQ)$_3$: Anal. For $C_{42}H_{30}N_{16}\cdot 2CH_3OH$ (822.89): calcd. C, 64.22; H, 4.65; N, 27.23; Found C, 63,43; H, 4.82; N, 26.91. I R (KBr): (cm^{-1}): 3243 (br, N–H$_{str}$), 3037 (br, C–H$_{olif}$), 2828 (br, C–H$_{aliph}$), 2170 (s, C≡N$_{uncomplexed}$), 2115 (vs, C≡N$_{complexed}$),

Table 1
Crystal data and structure refinement of the TREN-Picric.a, b

Compound	TREN-PIC
Empirical formula	$C_{25}H_{24}N_{13}O_{23}$
Formula weight, g/mol	874.535
Temperature/K	298
Crystal system	Triclinic
Crystal color	Yellow
Wavelength/Å	0.71073
Space group	P −1
a/Å	8.4224 (2)
b/Å	12.5440 (3)
c/Å	18.4015 (5)
α/°	72.0793 (12)°
β/°	83.4136 (10)°
γ/°	72.4234 (10)°
Volume/Å3	1762.94 (8)
Z	2
D_{calc}/(g/cm^3)	1.648
Absorption coefficient	None
F(000)	890
Crystal size/mm	
➜ range for data collection/°	2.910–27.485°
Reflections collected	12,068
Independent reflections	9448
R(int)	0.030
Observed (I > 2⇔(I))	3151
Goodness-of-fit on F2	1.17
R[I > 2⇔(I)][a]	0.065
wR (all data)[b]	0.1180

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.
[b] $R_W = [\Sigma w(F^2 - F^2)^2 / \Sigma w(F^2)^2]^{1/2}$.