# Synthesis, redox properties, and X-ray diffraction structure of 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide

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#### Received August 4, 2003

Refluxing 2,3-dichloromaleic anhydride with *p*-anisidine in benzene with water removal gives the condensation product 2,3-dichloro-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (1) 75% yield. This new maleimide compound reacts with added ethanethiol in the presence of Et<sub>3</sub>N or DBU to furnish the bidentate sulfide ligand 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) in 85% yield. Each product has been characterized in solution by IR, NMR, and UV-vis spectroscopies, and the solid-state structure of 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide was unequivocally established by single-crystal X-ray diffraction analysis. 2,3-*bis*(Ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide crystallizes in the monoclinic space group C2/c, a = 20.035(3) Å, b = 9.188(1) Å, c = 16.887(2) Å,  $\beta = 93.696(2)^{\circ}$ , V = 3102.3(8) Å<sup>3</sup>, Z = 8, and  $D_{calcd} = 1.385$  mg/m<sup>3</sup>; R = 0.0268,  $R_w = 0.0676$  for 2025 reflections with  $I > 2\sigma(I)$ . The nature of the LUMO in 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) has been determined by extended Hückel molecular orbital calculations, and these data are discussed relative to the cyclic voltammetry results and other structurally relevant compounds prepared in our labs.

KEY WORDS: Maleimide heterocycle; bidentate sulfide; cyclic voltammetry; extended Hückel MO calculations.

#### Introduction

The compounds 2,3-dichloromaleic anhydride and 4,5-dichloro-4-cyclopenten-1,3-dione serve as starting materials for the redoxactive diphosphine complexes 2,3-*bis*-(diphenylphosphino)maleic anhydride (bma) and 4,5-*bis*(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd).<sup>1</sup> The interest and continued investigation of these diphosphine ligands derive from their ability to function as electron reservoirs due to the availability of a low-lying LUMO,<sup>2,3</sup> whose nodal properties approximate that of  $\psi_4$  of common  $6\pi$  electron systems such as maleic anhydride and hexatriene,<sup>4</sup> coupled with facile P–C bond cleavage sequences that are often triggered upon the coordination of these ligands to a variety of mono- and polynuclear metal complexes.<sup>5</sup>

Recently, our groups have embarked on the synthesis of disulfide compounds derived from 2,3-dichloromaleic anhydride and 4,5-dichloro-4-cyclopenten-1,3-dione.<sup>6,7</sup> Three such bidentate disulfide compounds prepared by our groups are shown subsequently, and one of the more interesting aspects that has emerged from our studies of these disulfides is the quasi-reversible one-electron reduction found for 4,5-bis(p-tolylthio)-4-cyclopenten-1,3-dione. The quasi-reversible

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nature of the  $0/1^-$  redox couple in 4,5-*bis*(*p*-tolylthio)-4-cyclopenten-1,3-dione was totally unexpected, as the site of electron accession in this and related complexes is associated with the  $\pi^*$  of the dione moiety, which has typically afforded stable reduction products. However, the kinetic instability of the radical anion relative to the known diphosphine and other disulfide derivatives is due to the cleavage of the C(dione)—S(*p*-tolyl) bond and release of the stable *p*-tolylthiolate anion.



Herein, we report our data on the synthesis and solution characterization of the new bidentate sulfide ligand 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (**2**). The solid-state structure was established by X-ray crystallography and the results of extended Hückel molecular orbital calculations reveal that the LUMO in 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (**2**) is essentially identical to that found in other such  $6\pi$  electron systems. The electrochemical properties of 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (**2**) have been studied by cyclic voltammetric and double-potential step chronocoulometric experiments.

### **Experimental section**

#### General

The compounds *p*-anisidine, ethanethiol, 2,3-dichloromaleic anhydride, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich Chem. Co. and were used as received. The IR and cyclic voltammetry

(CH<sub>2</sub>Cl<sub>2</sub>) and NMR (CDCl<sub>3</sub>) solvents used in these studies were distilled from  $P_2O_5$ . The above solvents were distilled under argon using standard inert atmosphere techniques and were stored in Schlenk storage vessels under argon.<sup>8</sup> All other solvents were of reagent grade and used as received. The tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate/hexane, followed by drying under vacuum for at least 48 h before use. The reported melting points were recorded on a Meltemp apparatus and are uncorrected.

Routine infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, using PC control and OMNIC software, while the <sup>1</sup>H NMR spectrum was recorded at 200 MHz on a Varian Gemini-200 spectrometer. The UV-vis spectrum was collected on a Hewlett-Packard 8425A diode array spectrophotometer in a 1.0 cm quartz cell.

## Synthesis of 2,3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>) maleimide

To 2.00 g (16.0 mmol) of *p*-anisidine in 60 mL of toluene was added 2.70 g (16.0 mmol) of 2,3-dichloromaleic anhydride, after which 50 mg of the acid catalyst *p*-toluenesulfonic acid (PTSA) was added. The reaction was refluxed at 110 °C overnight, while the water was removed through the use of a Dean-Stark trap. After the solution was allowed to cool to room temperature, the solvent was removed and the initial product, 2,3-dichloro- $N-(p-\text{MeOC}_6\text{H}_4)$  maleimide (1), was obtained by column chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (60:30 mixture) as the eluent. 2,3-Dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (1): yield 3.20 g (75%). mp: 212-213 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 1739 (antisymm, maleimide) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDC1<sub>3</sub>): δ 7.09 (aromatic AB quartet,  $J_{H-H} = 9.0 \text{ Hz}$ ), 3.82 (MeO).

Compound 1 was next employed in the synthesis of 2,3-*bis*(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)-maleimide (**2**). Here, 0.5 g (1.80 mmol) of

2,3-dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was treated with 0.4 mL (5.40 mmol) of ethanethiol, followed by the dropwise addition of 0.67 mL of DBU. The reaction was stirred for 2 h at room temperature, at which time TLC analysis confirmed the presence of the desired disulfide product. 2.3-bis(ethylthio)-N- $(p-MeOC_6H_4)$  maleimide was isolated by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (60:30 mixture) as the eluent. 2,3-bis(Ethylthio)- $N-(p-\text{MeOC}_6\text{H}_4)$  maleimide (2): yield 0.5 g (85%). mp: 56–58 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 1772 (w, symm, maleimide), 1715 (s, antisymm, maleimide) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.07 (aromatic AB quartet,  $J_{H-H} = 8.5 \text{ Hz}$ ), 3.80 (s, MeO), 3.34 (q, methylene), 1.35 (t, methyl). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  421 ( $\epsilon = 2480$ ), 309  $(\epsilon = 2790), 250 \ (\epsilon = 3360).$ 

# X-ray diffraction structure of 2,3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide

Single crystals of 2,3-bis(ethylthio)-N- $(p-MeOC_6H_4)$  maleimide suitable for X-ray crystallography were obtained from a CH<sub>2</sub>Cl<sub>2</sub> 2,3-bis(ethylthio)-N-(psolution containing MeOC<sub>6</sub>H<sub>4</sub>)maleimide that had been layered with hexane. X-ray data were collected on a Bruker SMART<sup>™</sup> 1000 CCD-based diffractometer at 213 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm,<sup>9</sup> and the structure was solved and refined using the SHELXTL program package.<sup>10</sup> The molecular structure was checked by using PLATON.<sup>11</sup> All nonhydrogen atoms were refined anisotropically. Refinement converged at R = 0.0268 and  $R_w = 0.0676$  for 2025 independent reflections with  $I > 2\sigma(I)$ .

#### Extended Hückel MO calculations

The extended Hückel calculations on 2,3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide were conducted with the original program developed by Hoffmann,<sup>12</sup> as modified by Mealli and Proserpio,<sup>13</sup> using weighted H'*ijs*. The input Z matrix for 2,3-*bis*(thio)-maleimide was constructed upon a model possessing  $C_{2\nu}$  symmetry, using bond distances and angles from the X-ray diffraction coordinates for 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide. Here, the p-MeOC<sub>6</sub>H<sub>4</sub> and the ethyl groups were replaced by hydrogen atoms in order to simplify the calculations, with the N–H and S–H bond lengths assigned to values of 1.05 Å and 1.35 Å, respectively.<sup>14</sup>

#### Cyclic voltammetry data

The cyclic voltammetric and doublepotential step chronocoulometric studies were recorded on a PAR Model 273 potentiostat/galvanostat, equipped with positive feedback circuitry to compensate for *i*R drop. The airtight CV cell used was based on a three-electrode design, and a platinum disk was employed as the working and auxiliary electrodes. The reference electrode utilized a silver wire as a quasireference electrode. All potential data reported have been referenced to the formal potential of the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> (internally added) redox couple, taken to have  $E_{1/2} = 0.307 \text{ V.}^{15}$ 

### Discussion

## *Synthesis, spectroscopic data, and molecular structure*

The p-toluenesulfonic acid-catalyzed reaction between 2,3-dichloromaleic anhydride and *p*-anisidine proceeds in toluene under reflux, coupled with removal of water, to furnish the corresponding condensation prod-2,3-dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide. uct 2,3-Dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide was isolated as the sole isolable product by column chromatography and was characterized in solution. The IR spectrum of 2,3-dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide in CH<sub>2</sub>Cl<sub>2</sub> exhibits a strong IR stretch at  $1739 \text{ cm}^{-1}$ , readily assignable to antisymmetric carbonyl stretch belonging to the maleimide moiety.<sup>16</sup> The expected higher frequency symmetric counterpart of this latter  $\nu$ (CO) stretch is extremely weak and was not observed.<sup>16a</sup> The <sup>1</sup>H NMR spectrum of 2,3dichloro-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide exhibits a methoxy singlet at  $\delta$  3.82 and an aromatic resonance that appears as an AB quartet centered at  $\delta$  7.09 (*J*<sub>H-H</sub> = 9.0 Hz).

Treatment of 2,3-dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>) maleimide (1) with a slight excess of ethanethiol in the presence of DBU or Et<sub>3</sub>N, which were employed to scavenge the liberated HC1, gives the desired compound 2,3-bis(ethylthio)- $N-(p-\text{MeOC}_6\text{H}_4)$  maleimide in good yield. TLC analysis of the crude reaction solution using a 6:4 mixture of CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether revealed the presence of a new spot ( $R_{\rm f} =$ 0.30), which was subsequently isolated by column chromatography over silica gel using the same solvent system as the eluent. The IR spectrum of the 2,3-bis(ethylthio)-N-(p- $MeOC_6H_4$ )maleimide revealed the presence of a pair of v(CO) stretches at 1772 (w) and 1715 (vs) that belong to the kinematically coupled carbonyl groups of the maleimide ring.<sup>16</sup> The <sup>1</sup>H NMR spectrum of compound 2,3-bis(ethylthio)-N-(p- $MeOC_6H_4$ )maleimide (2) exhibits an AB quartet for the aromatic protons at  $\delta$  7.07 ( $J_{\rm H-H} =$ 8.5 Hz), with additional high-field resonances at  $\delta$  3.80 (s), 3.34 (q), and 1.35 (t), belonging to the p-OMe group, and the ethylthio methylene and methyl moieties, respectively. Finally, the UV-vis spectrum of 2,3-bis(ethylthio)-N-(p- $MeOC_6H_4$ )maleimide (2) in  $CH_2C1_2$  displayed moderately intense absorbances at 421, 309, and 250 nm.

The molecular structure of 2,3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) was next established by X-ray diffraction analysis. Single crystals of 2,3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) were found to exist as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters are listed in Table 1, whereas Table 2 gives selected bond distances and angles.

 Table 1. X-ray Crystallographic Data and Processing Parameters for

 2.3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2)

CCDC entry no.	21269
Space group	Monoclinic, C2/c
<i>a</i> (Å)	20.035(3)
<i>b</i> (Å)	9.188(1)
<i>c</i> (Å)	16.887(2)
$\beta$ (°)	93.696(2)
V (Å <sup>3</sup> )	3102.3(8)
Molecular formula	C15H17NO3S2
fw	323.42
Formula units per cell $(Z)$	8
$D_{\text{calcd}} (\text{Mg/m}^3)$	1.385
$\lambda (MoK_{\alpha}) (Å)$	0.71073
Absorption coefficient $(mm^{-1})$	0.352
R <sub>merge</sub>	0.0400
Absolute correlation factor	0.2747/0.2127
Total reflections	6178
Independent reflections	2025
Data/res/parameters	2025/0/194
R	0.0268
$R_{ m w}$	0.0676
GOF	1.052
Weights	$[0.04F^2 + (\sigma F)^2]^{-1}$

The thermal ellipsoid drawing of 2,3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) shown in Fig. 1 confirms the functionalization of the C(2) and C(3) ring atoms of the maleimide

**Table 2.** Selected Bond Distances (Å) and Angles (°) in for 2,3*bis*(erthylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (**2**)<sup>*a*</sup>

Bond distances			
S(1) - C(2)	1.732(2)	S(1) - C(12)	1.806(2)
S(2) - C(3)	1.737(2)	S(2) - C(14)	1.816(2)
O(1) - C(1)	1.208(2)	O(2)-C(4)	1.204(2)
O(3) - C(8)	1.366(2)	O(3) - C(11)	1.427(2)
N(1)-C(1)	1.385(2)	N(1)-C(4)	1.402(2)
N(1)-C(5)	1.431(2)	C(1)-C(2)	1.499(3)
C(2)-C(3)	1.351(2)	C(3)-C(4)	1.501(3)
Bond angles			
C(2)-S(1)-C(12)	104.83(9)	C(3) - S(2) - C(14)	104.66(8)
C(8) - O(3) - C(11)	118.1(1)	C(1)-N(1)-C(4)	109.9(1)
C(1)-N(1)-C(5)	124.8(1)	C(4)-N(1)-C(5)	125.3(1)
O(1)-C(1)-N(1)	125.2(2)	O(1)-C(1)-C(2)	127.6(2)
N(1)-C(1)-C(2)	107.2(1)	C(3)-C(2)-C(1)	108.2(2)
C(3) - C(2) - S(1)	136.4(1)	C(1) - C(2) - S(1)	115.4(1)
C(2)-C(3)-C(4)	107.9(2)	C(2)-C(3)-S(2)	128.1(1)
C(4)-C(3)-S(2)	123.0(1)	O(2)-C(4)-N(1)	124.7(2)
O(2) - C(4) - C(3)	128.5(2)	N(1)-C(4)-C(3)	106.8(1)

<sup>*a*</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.



Fig. 1. Thermal ellipsoid plot of 2,3-*bis*(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) showing the thermal ellipsoids at the 50% probability level.

residue by an ethylthio group. The C(1)–C(2)[1.499(3) Å] and C(3)–C(4) [1.501(3) Å] C–C single-bond distances, along with the C(2)–C(3)[1.351(2) Å] bond length for the C=C  $\pi$  bond exhibit acceptable values for C--C and C=-C bond lengths.<sup>6,14</sup> The three different C-N distances range from 1.385(2) Å [N(1)–C(1)] to 1.431(2) Å [N(1)–C(5)], with an average length of 1.406 Å.<sup>6,14</sup> The five- and six-membered rings are planar and the interplanar angle between the two rings reveals a dihedral angle of  $59.4(1)^{\circ}$ . The torsion angles of  $27.1(2)^{\circ}$  and  $-146.2(2)^{\circ}$ for the atoms C(3)-C(2)-S(1)-C(12) and C(2)-C(3)-S(2)-C(14), respectively, indicate that the ancillary ethyl groups are tipped out of the plane defined by the maleimide ring. There are three intermolecular nonclassical hydrogen-bond like interactions in the structure: C(9)-H(9)···O(3) with distances of 0.94 Å, 2.50 Å, 3.371(2) Å and an angle of 154°; C(10)-H(10)···O(2) with distances of 0.94 Å. 2.51 Å, 3.421(2) Å and an angle of  $161^{\circ}$ ; C(11)-H(11c)···O(1) with distances of 0.97 Å, 2.59 Å, 3.320(2) Å and an angle of  $132^{\circ}$ . The remaining bond distances and angles in 2 are unexceptional and do not require comment.

Cyclic voltammetry data and extended Hückel molecular orbital calculations

The redox chemistry of 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (**2**) was initially studied by cyclic voltammetry at a platinum electrode in CH<sub>2</sub>Cl<sub>2</sub> solvent containing 0.2 M TBAP at room temperature. Scanning the sample at a rate of 200 mV/s over a potential range of 1.0 V to -1.7 V revealed the presence of single redox response at  $E_{1/2} = -1.22$  V, with Fig. 2 showing the cathodic scan CV over the region of -0.6 V out to the switching potential of -1.7 V and back to -0.6 V. Normal electrochemical criteria indicate that this  $0/1^-$  redox couple corresponds to a reversible one-electron reduction,<sup>15,17</sup> a feature that is consistent with the CV behavior reported for the diphosphine ligands bma and bpcd.<sup>3e,18</sup>

Of interest to us is the fact that 2,3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) forms a relatively stable radical anion upon reduction with no evidence for cleavage of either the S—C(dione) or the S—Et bond on the CV time scale. The kinetic stability of 2, 3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) during one-electron reduction was validated



**Fig. 2.** Cathodic scan cyclic voltammogram for 2,3*bis*(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) ca. 10<sup>-3</sup> M in CH<sub>2</sub>C1<sub>2</sub> containing 0.25 M TBAP at 200 mV/s at room temperature (top), and the CACAO drawing for the LUMO of 2,3-*bis*(thio)-maleimide (bottom).

by double-potential step chronocoulometric (DPSC) studies.<sup>19</sup> The DPSC data revealed that the stability of 2,3-*bis*(ethylthio)-*N*-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)maleimide ( $2^{-\bullet}$ ) was on the order of 3–5 s at room temperature, and these results stand in sharp contrast to the stability of the radical anion derived from 4,5-*bis*(*p*-tolylthio)-4-cyclopenten-1,3-dione,<sup>7</sup> whose half-life may be estimated at ca. <0.5 s by both DPSC and dimensionless CV current ratio measurements at room temperature.<sup>20</sup> The latter radical anion decomposes according to the pathway depicted in Eq. (1) with the expulsion of the weak *p*-tolylthiolate anion.



The nature of the LUMO in 2.3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2)was explored by extended Hückel MO calculations, in order to establish the site of electron accession in the corresponding radical anion. The bottom portion of Fig. 2 shows the three-dimensional CACAO drawing<sup>13</sup> for the a<sub>2</sub>-based LUMO in the model compound (HS)C = C(SH)C(O)NHC(O). The calculated LUMO energy level (-10.05 eV) and nodal pattern found in (HS)C = C(SH)C(O)NHC(O)are similar to the  $\pi^*$  LUMO ( $\psi_4$ ) reported for the  $6\pi$  electron systems maleic anhydride and 1,3,5-hexatriene,<sup>4,21</sup> the diphosphine ligands bma and bpcd,<sup>1-3,22</sup> and the monosubstituted cyclopenten-1,3-dione compound  $(Cl)C = C(NMe_2)C(O)CH_2C(O)$ .<sup>23</sup> Minor outof-phase  $\pi^*$  contributions to the LUMO from a lone-electron pair associated with each thiol group are also observed. Mulliken population analysis confirms that the  $\pi^*$  thiol interactions contribute less than 5% to the LUMO. This latter antibonding interaction between the thiol groups and the carbocyclic ring system provides the basis by which thiolate expulsion is achieved during electrochemical reduction. We have also replaced the maleimide hydrogen in (HS)C = C(SH)C(O)NHC(O) with a phenyl group and have studied the effect that the ancillary phenyl group has on the LUMO in (HS)C=C(SH)C(O)NPhC(O).<sup>(3)</sup> The MO calculations on (HS)C=C(SH)C(O)NPhC(O) revealed that the LUMO (not shown) possessed a  $\pi^*$ -based orbital consistent with that of  $\psi_4$  of other  $6\pi$ electron systems and exhibited a calculated energy of -10.05 eV. Clearly, the substitution of the N—Ph versus a N—H group does not dramatically alter the nature and energy level of the LUMO

<sup>&</sup>lt;sup>(3)</sup>In the original calculations on (HS)C=C(SH)C(O)NPhC(O), the thiol linkages were constrained to the plane defined by the maleimide ring and were set coincident with the closest carbonyl group (torsion angle = 0°). Setting the rotation of the phenyl group about the N-C(aryl) bond as a free variable in the calculations showed only a small variation in the energy level of the LUMO. No major change was observed in the gross composition of the LUMO.

in (HS)C=C(SH)C(O)NRC(O). On the basis of these data, the maleimide ring is expected to serve as the main site for electron accession during the electrochemical reduction of compound 2,3bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2).

#### Conclusions

The synthesis of the maleimide compound 2,3-dichloro-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (1), followed by its conversion into the disulfide compound 2,3-bis(ethylthio)-N-(p- $MeOC_6H_4$ )maleimide (2) has been described. Both new compounds have been fully characterized in solution by IR and NMR spectroscopies, and the X-ray diffraction structure of the latter compound has been determined. The one-electron reduction product observed by cyclic voltammetry for 2,3-bis(ethylthio)-N- $(p-MeOC_6H_4)$  maleimide (2) derives from the occupation of a  $\pi^*$  orbital on the maleimide ring in keeping with this genre of redox-active compounds. The site of the electron accession in 2,3-bis(ethylthio)-N-(p-MeOC<sub>6</sub>H<sub>4</sub>)maleimide (2) was verified by extended Hückel MO calculations.

#### Acknowledgment

Financial support from the Robert A. Welch Foundation (Grants P-0074-WHW and B-1093-MGR) is appreciated.

#### References

- (a) Fenske, D.; Becher, H.J. Chem. Ber. 1974, 107, 117;
   (b) Fenske, D. Chem. Ber. 1979, 112, 363.
- (a) Fenske, D. Angew. Chem. Int. Ed. Engl. 1976, 75, 381;
   (b) Bensmann, W.; Fenske, D. Angew. Chem. Int. Ed. Engl. 1978, 17, 462; 1979, 18, 677.
- (a) Mao, F.; Tyler, D.R.; Keszler, D. J. Am. Chem. Soc. 1989, 777, 130; (b) Fei, M.; Sur, S.K.; Tyler, D.R. Organometallics

**1991**, *10*, 419; (c) Mao, F.; Tyler, D.R.; Bruce, M.R.M.; Bruce, A.E.; Rieger, A.L.; Rieger, P.H. *J. Am. Chem. Soc.* **1992**, *114*, 6418; (d) Schut, D.M.; Keana, K.J.; Tyler, D.R.; Rieger, P.H. *J. Am. Chem. Soc.* **1995**, *117*, 8939; (e) Duffy, N.W.; Nelson, R.R.; Richmond, M.G.; Rieger, A.L.; Rieger, P.H.; Robinson, B.H.; Tyler, D.R.; Wang, J.C.; Yang, K. *Inorg. Chem.* **1998**, *37*, 4849.

- 4. Albright, T.A.; Burdett, J.K.; Whangbo, M.H. Orbital Interactions in Chemistry; Wiley- Interscience: New York, 1985.
- (a) Yang, K.; Smith, J.M.; Bott, S.G.; Richmond, M.G. Organometallics 1993, 12, 4779; (b) Yang, K.; Bott, S.G.; Richmond, M.G. Organometallics 1994, 13, 3788; 1995, 14, 2718. (c) Shen, H.; Bott, S.G.; Richmond, M.G. Organometallics 1995, 14, 4625; (d) Yang, K.; Martin, J.A.; Bott, S.G.; Richmond, M.G. Organometallics 1996, 15, 2227; (e) Yang, K.; Bott, S.G.; Richmond, M.G. J. Organomet. Chem. 1996, 516, 65; (f) Bott, S.G.; Yang, K.; Wang, J.C.; Richmond, M.G. Inorg. Chem. 2000, 39, 6051; (g) Watson, W.H.; Bodige, S.G.; Liu, J.; Richmond, M.G. Struct. Chem. 2003, 14, 367; (h) Bott, S.G.; Yang, K.; Richmond, M.G. Organometallics 2003, 22, 1383; (i) Bott, S.G.; Shen, H.; Senter, R.A.; Richmond, M.G. Organometallics 2003, 22, 1953.
- Bodige, S.G.; Meńdez-Rojas, M.A.; Watson, W.H. J. Chem. Crystallogr. 1999, 29, 57.
- Watson, W.H.; Wu, G.; Richmond, M.G. J. Chem. Crystallogr. 2004, 34, 709.
- Shriver, D.F. The Manipulation of Air-Sensitive Compounds; McGraw-Hill: New York, 1969.
- SAINT (v 6.02); Bruker Analytical X-ray Systems, Inc.: Copyright 1997–1999.
- SHELXTL 5.1, Bruker Analytical X-ray Systems, Inc.: Copyright 1998.
- PLATON (A Multipurpose Crystallographic Tool); Utrecht University: Utrecht, The Netherlands, Speck, A.L., 2001.
- (a) Hoffmann, R.; Lipscomb, W.N. J. Chem. Phys. 1962, 36, 2179; (b) Hoffmann, R. J. Chem. Phys. 1963, 39, 1397.
- 13. Mealli, C.; Proserpio, D.M. J. Chem. Ed. 1990, 67, 399.
- Weast, R.C., Ed.; *Handbook of Chemistry and Physics*, 56th ed.; CRC Press: Cleveland, OH, 1975.
- Bard, A.J.; Faulkner, L.R. *Electrochemical Methods*; Wiley: New York, 1980.
- (a) Rao, C.N.R. Chemical Applications of Infrared Spectroscopy; Academic Press: New York, 1963; (b) Dolphin, D.; Wick, A. Tabulation of Infrared Spectral Data; Wiley-Interscience: New York, 1977.
- (a) Kissinger, P.T.; Heineman, W.R. Laboratory Techniques in Electroanalytical Chemistry; Marcel Dekker, Inc.: New York, 1984; (b) Gosser, D.K., Jr.; Cyclic Voltammetry; VCH Publishers: New York, 1993.
- (a) Becher, H.J.; Fenske, D.; Heymann, M. Z. Anorg. Allg. Chem. 1981, 475, 27; (b) Meyer, R.; Schut, D.M.; Keana, K.J.; Tyler, D.R. Inorg. Chim. Acta 1995, 240, 405.
- Ridgway, T.H.; Van Duyne, R.P.; Reilley, C.N. J. Electroanal. Chem. 1972, 34, 267.
- 20. Nicholson, R.S.; Shain, I. Anal. Chem. 1964, 36, 706.
- 21. Hayakawa, K.; Mibu, N.; Osawa, E.; Kanematsu, K. J. Am. Chem. Soc. **1982**, 104, 7136.
- 22. Yang, K.; Bott, S.G.; Richmond, M.G. Organometallics 1995, 14, 2387.
- Shen, H.; Bott, S.G.; Richmond, M.G. J. Chem. Crystallogr. 1997, 27, 19.23.