

# Bis-(S-Benzylthiuronium) Chloranilate Supramolecular Crystal Structure: Preparation and Characterization

Dimitrios V. Stergiou,<sup>†</sup> Stavroula Skoulika,<sup>‡</sup> Nikolaos P. Evmiridis,<sup>†</sup> and Panayotis G. Veltsistas<sup>\*,†</sup>

Laboratory of Analytical Chemistry and Laboratory of Physical Chemistry, Department of Chemistry, University of Ioannina, 451 10, Ioannina, Greece

Received July 29, 2004. Revised Manuscript Received December 6, 2004

A novel supramolecular structure,  $[\text{C}_8\text{H}_{11}\text{N}_2\text{S}]_2^+(\text{C}_6\text{Cl}_2\text{O}_4)_2$ , based on hydrogen bonding of the organic S-benzylthiuronium (SBT) cation and the chloranilate dianion, is presented. Chloranilic acid or 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, is a strong quinoidal diphenic acid ( $\text{p}K_1 = 1.09$  and  $\text{p}K_2 = 2.42$ ), with molecular formula  $\text{C}_6\text{Cl}_2\text{O}_4\text{H}_2$  ( $\text{H}_2\text{CA}$ ). The CA-dianions and the aromatic rings of the SBT-cations form columns along the *c*-axis giving an ordered pattern of dianions surrounded by densely populated areas of SBT-cations. Each CA-dianion forms eight hydrogen bonds with the amine protons of six SBT-cations, through its oxygen atoms. In this way, an extended H-bond network, containing infinite chains of alternative  $\text{R}_4^2(8)$  and  $\text{R}_2^2(9)$  cyclic patterns, is obtained. The whole arrangement leads to a  $\text{C}2/c$  space group crystal structure, with unit cell dimensions  $a = 15.109 \text{ \AA}$ ,  $b = 11.606 \text{ \AA}$ , and  $c = 14.390 \text{ \AA}$  and with unit cell angles of  $\alpha = \gamma = 90^\circ$ , and  $\beta = 97.01^\circ$ , and average density of  $1.43 \text{ g/cm}^3$ . Dissolution of the crystalline material in DMSO leads to the formation of associated organic ions or charge-transfer complexes as evidenced from the bathochromic shift of the absorption band of chloranilic acid from 420 to 520 nm.

## Introduction

Physical properties of organic solid materials depend on supramolecular structure, which is the result of the aggregation of molecules by weaker than covalent bond interactions such as hydrogen-bond, dispersion forces,  $\pi$ – $\pi$  orbital interactions, etc. Such interactions lead to 1-D, 2-D, or 3-D structures by proper choice of the functional groups in the organic molecules involved.<sup>1,2</sup>

Ionic organic compounds enhance interactions of hydrogen bonding by electrostatic forces and provide structures that depend on the size, charge, and the proximity of the hydrogen-bond donors and acceptors of the ionic species involved.<sup>2</sup>

Crystal architecture is the field that exploits these interactions to design crystals with tailor-made properties based on weak interactions; the field is expanding very quickly because of the huge amount of data available in the literature and the rapid development of computer technology.<sup>3,4</sup> However, apart from the existing structure data the field now experiences the need for more data oriented to a crystal engineering view of the subject. Therefore, data are needed for organic molecules that contain a larger charge, or multiple functional groups, and/or  $\pi$ -electron donors and acceptors.

Dihydroxybenzoquinone ( $\text{H}_2\text{dmbq}$ ) is an organic molecule that possesses  $\pi$ -electrons, C–OH groups, and C=O groups for  $\pi$ -electron donor and acceptor interactions. The molecule has the property of resonance, it can be ionized stepwise to give anion species of different charge by gradual increase of pH; it can also be reduced through various steps to produce anion species of higher charge; and finally, it possesses coordinative properties.<sup>1</sup> Because of all these interesting properties the molecule is useful for optical, electrochemical, and physicochemical applications; for instance, chloranilate anions ( $\text{Cl}_2\text{dmbq}$ ) are known for their charge-transfer properties giving colored products<sup>5–10</sup> that are useful in extended spectrophotometric analyses<sup>11</sup> or when combined with transition metal ions give complexes with a variety of either monomer or polymer structures that provide interesting materials in the field of electrochemical and optical sensors.<sup>1,12</sup>

Ionic organic derivatives of chloranilates ( $\text{Cl}_2\text{dmbq}$ ), with various organic cation species<sup>13</sup> are a matter of significant interest in fine-tuning the formation of crystalline structures

\* Corresponding author: E-mail: panavelt@cc.uoi.gr. Tel: +30-26510-98411. Fax: +30-26510-44831.

<sup>†</sup> Laboratory of Analytical Chemistry.

<sup>‡</sup> Laboratory of Physical Chemistry.

- (1) Kitagawa, S.; Kawata, S. *Coord. Chem. Rev.* **2002**, *224*, 11.
- (2) Aakeroy, C. B. *Acta Crystallogr., Sect. B: Struct. Sci.* **1997**, *53*, 569.
- (3) Nangli, A.; Desiraju, G. R. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1998**, *54*, 934.
- (4) Wright, J. D. *Encyclopedia of Materials: Science and Technology*; Elsevier and Science Ltd: New York, 2000.

- (5) Rodriguez, V.; Gutierrez-Zorrilla, J. M.; Vitoria, P.; Luque, A.; Raman, P.; Martinez-Ripoll, M. *Inorg. Chim. Acta* **1999**, *290*, 57.
- (6) Zaman, M. B.; Morita, Y.; Toyoda, J.; Yamochi, H.; Saito, G.; Yoneyama, N.; Enoki, T.; Nagasuiji, K. *Chem. Lett.* **1997**, *26*, 729.
- (7) Zaman, M. B.; Tomura, M.; Yamashita, Y. *Org. Lett.* **2000**, *2*, 273.
- (8) Ishida, H.; Kashino, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1149.
- (9) Ishida, H.; Kashino, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1923.
- (10) Ishida, H.; Kashino, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1714.
- (11) Ouah, J. Og.; Odeiani, J. E. *J. Pharm. Biomed. Anal.* **2002**, *29*, 639.
- (12) Beg, M.; Arshad, A. *Pak. J. Sci. Ind. Res.* **1971**, *6*, 452.
- (13) Horiuchi, S.; Yamochi, H.; Saito, G.; Sagaguchi, K.; Kusunoki, M. *J. Am. Chem. Soc.* **1996**, *118*, 8604.

with different redox, charge-transfer, magnetic, and other physical properties. Only a few studies have been made toward this end, using halogenated dehydroxybenzoquinone ( $X_2\text{d}h\text{bq}$ ) derivatives with bis-(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) and bis-(pentamethylcyclopentadienyl)-iron as well as 4,4'-bipyridine and 1,2-bis-(2-pyridyl)-ethylene.<sup>14</sup> Further structural studies were done with dicyano-dhbq using OMTTF.<sup>15,16</sup> Ionic organic crystalline materials can also be formed using a variety of ammonium or uronium or thiuronium compounds and their aromatic derivatives. The latter compounds are of special interest as reagents for selective detection/determination of Ni(II) and Co(II) or as reagents for separation and identification of carboxylic, sulfonic, and sulfinic acids.<sup>17</sup>

S-Benzylthiuronium chloranilate ion pair ( $\text{SBT}$ )<sub>2</sub>—CA combines the reactivity with transition metal ions, the redox properties, and the easy electron-transfer properties between molecular entities; the charge delocalization provides an excellent material for use in electrochemical processes and in optics, and among others, finds applications in analytical chemistry.<sup>18</sup>

This work reports the preparation, identification, physical properties, and crystal structure of the ionic compound ( $\text{SBT}$ )<sub>2</sub>—CA. In addition, spectral-data and the interactions of solved S-Benzylthiuronium—chloranilate ion pair salt are presented.

## Experimental Section

**Reagents.** S-Benzylthiuronium chloride ( $\text{C}_8\text{H}_{11}\text{N}_2\text{SCL}$ , Product 13520, >98%, MW = 202.71, mp = 172–77 °C) was purchased from Fluka (Buchs, Switzerland). The salts of chloranilic acid ( $\text{CAM}_2$ , M = Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>) are satisfactorily soluble in water. Chloranilic acid dilithium salt was synthesized in situ by suspending the stoichiometric quantities of chloranilic acid and lithium carbonate in the aqueous system (400 mL), under warming on a water bath for 1 h, until all the carbon dioxide was removed and all volatiles were expelled.<sup>18</sup> Lithium carbonate ( $\text{Li}_2\text{CO}_3$ , Product 5680, PA min. 99%) and chloranilic acid ( $\text{C}_6\text{H}_2\text{Cl}_2\text{O}_4$ , Product C-8136, >98%, MW = 208.99, mp >300 °C) were obtained from Merck (Darmstadt, Germany) and Sigma (Sigma, St. Louis, MO), respectively. All other reagents were of analytical grade, and distilled water was used throughout.

**Preparation of the ( $\text{SBT}$ )<sub>2</sub>—CA Ion Pair.** A 200.0 mL warm ethanolic solution of 61.66 mM (plus a 10% excess) of S-benzyl-isothiourrea hydrochloride salt ( $\text{SBT}\cdot\text{HCl}$ ) (Fluka, >98%) was introduced into 400.0 mL of warm aqueous solution of 30.83 mM lithium chloranilate ( $\text{C}_6\text{Cl}_2\text{O}_4\text{Li}_2$ ), under a continuous stream of Ar and stirring on a water bath (80 °C) for 1 h,<sup>17</sup> to complete the formation and the precipitation reaction of the ion-paired salt:



The reaction mixture was cooled to room temperature<sup>22</sup> and then frozen on an ice—salt bath. After 6 h the ion pair salt was separated into lustrous cherry-red monocrystals with metallic reflections and a peculiar characteristic odor. The crystals were separated from the aqueous solution through filtration with a Gooch No. 3 glass filter. After the crystals were rinsed three times with 30 mL of cold water and EtOAc, they were drained in an air stream and later in a vacuum over  $\text{P}_2\text{O}_5$ . The practical yield reached approximately 92% of the theoretical one.

**Characterization.** The thermochemical data were obtained by using a Chyo Balance (model TRDA<sub>3</sub>-H). The material was placed in the balance using  $\text{Al}_2\text{O}_3$  reference material and the thermograms were taken at a temperature increase rate of 5 K/min and under an atmosphere of a mixture of  $\text{N}_2$  and air obtained at flow rates of 20 and 30 mL per minute, respectively. The sample used was 29.200 mg versus 106.000 mg of the reference material.

UV—Vis spectra were obtained using a Perkin-Elmer 15 UV—Vis spectrophotometer from a 2.00 mL DMSO solution containing 38.0 mg of the ( $\text{SBT}$ )<sub>2</sub>—CA compound.

Fluorescence spectra were obtained using a Perkin-Elmer spectrofluorimeter. The solid material was dissolved in acetone and the emission spectrum was obtained using an excitation wavelength of 264 nm.

Diffuse reflectance spectra were obtained using a Shimadzu UV-2401 PC recording spectrophotometer. A small quantity of the compound (approximately 1%) was properly dispersed into a  $\text{BaSO}_4$  pellet, which was used both as support and reference material.

IR spectra were obtained using a Perkin-Elmer 580 spectrometer. The solid material was pressed with KBr into disc-pellet and the IR-spectra were run from 4000 to 400  $\text{cm}^{-1}$ .

<sup>1</sup>H- and <sup>13</sup>C NMR spectra were obtained using a Bruker NMR—spectrometer. The crystals were dissolved in DMSO-(*d*<sub>6</sub>) using TMS as reference material.

**Crystal Structure Analysis.** The X-ray diffraction intensities were obtained at room temperature on a Bruker P4 diffractometer employing graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined on F<sup>2</sup> with SHELXL97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by difference Fourier maps and were refined isotropically.

## Results and Discussion

**Elemental Analysis.** The experimental elemental analysis data and the calculated ones for the ( $\text{SBT}$ )<sub>2</sub>—CA ion-pair salt are tabulated in Table 1. The agreement between the experimental and the theoretical is found to be satisfactory.

**Physical Properties.** The prepared ( $\text{SBT}$ )<sub>2</sub>—CA salt was found to be moderately soluble in cold water and very soluble in hot water, ethanol, methanol, acetone, and dioxan, and less soluble in DMF, DMSO, TBP, MIK, and BenzOH. It is practically insoluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , and EtOAc. The density value of the solid salt, measured with a Quantachrome SPY 3(478)-type densitometer is found to be  $d = 1.43$  g/cm<sup>3</sup> (at 25 °C), which is in full agreement with

- (14) Zaman, M. B.; Tomura, M.; Yamashita, Yo. *Chem. Commun.* **1999**, 11, 999.
- (15) Zaman, M. B.; Toyoda, J.; Morita, Y.; Nakamura, S.; Yamochi, H.; Saito, G.; Nakasuji, K. *Synth. Met.* **1999**, 102, 1691.
- (16) Yamochi, H.; Nakamura, S.; Saito, G.; Zaman, M. B.; Toyoda, J.; Morita, Y.; Nagasuji, K.; Yamashita, Y. *Synth. Met.* **1999**, 102, 1729.
- (17) Donleavy, J. J. *J. Am. Chem. Soc.* **1936**, 58, 1004.
- (18) Veltsistas, P. G. Contribution to the chloranilate compounds. Synthesis and characterization of new chloranilate substances. Construction, study of the characteristics and analytical application of two liquid membrane chloranilate ion-selective electrodes. Doctoral Thesis, University of Ioannina, Ioannina, Greece, 1992.

- (19) Papadimitriou, Ch.; Veltsistas, P.; Marek, J.; Novosad, J.; Slawin, A. M. Z.; Woolins, J. D. *Inorg. Chem. Commun.* **1998**, 11, 418.
- (20) Rogers, R. D.; Zaworotko, M. J. *Crystal Engineering, ACA Transactions*; ACA Publications: Buffalo, NY, Vol. 33, 1999.
- (21) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N. L. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1555.
- (22) Mann, F.; Saunders, B. *Practical Organic Chemistry*, 4th edition; Longman: London, 1971.

Table 1. Elemental Analysis and Spectral Data

experimental procedure		theoretical	found
elemental analysis data	%Cl	13.09	12.57
	%C	66.61	65.98
	%N	7.28	7.19
	%H	4.14	4.17
fluorescence spectral data		SBT: 254 nm, 318 nm, CA: 420 nm	(SBT) <sub>2</sub> -CA: 254 nm, 318 nm, 514 nm
IR-wavelength (cm <sup>-1</sup> ) absorption data			460–480w, 570–700–765m, 840vs, 980–1075m, 1375–1410–1445w, 1530vs(broad), 1630vs, 3060–3260m, 3440s (broad)
UV–Vis molar absorptivity data			log <sub>10</sub> $\epsilon_{514.8}$ = 2.84, log <sub>10</sub> $\epsilon_{318.8}$ = 4.38, log <sub>10</sub> $\epsilon_{256.4}$ = 3.88 in anhydrous solvent DMSO

Table 2. NMR Data in DMSO-*d*<sub>6</sub>

compound	<sup>1</sup> H NMR data (ppm)	<sup>13</sup> C NMR data (ppm)
CA	not obtained	109.5 (C <sub>3,6</sub> )/166.1 (C <sub>1,2,4,5</sub> )
SBT-chloride	2.52 (5-plet)/3.34/4.53/7.4 (6-plet)/9.26	33.1/39.5 (7-plet)/128/128.9 (doublet)/135/168.5
(SBT) <sub>2</sub> -CA	2.5 (5-plet)/4.48/7.4 (12-plet)	34.1/39.5 (7-plet)/104.7/128/128.9 (doublet)/135/168.7

that calculated from the crystal structure. The ion-pair salt was found to have a mp of 168.0 °C and melts without decomposition to a red oily liquid. Heated in a porcelain crucible, it undergoes pyrolytic decomposition with no residue.

**Thermochemical Data.** From the TG curve it is realized that after the melting point of (SBT)<sub>2</sub>-CA, at 175 °C, there is a drop of the weight. The drop continues in steps until 660 °C, when all the material is lost. The DTG curve shows the stepwise loss of the weight more clearly as follows: (1) four sharp peaks in the temperature range of 175–200 °C; (2) several small peaks in the range of 200–300 °C; and (3) a very broad peak with minimum at 560 °C in the range of 300–660 °C.

The DTA curve shows the following: (1) a sharp exothermic peak at 175 °C, which extends all over the temperature range of 175–200 °C; (2) a rather flat segment in the range of 200–350 °C; (3) a sigmoid-like drop in the temperature range of 200–250 °C; (4) a broad exothermic peak in the range of 350–660 °C with a minimum at 568.1 °C and some other features and small minima especially at the high-temperature end.

From the thermochemical data presented (Figure 1) it is realized that immediately after the melting point the material

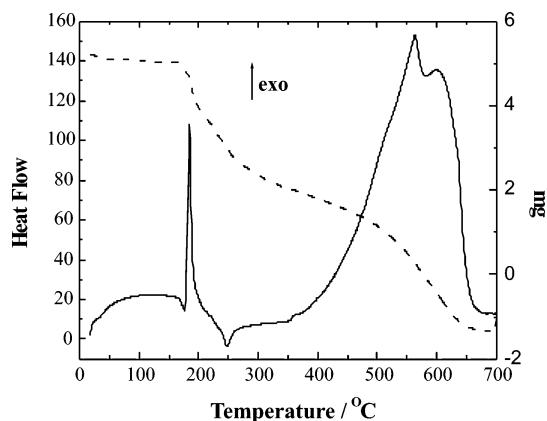


Figure 1. DTA (solid line) and TG (dashed line) analysis of the novel ion-paired compound *S*-benzylthiuronium chloranilate.

decomposes to volatile products, some of which are combustion products. The exothermic peak in the range of 175–200 °C gives evidence of the formation of combustion

products. However, the flat segment of the curve in the range of 200–350 °C suggests that the loss of weight is taking place in the absence of exothermic process. Furthermore, the broad exothermic peak with the minimum at 568.1 °C is due to the combustion of carbon to CO<sub>2</sub>, which amounts to 49% of the formula weight of the (SBT)<sub>2</sub>-CA ion pair salt.

**Spectral Data.** Infrared absorption data of the (SBT)<sub>2</sub>-CA ion-pair salt, as prepared in this work, were obtained and are given in Table 1. The IR data found are as expected since the bonds C–H, N–H, C=C, C–S and C–N stretch frequencies of the SBT cation and the corresponding C=O and C–Cl of the CA-dianion are also present in the overcrowded IR spectrum obtained. The principal absorbance band appears at 1530 cm<sup>-1</sup> (vs-broad) and is partly attributed to the vibration of the C–O bond corresponding to a bond order of 1.5, in contrast to the C–O bond vibration which for *p*-chloranilates appears at 1175 cm<sup>-1</sup>.<sup>19</sup>

UV–Vis absorption data of the (SBT)<sub>2</sub>-CA ion-pair salt, as prepared in this work, were obtained, and the logarithmic absorption coefficients at the wavelength in the maximum of the absorption peaks are given in Table 1. The UV–Vis data reveal absorption bands of excitation from (a) S<sub>0</sub>→S<sub>1</sub> state ( $\pi$ ,  $\pi^*$ ) transition at 254 nm due to the presence of aromatic ring, and (b) from the S<sub>0</sub>→S<sub>1</sub> state by ( $\pi$ ,  $\pi^*$ ) transition of the C=N bond in SBT molecule at 318 nm; finally, the band at 514 nm represents a bathochromic shift of the chloranilic acid band that normally absorbs at 420 nm.<sup>11</sup>

The fluorescence spectrum of (SBT)<sub>2</sub>-CA ion-pair salt obtained by excitation at 264 nm (UV-absorption band) gives an emission band at 530 nm with effective bandwidth of 25 nm, which is in agreement with the bathochromic shift of the ion pair (SBT)<sub>2</sub>-CA observed in the UV–Vis spectrum.

The DRS spectrum (Figure 2) shows a rather narrow diffuse reflectance band in the range of 300–380 nm, with a maximum at 340 nm and a broad one from 500–700 nm, with a maximum at 560 nm.

**NMR Spectroscopy Data.** <sup>1</sup>H NMR Data. (Table 2). The <sup>1</sup>H NMR spectrum of SBT·HCl gives (a) a shift at 2.5 ppm due to the benzylic hydrogen atoms, (b) a shift at 3.34 ppm due to amino hydrogen atoms, (c) a shift at 4.53 ppm due to imino hydrogen atom, and (d) a shift at around 7.4 ppm (6-multiplet) due to aromatic hydrogen atoms.

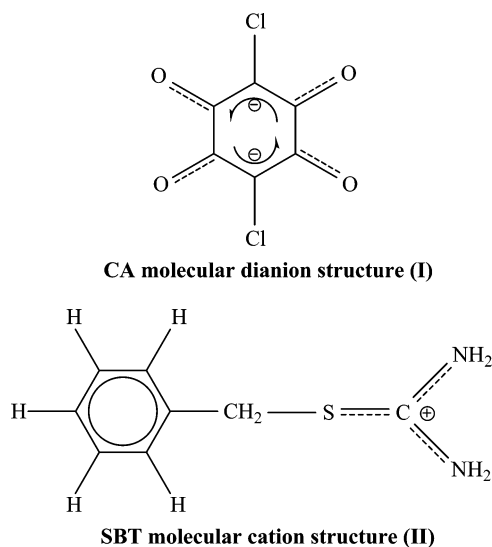


$^1\text{H}$  NMR shifts of  $(\text{SBT})_2\text{-CA}$  have all the previous shifts except the one at 3.34 ppm assigned to the amino hydrogen atoms, and the imino hydrogen peak is shifted by 0.05 ppm. In addition, the shift at 7.4 ppm (6-multiplet) due to aromatic hydrogen atoms has moved slightly and changed to 12-multiplet.

$^{13}\text{C}$  NMR Data (Table 2). The  $^{13}\text{C}$  NMR spectrum of  $(\text{SBT})_2\text{-CA}$  ion-pair salt gives (a) a 34 ppm shift assigned to benzylic carbon, (b) a shift at 39.5 ppm (heptaplet) assigned to thiuronium carbon atom, (c) a shift of 104.7 ppm (small) assigned to  $=\text{C}-\text{Cl}$  carbon atoms, (d) a triplet shift centered at 128.5 ppm assigned to aromatic carbons, (e) a 135 ppm shift assigned to aromatic carbons, and (f) a shift at 168.7 assigned to the quinonoid (or carbonyl group) carbon atoms.

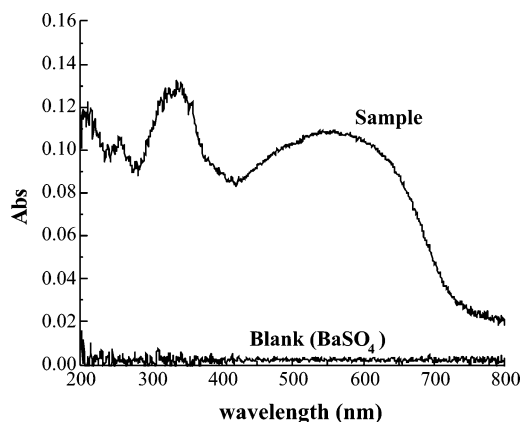
**X-ray Crystal Structure Data.** Crystallographic data are presented in Table 3. The  $(\text{SBT})_2\text{-CA}$  ion-pair salt crystallizes in the monoclinic system, space group  $C2/c$ . The asymmetric unit consists of one benzylthiuronium cation and half of a chloranilate dianion (Figure 3). The chloranilate unit has four C–O bonds of equal length (1.248(6) and 1.250(6) Å). Considering the C–C bond lengths (Figure 3), the resonance structure (I) is proposed for the chloranilate dianion.

The bond lengths of the SBT-cation (Figure 3) indicate that all bonds in the  $-\text{S}-\text{C}-(\text{NH}_2)_2$  terminal group have a partially double bond character. Consequently, the positive charge may be considered delocalized over all these atoms (resonance structure II).

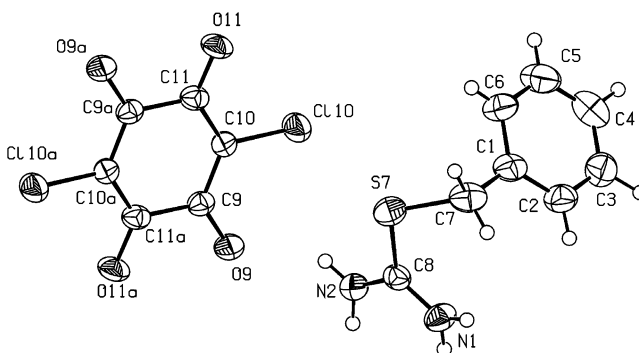


From the crystal packing (Figure 4) it is evident that the terminal  $-\text{S}-\text{C}-(\text{NH}_2)_2$  group points toward the negatively charged oxygen atoms of the dianion moiety. The chloranilate units are arranged in columns parallel to the  $c$  crystallographic axis (Figure 4). Inside a column the rings are inclined, relative to each other by an angle of  $63.45^\circ$  (Figure 5a) and no aromatic interactions are observed between them. The organic cations arranged, also, in columns parallel to the  $c$ -axis, surround the chloranilate dianions (Figure 4). Inside the cationic columns, extensive  $\pi-\pi$  aromatic interactions are present (Figure 5b).

The crystal packing is reinforced by the formation of an extended network of hydrogen bonds (Figures 4, 6, and 7)



**Figure 2.** Diffuse reflectance spectrum of the novel compound *S*-benzylthiuronium chloranilate.

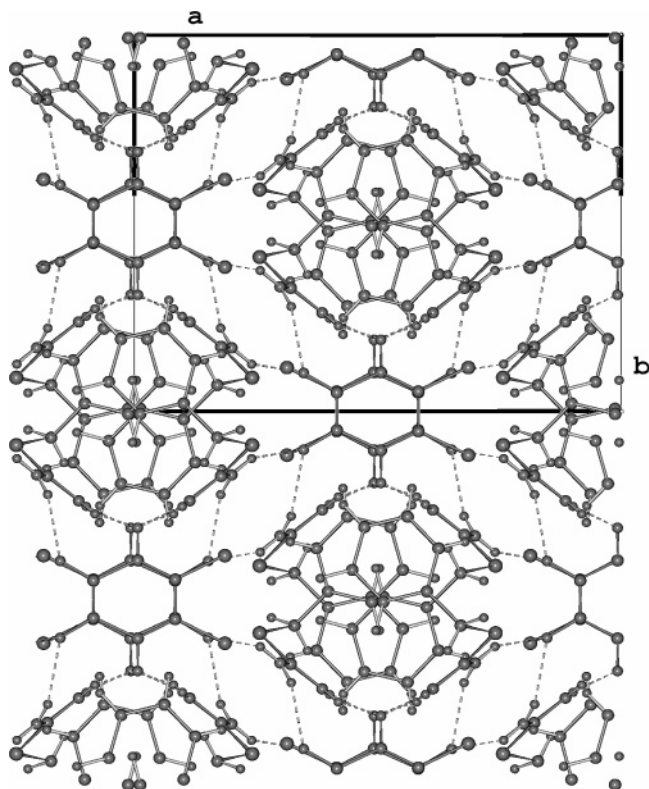


**Figure 3.** ORTEP drawing of the molecular structure of the dianion (left) and the cation (right), with the atom numbering scheme. Selected bond lengths (Å): C(9)–C(10), 1.394(7); C(10)–C(11), 1.399(7); C(9)–C(11), 1.536(7); C(9)–O(9), 1.250(6); C(11)–O(11), 1.248(6); C(10)–Cl(10), 1.740(5); C(1)–C(7), 1.480(9); C(7)–S(7), 1.834(7); S(7)–C(8), 1.737(5); C(8)–N(1), 1.289(7); C(8)–N(2), 1.320(7).

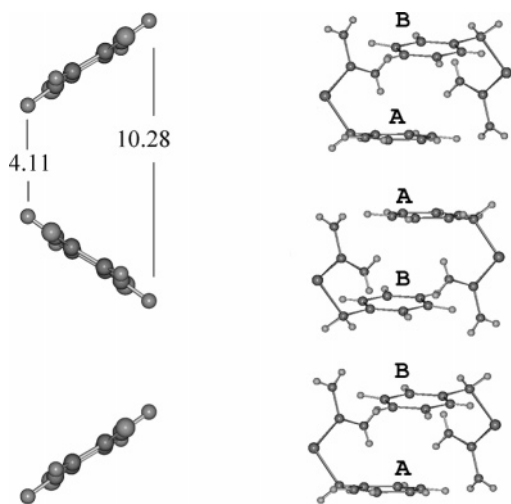
**Table 3. Crystallographic Data for  $[\text{C}_8\text{H}_{11}\text{N}_2\text{S}]_2(\text{C}_6\text{Cl}_2\text{O}_4)$**

empirical formula	$\text{C}_{11}\text{H}_{11}\text{ClN}_2\text{O}_2\text{S}$
formula weight	270.73
space group	$C2/c$
$T$ (K)	293(2)
$a$ (Å)	15.109(1)
$b$ (Å)	11.606(2)
$c$ (Å)	14.390(2)
$\beta$ (deg)	97.01(1)
$V$ (Å <sup>3</sup> )	2504.5(6)
$Z$ , $\rho_{\text{calc}}/\rho_{\text{meas}}$ (gcm <sup>−3</sup> )	8, 1.436/1.43
reflns collected/unique	2520/2198 ( $R_{\text{int}}=0.0261$ )
$R1$ [ $I > 2\sigma(I)$ ]	0.0505
$wR2$ [ $I > 2\sigma(I)$ ]	0.1197
GO $F$	1.077

involving all oxygen atoms of the chloranilate unit and all amine hydrogen atoms of the SBT-cation (Table 4). Each oxygen of the CA-dianion is involved in two hydrogen bonds with two neighboring cations, through an amine proton of each cation. The second proton of the same amine groups is connected with the crystallographically equivalent oxygen atom of the neighboring dianion, thus forming characteristic cyclic patterns<sup>20</sup> with graph-set notation  $R_4^2(8)^{21}$  (R1 in Figure 6). By means of these bonds two neighboring oxygen atoms (O9, O11) of a chloranilate unit are bonded to the amine groups of the same cation, forming thus cyclic rings with the graph-set notation  $R_2^2(9)$  (R2 in Figures 6 and 7). In this way, an infinite chain of alternative edge-fused  $R_4^2(8)$  and  $R_2^2(9)$  rings is formed along  $c$ . Consequently, each CA-dianion is bridged via its four oxygen atoms with four neighboring ones, two along the  $c$ -axis (above and below it,



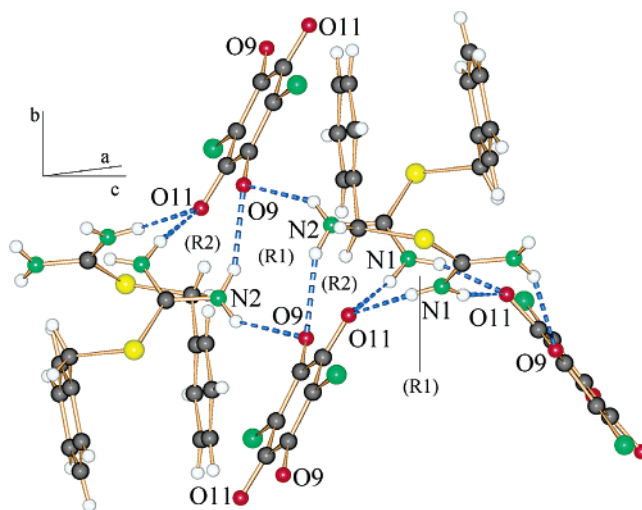
**Figure 4.** Projection of the crystal structure along the *c*-axis. Dashed lines represent hydrogen bonds.



**Figure 5.** (Left) Column of chloranilate dianions formed along the *c*-axis. (Right) An infinite column formed along the *c*-axis by the SBT units. Aromatic rings labeled with the same letter are parallel between them. Interplanar distances: A–A = B–B = 3.40 Å, A–B = 3.59 Å. Slipping distances: A–A = B–B = 2.90 Å, A–B = 1.26 Å.

inside the same anionic column), and two along the diagonals of the *ab* plane, belonging to two neighboring anionic columns, as shown in Figure 4.

Dissolution of the crystalline material in DMSO (data obtained through spectra of UV–Vis absorptiometry, fluorometry, and NMR spectroscopy) results in an association product that is either an ion pair salt or an organic complex; this is revealed from shift changes and/or the complete absence of peaks between  $^1\text{H}$  NMR spectra of  $\text{SBT}\cdot\text{HCl}$  and  $(\text{SBT})_2\text{--CA}$ , and moreover from the change of multiplicity of aromatic hydrogens of the SBT-cation. The presence of a strong H-bonded network is also supported by the batho-



**Figure 6.** Detailed representation of the hydrogen bond network. A chain of alternative edge-fused  $\text{R}_4^2(8)$  (labeled as R1) and  $\text{R}_2^2(9)$  (labeled as R2) rings is shown.

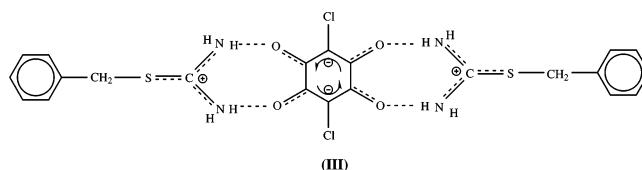
chromic shift of absorption band at 420 nm of the chloranilic acid in the UV–Vis absorption spectrum. Other research works<sup>11</sup> investigating the thermodynamics of the charge transfer complexes formed by the chloranilate dianion with other proton transfer cations have established the rather increased stability of such complexes that results from the relatively strong hydrogen bonding.

## Conclusions

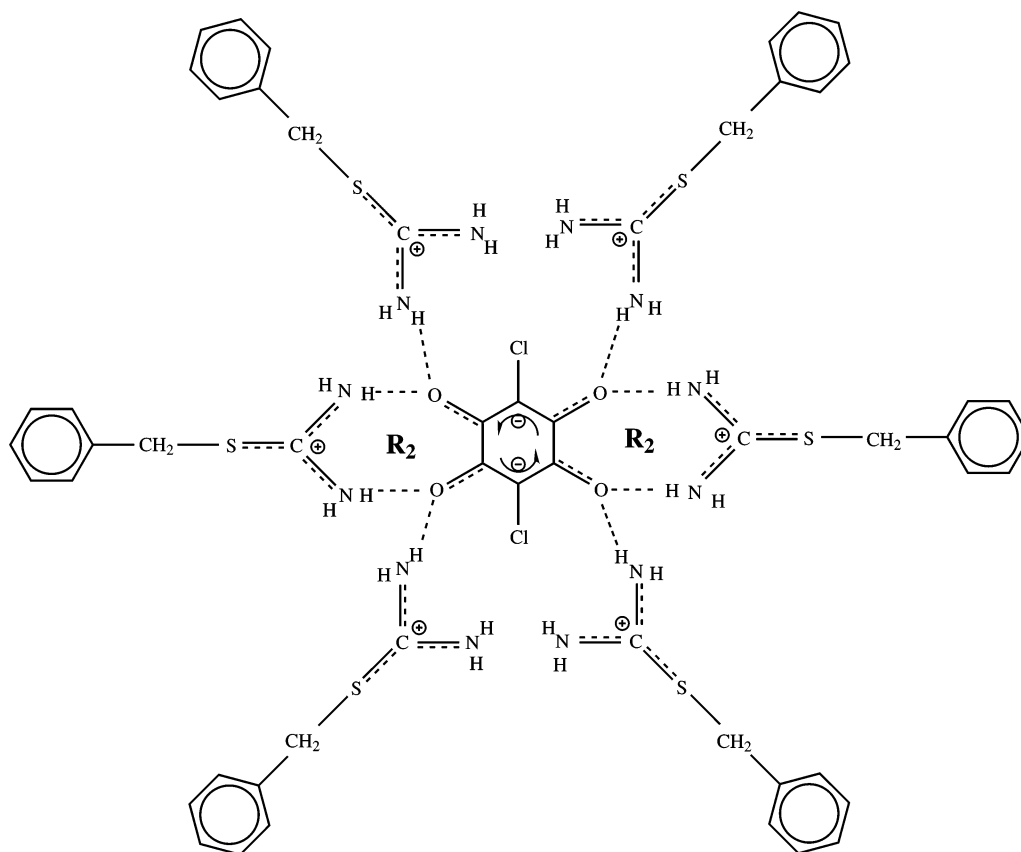
The  $(\text{SBT})_2\text{--CA}$  supramolecular structure consists of chloranilate dianions and SBT-cations arranged in columns anionic and cationic, respectively, along the *c*-axis. An extended network of cyclic H-bonds between the oxygen atoms of the anions and the amine protons of the cations is formed. By this means, each chloranilate dianion interacts with six cations, two by R2 and four by R1 ring-type bonding, as schematically shown in Figures 6 and 7.

The  $(\text{SBT})_2\text{--CA}$  supramolecular structure is not totally destroyed by dissolution in solvents and it may take the form of (a) an association compound through strong H-bond interaction between quinonoid-like oxygen and imino-group of isothiuronium compound producing a rather stable radical compound, or (b) an association compound through the interaction between quinonoid-oxygen and amino-group of the isothiuronium compound, and (c) a charge-transfer complex.

However, because of the increased strength of the R2 ring-type bonding (two HBs formed between a cation and an anion) compared to the R1 type, it is more reasonable to suggest that the molecule that remains intact in solution may have the partly dissociated supramolecular (synthon) structure (III).



This is in agreement with  $^1\text{H}$  NMR data (where the band at 3.3 ppm is absent and the shift upfield of the peak at 4.3



**Figure 7.** Schematic representation of the six-coordinated CA dianion within the crystal. Only  $R_2^2(9)$  cyclic patterns are shown.

**Table 4. H-bond Lengths (Å) and Angles (deg)<sup>a</sup>**

D-H...A	length	angle
N (1)-H (11)····O (11) <sup>ii</sup>	2.802 (7)	165.0 (6)
N (1)-H (12)····O (11) <sup>iii</sup>	2.808 (7)	155.9 (6)
N (2)-H (13)····O (9) <sup>iv</sup>	2.934 (6)	146.5 (5)
N (2)-H (14)····O (9) <sup>i</sup>	2.934 (6)	149.5 (5)

<sup>a</sup> *i*:  $-x + 1, -y, -z + 1$ . *ii*:  $x - 0.5, -y - 0.5, z - 0.5$ . *iii*:  $-x + 0.5, -y - 0.5, -z + 1$ . *iv*:  $-x, -y, -z + 0.5$ .

ppm in spectra of (SBT)<sub>2</sub>–CA compared with spectra of SBT·HCl) and gives evidence of stability of some hydrogen bondings in the supramolecular (synthon) structure and

furthermore, justifies the charge-transfer transition observed by UV–Vis absorptiometry.

**Acknowledgment.** We thank the authorities of the region of Epirus for the purchase of the X-ray equipment.

**Supporting Information Available:** Five tables containing complete information on data collection and refinement, final atomic coordinates, anisotropic thermal parameters, and all bond lengths and angles for  $[\text{C}_8\text{H}_{11}\text{N}_2\text{S}]_2(\text{C}_6\text{Cl}_2\text{O}_4)$  (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM040182M