

Table 1. Parameters for Dorn curve fits

Type	$\tau_1(\text{yr})$	$k_1(\text{yr})^{-1}$	$C_1$	$\tau_2(\text{yr})$	$k_2(\text{yr})^{-1}$	$C_2$	$\tau_3(\text{yr})$	$k_3(\text{yr})^{-1}$	$C_3$
Respiratory System (M)	55	0.146	0.95	85	0.082	0.05			
Respiratory System (F)	55	0.146	0.985	92	0.11	0.015			
Esophagus (M)	58	0.172	1						
Esophagus (F)	64	0.172	1						
Intestines (M)	61	0.164	1						
Intestines (F)	62	0.113	1						
Rectum (M)	60	0.133	1						
Rectum (F)	61	0.115	1						
Brain (M)	0.5	0.15	0.07	57	0.11	0.15	129	0.20	0.78
Brain (F)	0.5	0.155	0.12	55	0.12	0.08	135	0.11	0.80
Liver (M)	62	0.177	1						
Liver (F)	57	0.158	1						

To test the equation (1), for example, the age at death of each these 32 protected control beagles or protected but epileptic beagles are illustrated by the step function for fractional survival<sup>4</sup> in Figure 1.

The smooth curves are calculated from our water environment theory. The survival parameter = 4778 (controls) or 2335 (epileptics) days and  $k = 1.77 \times 10^{-3}$  (controls) or  $1.86 \times 10^{-3}$  (epileptics) day<sup>-1</sup> are used to get the smooth curve in Figure 1.

Case II; Nonsurvival from the diseases due to the multiple causes or the agings due to the heterogeneous populations.

For the case II, survival  $S$  is the product that results from several independent causes or homogeneous populations and is given by

$$S = \Sigma C_i S_i \quad (7)$$

Here

$$S_i = C_i [1 + \exp - k_i (\tau - t)]^{-1} \text{ and } \Sigma C_i = 1 \quad (8)$$

$C_i$  is the probability of  $i$ th causes or homogeneous population.

Dorn<sup>5</sup> has reported death rates per 100,000 at age  $t$  from 21 different kinds of cancer for both men and women.

Some of the statistics are for the years 1937-1939 for the white population of the United States.

Representative curves are shown in Figures 2 and 3.

The following survival parameters in Table 1 are used to fit the Dorn curve. The agreements are quite satisfactory.

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## Reduction of *o*-Cyanobenzenesulfonyl Chloride with Zinc in an Acidic Medium

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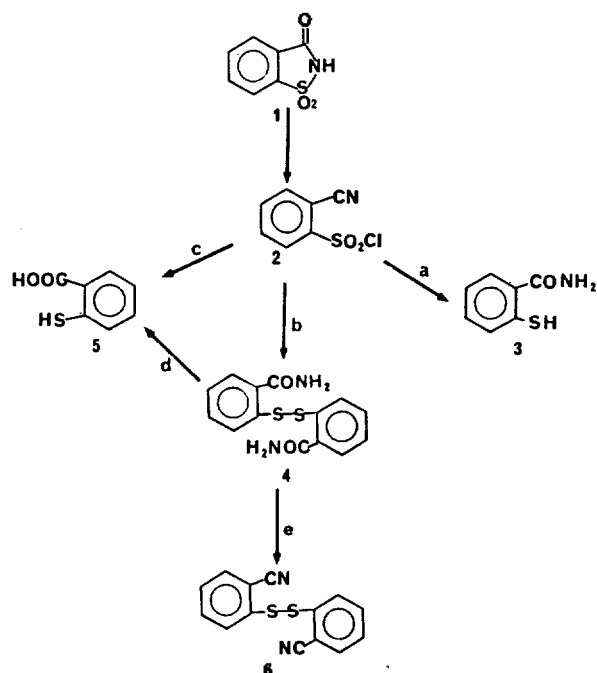
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In our research on new heterocyclic compounds containing sulfur and nitrogen, it became important to prepare some 2-substituted benzenethiols and the corresponding disulfides such as 2-mercaptobenzamide(3), dithiosalicylamide(4) and bis(*o*-cyanophenyl) disulfide(6). These compounds are not available commercially, and few synthetic procedures for these compounds have been reported.<sup>1-11</sup> Because the reported methods are inconvenient, we designed new synthetic methods and report the results herein.

We selected *o*-cyanobenzenesulfonyl chloride(2) as the starting material for our study, because it useful functional groups such as -CN and -SO<sub>2</sub>Cl on 1,2-position of benzene

ring. In a previous report,<sup>12</sup> we described a synthesis of *o*-cyanobenzenesulfonyl chloride(2) from saccharin(1) in 85% yield.

Treatment of *o*-cyanobenzenesulfonyl chloride(2) with zinc and concentrated HCl in refluxing EtOH gave 2-mercaptobenzamide(3) in 85% yield. Reduction of *o*-cyanobenzenesulfonyl chloride(2) with zinc-dust and 6N-HCl in methanol at 5°C afforded dithiosalicylamide(4) in 76% yield, whereas in refluxing MeOH the product was 2-mercaptobenzoic acid(5, 71% yield). Treatment of dithiosalicylamide(4) with zinc-dust and concentrated HCl in refluxing water gave 2-mercaptobenzoic acid(5) in 50% yield. On the other hand, the reac-



a Zn-dust, conc-HCl(36%), EtOH, Reflux. b Zn-dust, 6N-HCl, MeOH, 5°C. c Zn-dust, 6N-HCl, MeOH, Reflux. d Zn-dust, conc-HCl, H<sub>2</sub>O, Reflux. e POCl<sub>3</sub>, at 90°C.

Scheme 1

tion of dithiosalicylamide(4) with POCl<sub>3</sub> at 90°C gave bis(o-cyanophenyl) disulfide(6) in quantitative yield. We have also found that the final product in the o-cyanobenzenesulfonyl chloride(2) with zinc-dust in acidic medium is 2-mercaptobenzoic acid(5, R<sub>f</sub> = 0.17) forming via dithiosalicylamide(4, R<sub>f</sub> = 0.26) and 2-mercaptobenzamide(3, R<sub>f</sub> = 0.83) by tlc.

Proof of the structure of each compound is based on analytical and spectroscopic data reported in detail in the experimental section.

## Experimental

Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Hitachi 270-50 spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker AW-80MHz spectrometer with chemical shift values reported in δ units (part per million) relative to an internal standard (tetramethylsilane). Elemental analyses were performed by the Central Laboratory, Gyeongsang National University, Chinju, Korea. Thinlayer chromatography was performed on glass plates coated with silica gel (0.25 mm, Silica Gel 60 F-254, Merck), developing solvent; CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9:1 (v/v).

**2-Mercaptobenzamide(3).** To a mixture of o-cyanobenzenesulfonyl chloride(2, 0.05 mol, 11.5 g), concentrated HCl (36%, 25 ml) and ethanol (120 ml) as the solvent was added zinc-dust (0.13 mol, 8.4 g) for 1h at below 10°C. The reaction mixture was then refluxed for 1h. After the solvent was evaporated by rotary evaporator, 50 ml of water was added to the residue. The resulting mixture was stirred for 30 min, and then filtered. The solid was washed with water (10 ml × 2) and dried in air to give the compound 3 as a white powder in 85% (6.5 g) yield; mp 142-144°C (lit.<sup>2,7</sup> mp

145-146°C); IR(KBr) 3336, 3188, 3060, 2564, 1668, 1614, 1478, 1272, 1134, 896, 746, 638 cm<sup>-1</sup>; <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 5.4(bs, 1, SH), 7.0-7.7(m, 4, aromatic H), 8.0(bs, 2, NH<sub>2</sub>). Anal. Calcd. for C<sub>7</sub>H<sub>7</sub>NOS: C, 54.88; H, 4.61; N, 9.14; Found; C, 54.90; H, 4.59; N, 9.00.

**Dithiosalicylamide(4).** A solution of 5 g (0.025 mol) of 2 and 20 ml of 6N-HCl in 20 ml of MeOH was adjusted to 5°C with stirring in an ice bath. Zinc-dust (3.5 g, 0.054 mol) was added for 1h with stirring at below 5°C and the reaction mixture was then stirred for 1h at same temperature. The reaction mixture was poured into 200 ml of water with stirring, and filtered. The solid was washed with water (10 ml × 3) and dried in air to give the compound 4 as a white powder in 76% (2.9 g) yield. Analytical sample was recrystallized from MeOH. mp 238-240°C (lit.<sup>6</sup> mp 239°C); IR(KBr) 3370, 3192, 1640, 1616, 1400, 1128, 746, 628 cm<sup>-1</sup>; <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 7.0-7.6(m, 8, aromatic H), 8.0(bs, 4, 2NH<sub>2</sub>); Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>; C, 55.24; H, 3.97; N, 9.20; Found; C, 55.11; H, 3.28; N, 9.25.

**2-Mercaptobenzoic acid(5).** A) A solution of o-cyanobenzenesulfonylchloride(2, 0.01 mol, 2.01 g) and 10 ml of 6N-HCl in 20 ml of MeOH was adjusted to 5°C with stirring in an ice bath. Zinc-dust (0.028 mol, 1.8 g) was added for 10 min with stirring at same temperature. The reaction mixture was then refluxed for 1h. To the above solution, 20 ml of concentrated HCl (36%) was added and the reaction mixture was then refluxed for 2h. The reaction mixture was cooled to 4°C in an ice bath, and filtered. The solid was washed with water (10 ml × 2), and dried in air to give the compound 5 as yellow crystalline solid in 71% (1.1 g) yield; mp 164-165°C (lit.<sup>10</sup> mp 163-164°C); IR(KBr) 3356-2900(broad), 2550, 1682, 1590, 1564, 1472, 1418, 1320, 1270, 1172, 1064, 1042, 904, 802, 746 cm<sup>-1</sup>; <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 4.6(bs, 1, SH), 6.8-7.4(m, 4, aromatic H), 8.0(bs, 1, OH). 5 was identical with an authentic sample.

B) To a mixture of 4(0.005 mol, 1.56g), concentrated HCl (36%, 13 ml) and 2 ml of H<sub>2</sub>O was added slowly zinc-dust (0.01 mol, 0.66g) with stirring. The reaction mixture was then refluxed for 1h. The hot solution was filtered. The resulting solution was cooled to 5°C in ice bath and filtered. The solid was washed with cold water (10 ml × 2) and dried in air to give the compound 5 as yellow crystalline solid in 50% (0.77 g) yield; mp 164-165°C (lit.<sup>10</sup> mp 163-164°C); IR(KBr) 3450-2900 (broad), 2550, 1695, 1596, 1564, 1472, 1417, 1320, 1270, 1174, 1064, 1042, 904, 802, 746 cm<sup>-1</sup>; <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 4.6(bs, 1, SH), 6.8-7.4(m, 4, aromatic H), 8.0(bs, 1, OH).

**Bis(o-cyanophenyl)disulfide(6).** The mixture of dithiosalicylamide(4, 0.005 mol, 1.56 g) and 15 ml of POCl<sub>3</sub> was stirred for 4h at 90°C. Excess POCl<sub>3</sub> was distilled off under reduced pressure. The residue was poured into 200 ml of water with stirring and filtered. The solid was washed with water (20 ml × 2) and dried in air to give the compound 6 as yellow crystalline solid in 99% (1.32 g) yield; mp 102-103°C (lit.<sup>8</sup> mp 103-104°C, 102-103°C<sup>3</sup>); IR(KBr) 3092, 2224, 1586, 1462, 1286, 778, 762, 578 cm<sup>-1</sup>; <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 7.4-8.3(m, 8, aromatic H). 6 was identical with an authentic sample.

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## Magnetism and X-Ray Photoelectron Spectroscopic Study on $\text{FeMoO}_4\text{Cl}$ and $\text{LiFeMoO}_4\text{Cl}$

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The general mechanism of intercalation reaction is still not experimentally clarified. All of the compounds that exhibit intercalation reaction have in common two-dimensional structure.  $\text{FeMoO}_4\text{Cl}$  is one of the good host candidates to investigate intercalation mechanism for more insight into the unique role of interlayer bonding character.

$\text{FeMoO}_4\text{Cl}$  is a layer type compound whose synthesis, structure and some physical properties have been reported<sup>1</sup>. It has tetragonal symmetry with unit cell parameters  $a = 6.672$  and  $c = 5.223\text{\AA}$  in the space group  $P4/nmm$  ( $Z = 2$ ). Individual layers consist of  $\text{MoO}_4$  tetrahedra and  $\text{FeO}_4\text{Cl}$  square pyramids by sharing the corner-oxygen. The octahedral coordination of ferric ion of  $\text{FeO}_4\text{ClCl}'$  is achieved by stacking layers on top of one another in such a way that each chlorine in the adjacent layer is in contact with ferric ion in the layer below or above it (Cl and Cl' denote the chlorine coordinated around Fe in intralayer and interlayer, respectively).

Recently intercalation reaction of  $\text{FeMoO}_4\text{Cl}$  with *n*-alkylamines has been systematically studied<sup>2</sup>, and with alkali metals (e.g., lithium and sodium) has also been investigated by electrochemical as well as chemical methods<sup>2,3</sup>. As reported in the previous paper<sup>3</sup>, we could see that the crystal was changed from tetragonal ( $\text{FeMoO}_4\text{Cl}$ ) to monoclinic ( $\text{LiFeMoO}_4\text{Cl}$ ) symmetry with cell parameters  $a = 6.994$ ,  $b = 6.871$ ,  $c = 5.015\text{\AA}$  and  $\beta = 91.27^\circ$  by electrochemical and chemical lithiations.

In this report, an attempt was made to analyze the elements participating in the redox reaction and also to understand the bonding nature of intra and interlayer before and

after lithium intercalation into  $\text{FeMoO}_4\text{Cl}$ -host lattice. To achieve these purposes, we have performed magnetic susceptibility measurements and X-ray photoelectron spectroscopic analysis.

The host material,  $\text{FeMoO}_4\text{Cl}$ , has been synthesized with  $\text{Fe}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $\text{FeCl}_3$  by chemical vapor transport (CVT) technique as described elsewhere<sup>2</sup>. Lithiation has been carried out with excess LiI in purified acetonitrile at ambient temperature for a week under an inert atmosphere. Considering the coincidence of EMF vs. Li/Li' for LiI (2.8V) with the open circuit voltage (OCV) of  $\text{LiFeMoO}_4\text{Cl}$  (2.2V)<sup>4</sup>, it is thought that LiI is more suitable reducing reagent than *n*-BuLi (-1V). In practice, the crystals of  $\text{FeMoO}_4\text{Cl}$  was turned out to be X-ray amorphous after reaction with *n*-BuLi.

Magnetic susceptibility measurements were performed in an inert atmosphere with Faraday-type magnetobalance from 77K to 350K.

X-ray photoelectron spectra using an unmonochromatized Mg-K $\alpha$  radiation (1253.6 eV) were recorded on an PHI 5100 Perkin-Elmer X-ray photoelectron spectrometer equipped with PE 7700 computer system. The base pressure was maintained in the  $\sim 10^{-9}$  torr throughout all operations. Instrumental work function was calibrated by the Au(4f<sub>7/2</sub>) binding energy at 83.8 eV. Samples were mixed with graphite ( $C_{1s} = 284.4$  eV) as an internal standard, which were mounted on the specially designed sample holder covered with gold sheet and put into the chamber without exposure to air.

Molar susceptibility ( $\chi'_m$ ), reciprocal susceptibility ( $\chi'_m{}^{-1}$ ) and effective magnetic moment ( $\mu_{eff}$ ) for  $\text{FeMoO}_4\text{Cl}$  and  $\text{LiFeMoO}_4\text{Cl}$  have been measured over the temperature range from 77K to 350K as shown in Figures 1 and 2. The reciprocal susceptibility vs. temperature for  $\text{FeMoO}_4\text{Cl}$  exhibits a typical two dimensional antiferromagnetic behavior in

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