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Synthesis of 2,3-Diaryltetrazole-5-thiones and Theoretical Studies on Atomic Charge Distributions of 2,3-Diphenyltetrazole-5-thione

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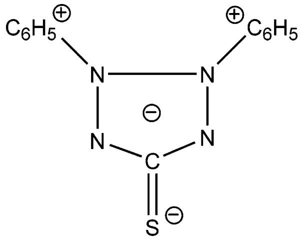

Four 2,3-diaryltetrazole-5-thiones have been synthesized in high yields using a new synthetic method under mild reaction conditions. Theoretical calculations of the structure, vibrational frequencies, and natural population analysis (NPA) of atomic charge distributions on 2,3-diphenyltetrazole-5-thione **1** have been performed by DFT-B3LYP, HF, and MP2 methods using several basis sets. According to the NPA results a new resonance hybrid structure of **1** has been proposed with an exocyclic sulfur atom and a tetrazole ring carrying negative charges and two phenyl rings having positive charges. On the basis of this new proposed structure, the calculated results can explain experimental facts logically. In addition, a new chemical property of **1** has been predicted: the protonation should occur not only on the exocyclic S atom, but also on the N atoms having negative charges.

Introduction

2, 3-Diphenyltetrazole-5-thione **1** (Scheme 1) is a well-known *meso*-ionic compound which exhibits various physical and chemical properties.[1,2] In 1937 Fischer published a procedure for the synthesis of **1**.[1b] Using this procedure **1** can be obtained from the oxidation of dithizone with potassium hexacyanoferrate(III).

However, yield and purification of this procedure were not satisfying. To date, no other synthetic routes to **1** have been reported. Although there are common synthetic routes to tetrazoles, such as by the facile addition of metal azide to nitriles, thiocyanates, cyanates, and cyanamides[3] or by Huisgen 1,3-dipolar cycloaddition,[4] they cannot obtain 2,3-diaryltetrazole-5-thiones. Recently, our group made remarkable progress in improving the synthesis of **1**. Using this new method **1** can be prepared under mild conditions in a high yield (up to 95%). Initially, we only wanted to synthesize the dithiocarbamate of dithizone by reacting dithizone with carbon bisulfide under basic conditions. However, the anticipated product was not obtained. Instead, two different products were isolated. Crystal structure determinations carried out on both products reveal that they are 2,3-diphenyltetrazone-5-thione, **1**, and 3-phenyl-5-phenylazo-[1,3,4]-thiadiazole-5-thione. These results attracted our attention and promoted us to develop a new synthetic route to the preparation of **1**. Our investigation revealed that in the absent of carbon bisulfide **1** could be synthesized directly in very high yields simply using air to oxidize dithizone under basic conditions or using hydrogen peroxide to oxidize dithizone under nonbasic conditions. A similar method could be adopted to synthesize other 2,3-diaryltetrazole-5-thiones when dithizone was replaced

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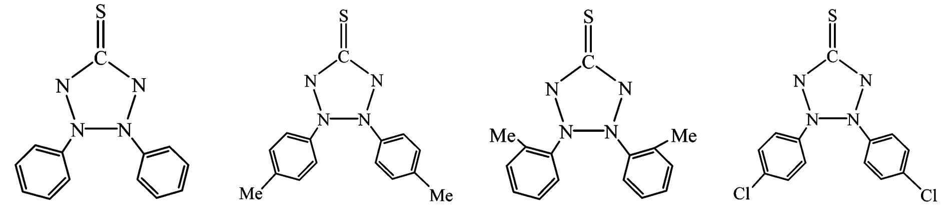
SCHEME 1. Four 2,3-Diaryltetrazole-5-thiones



1 **2** **3** **4**

by aryl-substituted dithizone. All of the features of this new method, such as mild reaction conditions, high yield, simple purification, and short reaction period, make this synthesis a promising method in industrial applications.

Many theoretical studies on 2,3-diaryltetrazole-5-thione have been published before.[5,6] Therefore, we also performed theoretical calculations on **1**. Surprisingly, the calculated results showed that the theoretical atomic charge distributions of **1** are different from the reported resonance hybrid structure of **1** (Figure 1). This resonance hybrid structure was proposed in 1961 by Ogilvie et al. according to the physical and chemical properties of **1**.[7] They proposed that the exocyclic sulfur atom had negative charges and the tetrazole ring had positive charges. In 1965 Yoshihiko and Quintus reported the crystal structure of **1,** and this structure supported Ogilvie's proposal based on the "sandwich-type" packing in the crystal lattice.[8] From then on the resonance hybrid structure of **1** as shown in Figure 1 has been used. This representation of **1** utilizes the accepted symbolism for *meso*-ionic compound and does not imply that a unit negative charge is associated with the exocyclic sulfur atom.

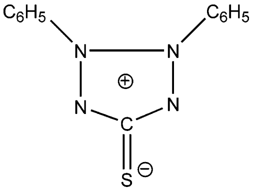


FIGURE 1. Reported atomic charge distributions for **1**.

However, our calculated results showed that this resonance hybrid structure was wrong, and the right structure is shown in Figure 2, where the exocyclic sulfur atom and tetrazole ring both have negative charges while two phenyl rings have positive charges. In this paper we report our studies based on the theoretical calculations.

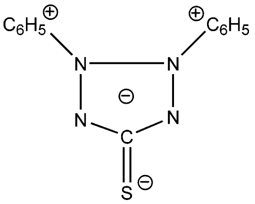


FIGURE 2. New atomic charge distributions for **1**.

Results and Discussion

Synthesis. Two methods have been developed to synthesize **1** using either hydrogen peroxide (method I) or air (method II) as oxidant to react with dithizone. Compounds **2**−**4** (Scheme 1) are synthesized using similar methods. Both methods I and II give high yield (up to 95%) under mild reaction conditions and are easy workup, which make them promising in industry applications.

X-ray single-crystal structure determinations of **1** and **2** (see crystallographic data and Figure S1 and Figure S2 in the Supporting Information) indicate that all the bond lengths of C=S and N−N are longer than their respective double-bond lengths and shorter than their respective single-bond lengths. The exocyclic sulfur atoms and tetrazole rings are coplanar. Therefore, conjugation among the sulfur atoms and the tetrazole rings exists. The bonds of C−N connecting the tetrazole ring with the phenyl rings are typical single bonds. The dihedral angles between the tetrazole rings with the phenyl rings are 44.92° for **1** and 89.82° for **2**.

Theoretical Calculations. Comparison of three methods (B3LYP, MP2, and HF) used in theoretical calculations (see Figure S3, Table S1, and Table S2) shows that DFT-B3LYP methods gave best bond parameters, which are very close to those observed in the crystal structure of **1**. The largest bond length difference between the calculated value and the corresponding experimental value is 0.0310 Å, and the largest bond angle difference is 2.09°. These differences indicate that the calculated precision is satisfactory.[9] HF methods gave the largest deviations in bond angles among the three methods. Despite this, in all calculations the resonance situation between the tetrazole ring and the exocyclic sulfur atom exists and the two C atoms connecting the phenyl ring with tetrazome ring are also coplanar with the tetrazole ring. These results suggest that all of above models can be used to predict the properties of **1** and the B3LYP calculations can best reproduce the structure of **1**. Therefore, the discussion hereafter is mainly based on the calculations using B3LYP. At the same time the data obtained from the calculations of HF and MP2 methods are also used to assist the interpretation of the properties of **1**.

To carry out the atomic charge distributions analyses we optimized **1** using DFT-B3LYP and HF methods at

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TABLE 1. NPA Atomic Charge Distributions

	B3LYP 6-31G*	B3LYP 6-311G**	B3LYP 6-31+G*	HF 6-31G*	HF 6-311G**	HF 6-31+G*	MP2 6-31G*	MP2 6-311G**
S	−0.25208	−0.28107	−0.24313	−0.41055	−0.44068	−0.40615	−0.34033	−0.39742
tetrazole ring	−0.3158	−0.29813	−0.33683	−0.21836	−0.1975	−0.23528	−0.28159	−0.23654
phenyl ring	0.2826	0.28965	0.29677	0.31445	0.31909	0.32071	0.31096	0.3170

TABLE 2. Total Energy of 2,3-Diphenyltetrazole-5-thione in the Gas Phase and Its Relative Energies in Solvents (kcal/mol)

		B3LYP 6-31G*	B3LYP 6-311G**	B3LYP 6-31+G*	HF 6-31G*	HF 6-311G**	HF 6-31+G*
total energy	gas phase	−701864.45356	−701986.86937	−701880.12373	−698596.00570	−698703.97184	−698607.84178
relative energies	ethanol	−15.92500	−14.53400	−13.23926	−16.11570	−7.93373	−18.42744
	water	−16.99428	−15.49290	−14.10102	−17.04749	−9.13271	−19.56386

6-31G*, 6-311G**, and 6-31+G* basis sets and MP2 methods at 6-31G* and 6-311G** basis sets.

It is evident that by using 6-31G* and 6-311G* basis sets all of the Mulliken atomic charge distributions analyses (Table S3) show that the exocyclic sulfur atom and tetrazole ring have negative charges while two phenyl rings have positive charges. However, use of the 6-31+G* basis set offers different results, which indicate that the exocyclic sulfur atom and the phenyl ring have negative charges but that the tetrazole ring has a positive charge. Above discrepant results prompted us to perform further study. Thus, based on the above optimized structures, natural population analysis (NPA) was performed.[10,11]

Of the numerous schemes proposed for atomic population analysis, only Mulliken population analysis has truly found widespread use. Unfortunately, Mulliken populations fail to give a useful and reliable characterization of the charge distribution in some cases.[11g,12] Mulliken population analysis may give two types of objections. One is that the Mulliken population can have unphysical negative values.[11g,12] This defect might be overlooked if the magnitudes were small, but the values are sometimes quite significant. The other defect is that Mulliken populations are unduly sensitive to basis set, particularly as the basis set is enlarged to higher accuracy.[11g] However, the NPA seems to offer several advantages over standard Mulliken analysis or alternative theoretical approaches. Unlike Mulliken population analysis, NPA gives intrinsically nonnegative quantities. The NPA also exhibits excellent numerical stability with respect to basis set changes.[11g] Table 1 gives the NPA atomic charge distributions (for detailed information on the atomic charges on each atom, see Table S4).

Indeed, no matter what method and what basis set are used, the NPA results in Table 1 show that all three methods produced consistent atomic charge distributions for **1** with the exocyclic sulfur atom and the tetrazole ring having negative charges while the two phenyl rings have positive charges.

On the basis of the Mulliken atomic charge distributions and natural population analyses, we propose a new structure for **1** as shown in Figure 2, which is different from the resonance structure proposed by Ogilvie et al.

Using this new structure we can explain the physical property of **1** presented in Ogilvie's paper: why **1** is easy to dissolve in polar solvents. For this purpose we carried out DFT-B3LYP and HF calculations using different basis sets for **1** and obtained its total energies in the gas phase and in solution (ethanol and water solutions). In the Onsager model the dielectric constants ϵ of ethanol and water are 24.55 and 78.39, respectively. Table 2 gives the total energy of **1** in the gas phase and its relative energies in solution calculated by different methods.

All the calculated data indicate that the total energy of **1** in solution is lower than that in the gas phase; on the other hand, the total energy in water is lower than that in ethanol. These results suggest that **1** is easy to dissolve in polar solvents and more stable in more polar solvent.[13]

In addition, we can also predict that the magnitude of negative charges on the sulfur atom and positive charges on the phenyl ring will increase in polar solvents as compared to their values in the gas phase. Accordingly, the dipole moment of **1** will increase with increasing the polarity of the solvent. The calculated results in the gas phase and in solvent are consistent with this prediction. Table 3 lists the NPA atomic charges on the sulfur atom, the tetrazole, and the phenyl rings in solvents (for detailed information about the atomic charges on each atom, see Tables S5 and S6). Table 4 gives the dipole moment values of **1** in the gas phase and in solution.

In solution, the values of negative atomic charge on the sulfur atom are marginally larger than those in the gas phase and the values of positive atomic charge on the phenyl rings are also marginally larger than those in the gas phase. At the same time these values in water are all larger than those in ethanol (Table 3). As seen in Table 4, the dipole moment values in solution are larger than those in the gas phase. The dipole moment values in water are marginally larger than those in ethanol.

Additionally, the NPA atomic charges in solution as listed in Table 3 support the new proposed resonance hybrid structure of **1** as shown in Figure 2.

In our new proposed resonance hybrid structure the sulfur atom has negative charges, which is similar to that in Ogilvie's structure. Therefore, this new structure

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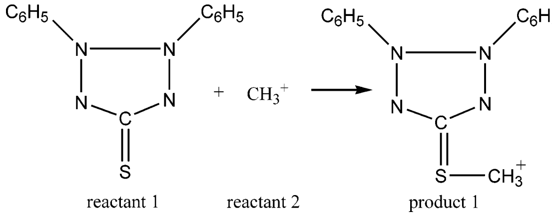
TABLE 3. NPA Atomic Charge Distributions in Solvent

		B3LYP 6-31G*	B3LYP 6-311G**	B3LYP 6-31+G*	HF 6-31G*	HF 6-311G**	HF 6-31+G*
ethanol	S	−0.42014	−0.43815	−0.39051	−0.51330	−0.56244	−0.52607
	tetrazole ring	−0.24486	−0.23344	−0.27465	−0.17321	−0.14563	−0.18180
	phenyl ring	0.33250	0.33580	0.33258	0.34327	0.35404	0.35392
water	S	−0.43058	−0.44775	−0.39961	−0.51877	−0.56925	−0.53282
	tetrazole ring	−0.24088	−0.22965	−0.27083	−0.17104	−0.14313	−0.17916
	phenyl ring	0.33573	0.33870	0.33522	0.34490	0.35617	0.3560

TABLE 4. Dipole Moment of 2,3-Diphenyltetrazole-5-thione in the Gas Phase and Solvents (in Debye)

	B3LYP 6-31G*	B3LYP 6-311G**	B3LYP 6-31+G*	HF 6-31G*	HF 6-311G**	HF 6-31+G*
gas phase	13.4701	13.5728	13.6049	15.9206	16.0120	15.9527
ethanol	20.3886	20.2141	19.9764	20.9019	22.3136	22.2489
water	20.8498	20.6470	20.3911	21.1889	22.6997	22.6395

SCHEME 2

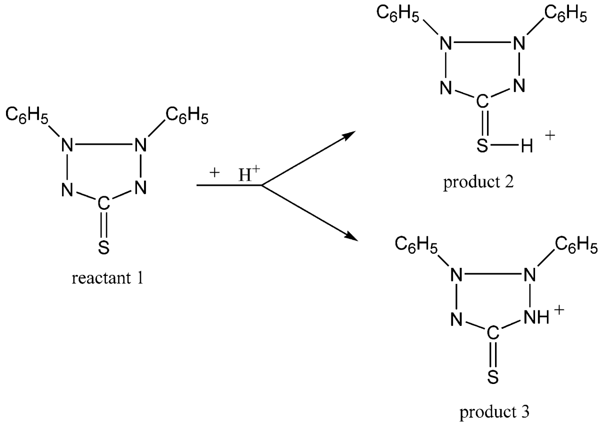


should also bestow a nucleophilic property upon the sulfur atom. To prove this property, we calculated the changes of Gibbs free energy for the methylation of **1**. Because the DFT-B3LYP method considers electron correlation and is less computationally demanding as well as predicts the structure and vibrational frequencies very well, we chose the DFT-B3LYP level of theory using the 6-311G** basis set to optimize the geometry of the reactants and product in Scheme 2 and to calculate their vibrational frequencies to ascertain that the structures are stable (no imaginary frequencies). On the basis of the obtained frequencies, thermodynamic properties are derived from statistical thermodynamics (Table S7).

On the basis of calculated data, all of the values for the standard entropy S°_m and standard enthalpy H°_m of the reactants and product in Scheme 2 increase with increasing temperature. This is attributed to enhancement of the molecular vibration. In the course of the methylation of **1** both the entropy and enthalpy decrease at temperatures ranging from 200.0 to 800.0 K ($\Delta S_\mathrm{T} < 0$, $\Delta H_\mathrm{T} < 0$), indicating that this reaction is an exothermic processes accompanied by the decrease of confusion degree. From the equation $\Delta G_\mathrm{T} = \Delta H_\mathrm{T} - T\Delta S_\mathrm{T}$, the changes of the Gibbs free energies (ΔG_T) in the reaction process are all negative, which implies that methylation of **1** can occur spontaneously from 200.0 to 800.0 K. At 298.15 K, on the calculated model of an ideal gas, the calculated equilibrium constant, based on the equation $\Delta G_\mathrm{T} = -RT \ln K_\mathrm{p}$, is 2.199×10^{99}, which suggests that product **1** is the main component at room temperature.

According to the new resonance hybrid structure, protonation of **1** can take place not only on the sulfur atom, but also on the nitrogen atoms having negative charges. This is in contrast to what was reported by Ogilvie et al. On the other hand, we obtained the optimized geometry of products **2** and **3** in Scheme 3-(Figure S3). Frequency calculations show that products **2** and **3** are stationary points in their respective potential-energy surfaces (no imaginary frequencies). The thermodynamic properties of reactant and products in Scheme 3 were calculated at the DFT-B3LYP/6-311G** level of theory (Table S8). The calculations show that the changes of the Gibbs free energies (ΔG_T) for the two reactions are all negative, and these negative values imply that the spontaneous protonation process can take place on the S and N atoms having negative charges. On the other hand, changes of Gibbs free energies (ΔG_T) for protonation on the sulfur atom are smaller than those on the N atoms, indicating that the protonation is easier to take place on the sulfur atom. In addition, the total energy of product **2** is lower than that of product **3**; hence, product **2** is more stable than product **3**. Therefore, product **2** could be obtained easier than product **3**.

SCHEME 3



Conclusions

Compound **1** and its derivatives have been synthesized using either hydrogen peroxide or air as an oxidant under mild reaction conditions. The new method features high yield and easy workup. These advantages make this new method promising in industrial applications.

On the basis of the optimized geometric structures of **1**, which are calculated by DFT-B3LYP, HF, and MP2 methods using several basis sets, the natural population analysis of atomic charge distributions were performed. According to the calculated NPA results, a new atomic charge distribution of **1** has been proposed. The NPA results show that the sulfur atom and the tetrazole ring have negative charges while the two phenyl rings have positive charges. This is different from the resonance hybrid structure proposed by Ogilvie et al. Using our new proposed structure for **1** and the calculated data, the physical and chemical properties of **1** can be explained logically. On the basis of the new structural feature, protonation of should take place not only on the S atom, but also on the N atoms having negative charges.

Experimental Section

Computational Methods. Since a proper structure is a primary condition for in-depth studies of a chemical system, it is necessary to select an appropriate computational model that can produce a reasonable structure for **1**. For this purpose we performed a large number of calculations for the system studied. The properties of **1** in the gas phase and in solvent are all investigated.

In the gas phase, considering the disk space and computational cost, the geometry of **1** was optimized at DFT-B3LYP,[14,15] HF, and MP2 levels of theory using 6-31G*, 6-311G**, and 6-31+G* standard basis sets for B3LYP and HF methods and 6-31G* and 6-311G** basis sets for MP2 methods by the Berny gradient optimization method.[16]

To investigate the solvent effect for the studied compound, the Onsager reaction filed model[17,18] was utilized to optimize the solvated systems and calculate relevant properties. In this method the solute occupies a fixed spherical cavity of radius a_0 within the solvent field. For each solvated species studied here the cavity size a_0 was derived from a tight molecular volume calculation provided in Gaussian 03 on the fully optimized gas-phase stationary states using the same quantum chemical model for consistency. In terms of disk space, computer time, and the size of the molecules studied here, using the Onsager reaction field model we only performed geometry optimization by Hartree–Fock and DFT-B3LYP levels of theory.

Normal-mode vibrational frequencies were calculated from the analytical harmonic force constants. Calculated vibrational frequencies ascertained that the structure was stable (no imaginary frequencies). Thermodynamic properties were derived from statistical thermodynamics based on the frequencies. Natural bond orbital analyses[11,19] were performed on the optimized structure in the gas phase and in solution.

All calculations were performed with the Gaussian 03 software package[20] on a Pentium IV computer and DELL PE 2650 server using the default convergence criteria.

Synthesis of 2,3-Diphenyltetrazole-5-thione (1) (Method I). Dithizone (1.0 g, 4 mmol) was dissolved in acetone (100 mL), and a dark-green solution was observed. Hydrogen peroxide (0.5 mL, 6 mmol) was then added dropwise with stirring. The mixture was stirred and kept at 40–60 °C, and the solution color changed from green to red gradually. After 3 h of stirring the reaction was stopped and cooled to room temperature. Evaporation of acetone gave a dark-red solid. The solid was washed with water and air-dried. The pure product was obtained by recrystallization from EtOH as red crystals. Yield: 98%. mp 167–169 °C. FTIR ν 3014(m), 1635(m), 1489(s), 1363(m), 1319(vs), 1245(m), 1160(m), 1017(m), 980(m), 765(s), 687(s) cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_4S$: C, 61.42; H, 3.94; N, 22.05. Found: C, 61.02; H, 3.71; N, 21.82.

Synthesis of 2,3-Diphenyltetrazole-5-thione (1) (Method II). Dithizone (2.0 g, 8 mmol) was dissolved in acetonitrile (80 mL), and a dark-green solution was observed. The mixture was heated to 50 °C, and an aqueous sodium hydroxide solution (50% 100 mL) was added dropwise with stirring. Fifteen minutes later the solution color changed from green to red. After 12 h the reaction was stopped and the solution cooled to room temperature. The acetonitrile was rotary evaporated, and a dark red solid was obtained. The solid was then washed with water and air-dried. The pure product was obtained by recrystallization from EtOH as red crystals. Yield: 96%. mp 167–169 °C. FTIR ν 3014(m), 1589(m), 1488(s), 1366(m), 1315(vs), 1244(m), 1159(m), 1022(m), 980(m), 764(s), 688(s). ^{1}H NMR ($CDCl_3$) δ 7.27–7.99 (m, 10H, ArH). ^{13}C NMR δ 125.04, 129.56, 132.86, 151.46, 187.23. Anal. Calcd for $C_{13}H_{10}N_4S$: C, 61.42; H, 3.94; N, 22.05. Found: C, 61.11; H, 3.80; N, 21.89.

Synthesis of 2,3-Di(*p*-methylphenyl)tetrazole-5-thione (2) (Method II). The same procedure as for **1** (Method II) was used. *p,p′*-Dimethyldithizone (2.3 g, 8 mmol) was used in place of dithizone, chloroform (80 mL) replaced acetonitrile, the reaction temperature was 40 °C, the reaction time was 4 h, and orange crystals formed. Yield: 95%. mp 170–171 °C. FTIR ν 3027(m), 2990(m), 2920(m), 1637(m), 1506(m), 1401(m), 1296(vs), 1241(s), 1040, 980(m), 826(s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 6H, CH_3), δ 7.35–7.59 (m, 8H, ArH). ^{13}C NMR δ 20.86, 126.06, 130.08, 131.06, 142.85, 181.27. Anal. Calcd for $C_{15}H_{14}N_4S$: C, 63.83; H, 4.96; N, 19.86. Found: C, 63.62; H, 4.62; N, 19.58.

Synthesis of 2,3-Di(*o*-methylphenyl)tetrazole-5-thione (3) (Method I). The same procedure as for **1** (Method I) was used. *o,o′*-Dimethyldithizone (2.3 g, 8 mmol) was used in place of dithizone, the reaction time was 1 h, and orange crystals formed. Yield: 96%. mp 168–169 °C. FTIR ν 3010(m), 2902(m), 2844(m), 1650(m), 1489(m), 1367(m), 1309(vs), 1246(m), 1082(s), 975(m), 770(s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 6H, CH_3), δ 7.16–7.49 (m, 8H, ArH). ^{13}C NMR δ 17.72, 127.41, 132.29, 134.66, 183.83. Anal. Calcd for $C_{15}H_{14}N_4S$: C, 63.83; H, 4.96; N, 19.86. Found: C, 63.47; H, 4.57; N, 19.39.

Synthesis of 2,3-Di(*p*-chlorphenyl)tetrazole-5-thione (4) (Method I). The same procedure as for **1** (Method I) was used. *p,p′*-Dichlorodithizone (2.6 g, 8 mmol) was used in place of dithizone, the reaction time was 6 h, and yellow crystals formed. Yield: 95%. mp 202–203 °C. FTIR ν 3220(m), 1641(m), 1559(m), 1488(m), 1410(m), 1293(vs), 1231(m), 1092(m), 1016(m), 981(m), 842(s), 770(s), 764 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.70–7.73 (m, 8H, ArH). ^{13}C NMR δ 128.20, 130.11, 131.91, 137.54, 181.97. Anal. Calcd for $C_{13}H_8N_4SCl_2$: C, 48.30; H, 2.48; N, 17.34. Found: C, 48.13; H, 2.52; N, 17.27.

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Supporting Information Available: CIF file for **1**–CCDC 252442 and **2**-CCDC 234730, all of the atomic coordinates calculated by three methods using different basis sets for **1** in the gas phase together with detailed information about the atomic charges on every atom in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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