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A DFT INVESTIGATION OF SUBSTITUENT EFFECTS ON THE INTERCONVERSIONS OF THIOPHENOLS TO CYCLOHEXA-2,4- AND -2,5-DIENE-1-THIONES. II. ENERGETICS

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Abstract

The effect of single substituents — chloro-, cyano-, fluoro-, nitro-, trifluoromethyl-, dimethylamino-, methoxy-, and methyl-groups — on the theoretical thione-enethiol tautomerism (the sulfur analog of the keto-enol tautomerism) between 1-thiophenols and cyclohexa-2,4- and -2,5-diene-1-thiones has been investigated using density functional computational methods at the ωB97X-D/6-311++G level of theory. Based on the calculated electronic energies of the isolated molecules in the gas phase, the equilibria heavily favor the thiophenol systems, as expected. The substituted-cyclohexadienethiones are unlikely to be synthetically accessible, except perhaps as isolated molecules in low temperature matrices, in the dilute gas phase, or in interstellar space, as they are predicted to overwhelmingly transform into the corresponding thiophenols due to the large computed electronic energy differences and the effect of the aromatic character of the thiophenols. The single substituents do affect the energy differences between the analogous thiophenol and the cyclohexadienethiones, but either increase the energy difference or do not decrease the energy difference sufficiently to allow an equilibrium between the molecules to be observable.**

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Introduction

In the first part of this investigation,[1] the structures and selected properties of thiophenol (**PhSH**), cyclohexa-2,4- and -2,5-diene-1-thione (**Chd^{24}=S** and **Chd^{25}=S**, respectively) and selected mono-substituted analogs of the parent molecules were reported. The substituents investigated were the chloro-, cyano-, fluoro-, nitro-, trifluoromethyl-, dimethylamino-, methoxy-, and methyl-groups. While the calculated results exposed no structural anomalies in these molecules, many of the molecules reported had not been previously studied either experimentally or computationally, making the structural information novel, if not surprising.

However, the original goal of the project was to determine whether the selected substituents could affect the theoretical thioketo-enethiol tautomerism between the substituted-thiophenol and either the substituted-cyclohexa-2,4- or the -2,5-diene-1-thione, potentially allowing a sufficient amount of either or both of the cyclohexadienethiones to be present so that experimental detection would be possible. For such an analysis, the calculated electronic energies for the molecules were required. Thus, herein are reported the electronic energies of all of the resulting molecules, calculated at the ωB97X-D/6-311++G** level of density functional theory. These data were then used to determine the relative energies of the isomeric substituted thiophenols and of the substituted cyclohexadienethiones, and the effect of each substituent on the potential thioketo-enethiol tautomerism between the cyclohexadienethiones and the corresponding thiophenols.

Computational methods

As previously described,[1] all computations were carried out with the *Spartan* program packages[2] at the ωB97X-D/6-311++G** level of density functional theory.[3] This method is reported to perform well for covalent systems.[4]

Results and Discussion

The calculated electronic energies of thiophenol, the cyclohexadiene-1-thiones, and the substituted analogs are discussed herein. Table 1 compares the energies of the thiophenols with those of the cyclohexa-2,4-diene-1-thiones, while Table 2 compares the energies of the thiophenols with cyclohexa-2,5-diene-1-thiones. Comparisons of the relative stabilities of the substituted-thiophenol and -cyclohexadienethione isomers are discussed first, followed by a discussion of the effect of the substituents on the potential thione-enethiol tautomerisms.

Relative isomeric stabilities within the thiophenols and the cyclohexadiene-1-thiones

Direct comparisons of the stabilities of the isomeric 2-, 3-, and 4-substituted thiophenols (calculated as if isolated in the gas phase at ambient temperature) can be made from the data in Table 1; the most negative electronic energy defines the most stable isomer at this level of theory. Thus, based on the relative calculated electronic energies, the most stable isomers are the *ortho*-substituted **2-CN-C_6H_4SH**, **2-OMe-C_6H_4SH**, and **2-Me-C_6H_4SH**, the *meta*-substituted **3-Cl-C_6H_4SH**, **3-F-C_6H_4SH**, and **3-NMe_2-C_6H_4SH**, and the *para*-substituted **4-NO_2-C_6H_4SH** and **4-CF_3-C_6H_4SH**. The least stable isomers were calculated to be the *ortho*-substituted **2-Cl-C_6H_4SH**, **2-NO_2-C_6H_4SH**, **2-CF_3-C_6H_4SH**, and **2-NMe_2-C_6H_4SH**, the *meta*- substituted **3-CN-C_6H_4SH**, and the *para*-substituted **4-F-C_6H_4SH**, **4-OMe-C_6H_4SH**, and **4-Me-C_6H_4SH**. However, the absolute energy differences were often found to be small, and the possibility exists that at a different level of theory the relative stabilities may change.

The relative stability results for the substituted thiophenols do not readily align themselves with the *ortho-para* directing influence of the thiol-group[5,6] in electrophilic aromatic substitution.

Because electrophilic aromatic substitution reactions are heavily dominated by the transition state structures, which can be either a π- or a -state,[7] such differences in stability in the ground state are not unexpected. The potential transition state structures, however, were not investigated.

Within the cyclohexa-2,4-diene-1-thiones, the most stable of the five possible isomeric molecules for each substituent were either 5- or 3-substituted systems: **5-Cl-Chd^{24}=S**, **5-CN-Chd^{24}=S**, **5-NO$_2$-Chd^{24}=S**, **5-CF$_3$-Chd^{24}=S**, and **5-Me-Chd^{24}=S**, and **3-F-Chd^{24}=S**, **3-NMe$_2$-Chd^{25}=S**, and **3-OMe-Chd^{24}=S**. On the other hand, the least stable were either 6- or 2-substituted species: **6-Cl-Chd^{24}=S**, **6-CN-Chd^{24}=S**, **6-F-Chd^{24}=S**, **6-NMe$_2$-Chd^{24}=S**, **6-OMe-Chd^{24}=S**. and **6-Me-Chd^{24}=S**, and **2-NO$_2$-Chd^{24}=S**, and **2-CF$_3$-Chd^{24}=S**. The reasons for these results are apparently based on an interplay of steric and electronic effects. For the least stable isomers, placing the substituent at the 6- or the 2-positions will be expected to increase the steric interactions of the substituent with the thione group (through substitution at position 2) or simply will increase the steric interactions of the saturated carbon atom (through substitution at position 6). Thus, any interactions, whether positive or negative, of the substituent with the conjugated system will be hindered. In positions 5 or 3, the substituents may have additional electronic interactions with the conjugated system, making those molecules more stable than with regard to substitution at other positions.

Within the cyclohexa-2,5-diene-1-thiones, a much simpler system evolves, but not only because there are fewer possible substituent positions: All of the most stable isomers contain the substituent at the 3-position (equivalent to the 5-position). This result seems straightforward, with the substituents placed to provide for the least steric interaction with the thione group while still allowing interactions of the substituent with the cross-conjugated unsaturated system. Similarly, the least stable isomers are either 2- (equivalent to the 6-position) or 4-substituted, and appeared to balance steric hindrance with electronic interactions (**2-Cl-Chd^{25}=S**, **2-NO$_2$-Chd^{25}=S**, and **2-CF$_3$-Chd^{25}=S**) or prioritized steric interactions with the thione group (**4-CN-Chd^{25}=S**, **4-F-Chd^{25}=S**, **4-NMe$_2$-Chd^{25}=S**, **4-OMe-Chd^{25}=S**, and **4-Me-Chd^{25}=S**).

With regard to the relative stabilities of the parent cyclohexadienethione isomers, the cross-conjugated **Chd^{25}=S** was calculated to be more stable than the linearly-conjugated **Chd^{24}=S** isomer by 10.8 kJ/mol. Such a result is also support for the detection of **Chd^{25}=S** in the Galactic Center molecular cloud G+0.693-0.027, rather than the **Chd^{24}=S** isomer.[8] However, not all of the substituted cyclohexa-2,5-diene-1-thiones were calculated to be more stable than the substituted cyclohexa-2,4-diene-1-thiones. In Tables 1 and 2, the most stable isomers when comparing the cyclohexa-2,5-diene-1-thiones with the cyclohexa-2,4-diene-1-thiones are highlighted in red. Substituents at the 2- and 6-positions of the cyclohexa-2,5-diene-1-thiones are compared to the 2-substituted cyclohexa-2,4-diene-1-thiones, the 3- and 5-positions of the cyclohexa-2,5-diene-1-thiones compared to the 3-substituted cyclohexa-2,4-diene-1-thiones, and the 4-position substituents were compared in each. Thus, although the majority of the cyclohexa-2,4-diene-1-thiones were calculated to be more stable than the corresponding cyclohexa-2,5-diene-1-thiones, five — **4-CN-Chd^{25}=S**, **4-F-Chd^{25}=S**, **4-NO$_2$-Chd^{25}=S**, **4-NMe$_2$-Chd^{25}=S**, and **4-OMe-Chd^{25}=S** — reversed that trend.

The potential reason for the reversal of stability mentioned

Table 1. Electronic energies of the thiophenols compared to the corresponding cyclohexa-2,4-diene-1-thiones

thiophenol[a]	electronic energy (eV)	cyclohexadiene-1-thione[c]	electronic energy (eV)	difference[b] (kJ/mol)	cyclohexadiene-1-thione	electronic energy (eV)	difference[b] (kJ/mol)
PhSH	-630.417139	**Chd^{24}=S**	-630.379175	99.67			
2-Cl-C$_6$H$_4$SH	-1090.023319	**2-Cl-Chd^{24}=S**	-1089.981450	109.93	**6-Cl-Chd^{24}=S**	-1089.980056	113.59
2-CN-C$_6$H$_4$SH	-722.647530	**2-CN-Chd^{24}=S**	-722.603943	114.44	**6-CN-Chd^{24}=S**	-722.595374	136.94
2-F-C$_6$H$_4$SH	-729.658723	**2-F-Chd^{24}=S**	-729.616323	111.32	**6-F-Chd^{24}=S**	-729.609226	129.95
2-NO$_2$-C$_6$H$_4$SH	-834.907909	**2-NO$_2$-Chd^{24}=S**	-834.862134	120.18	**6-NO$_2$-Chd^{24}=S**	-834.864058	115.13
2-CF$_3$-C$_6$H$_4$SH	-967.472348	**2-CF$_3$-Chd^{24}=S**	-967.430619	109.56	**6-CF$_3$-Chd^{24}=S**	-967.432026	105.87
2-NMe$_2$-C$_6$H$_4$SH	-764.380781	**2-NMe$_2$-Chd^{24}=S**	-764.339009	109.67	**6-NMe$_2$-Chd^{24}=S**	-764.332945	125.59
2-OMe-C$_6$H$_4$SH	-744.938881	**2-OMe-Chd^{24}=S**	-744.896451	111.40	**6-OMe-Chd^{24}=S**	-744.886075	138.64
2-Me-C$_6$H$_4$SH	-669.733913	**2-Me-Chd^{24}=S**	-669.696651	97.83	**6-Me-Chd^{24}=S**	-669.693463	106.20
3-Cl-C$_6$H$_4$SH	-1090.024303	**3-Cl-Chd^{24}=S**	-1089.987519	96.58	**5-Cl-Chd^{24}=S**	-1089.988254	94.65
3-CN-C$_6$H$_4$SH	-722.646039	**3-CN-Chd^{24}=S**	-722.605147	107.36	**5-CN-Chd^{24}=S**	-722.607609	100.90
3-F-C$_6$H$_4$SH	-729.658878	**3-F-Chd^{24}=S**	-729.623519	92.84	**5-F-Chd^{24}=S**	-729.622902	94.45
3-NO$_2$-C$_6$H$_4$SH	-834.912201	**3-NO$_2$-Chd^{24}=S**	-834.869616	111.81	**5-NO$_2$-Chd^{24}=S**	-834.873171	102.47
3-CF$_3$-C$_6$H$_4$SH	-967.475642	**3-CF$_3$-Chd^{24}=S**	-967.435937	104.25	**5-CF$_3$-Chd^{24}=S**	-967.438101	124.82
3-NMe$_2$-C$_6$H$_4$SH	-764.380885	**3-NMe$_2$-Chd^{24}=S**	-764.355188	67.47	**5-NMe$_2$-Chd^{24}=S**	-764.354675	68.81
3-OMe-C$_6$H$_4$SH	-744.937934	**3-OMe-Chd^{24}=S**	-744.910469	72.11	**5-OMe-Chd^{24}=S**	-744.908458	77.39
3-Me-C$_6$H$_4$SH	-669.733226	**3-Me-Chd^{24}=S**	-669.698893	90.14	**5-Me-Chd^{24}=S**	-669.698901	90.12
4-Cl-C$_6$H$_4$SH	-1090.024048	**4-Cl-Chd^{24}=S**	-1089.985146	104.14			
4-CN-C$_6$H$_4$SH	-722.647190	**4-CN-Chd^{24}=S**	-722.606305	107.34			
4-F-C$_6$H$_4$SH	-729.658238	**4-F-Chd^{24}=S**	-729.619054	102.88			
4-NO$_2$-C$_6$H$_4$SH	-834.913570	**4-NO$_2$-Chd^{24}=S**	-834.872559	107.67			
4-CF$_3$-C$_6$H$_4$SH	-967.476486	**4-CF$_3$-Chd^{24}=S**	-967.437858	101.42			
4-NMe$_2$-C$_6$H$_4$SH	-764.380871	**4-NMe$_2$-Chd^{24}=S**	-764.343259	98.75			
4-OMe-C$_6$H$_4$SH	-744.937649	**4-OMe-Chd^{24}=S**	-744.901592	94.67			
4-Me-C$_6$H$_4$SH	-669.732837	**4-Me-Chd^{24}=S**	-669.696488	95.43			

[a] **Ph** = C_6H_5, **Me** = CH_3.

[b] The difference is the electronic energy difference, $E_{Chd} - E_{PhSH}$, as the thiophenol was always calculated to be more stable (to exhibit a more negative calculated electronic energy) than the corresponding cyclohexadiene-1-thione(s); 1 a.u. = ~2625.5 kJ/mol.

[c] The superscript numbers indicate the locations of the C=C double bonds in the cyclohexa-**2,4**-diene-1-thiones (*i.e.*, Chd^{24}=S). When the cyclohexa-2,4-diene-1-thione is more stable than the corresponding cyclohexa-2,5-diene-1-thione, the molecule is highlighted in red.

may lie simply in the position of the saturated carbon in the cyclohexa-2,5-diene-1-thiones and the cyclohexa-2,4-diene-1-thiones. Neither the former 6-substituted molecules were ever the most stable of the cyclohexa-2,5-diene-1-thiones, nor were the latter 4-substituted isomers in the cyclohexa-2,4-diene-1-thiones. Thus, if there were to be any reversals of stability for corresponding molecules, that reversal would most likely occur when the less stable molecule contained the substituent at the saturated carbon center compared to the more stable molecule with the substituent at the same position, but not at the saturated carbon. This is what is apparently occurring here.

Substituent effects on potential thione-enethiol tautomerisms

As seen in Table 1 for the substituted cyclohexa-2,4-diene-1-thiones and in Table 2 for the cyclohexa-2,5-diene-1-thiones, all of the substituted thiophenols were calculated to be more stable than any of the substituted cyclohexadienethiones. The differences in stability ranged from 59.40 kJ/mol for the more stable **3-NMe$_2$-C$_6$H$_4$SH** compared to the less stable **3-NMe$_2$-Chd^{25}=S**, to 138.64 kJ/mol for the more stable **2-OMe-C$_6$H$_4$SH** compared to the less stable **6-OMe-Chd^{24}=S**. A "benchmark" can be set with the differences in energies between **PhSH** and **Chd^{25}=S** and **Chd^{24}=S**, 99.67 kJ/mol and 88.89 kJ/mol, respectively. Any energy difference larger than these values indicates that the thioketone moiety will be less likely to be observable, while any energy difference smaller than these values indicates that the amount of the thioketone will be greater. Thus, substituents can and do directly affect the potential tautomerism between a substituted thiophenol and a substituted cyclohexadienethione, both positively and negatively. Could these effects be experimentally observable?

Table 2. Electronic energies of the thiophenols compared to the corresponding cyclohexa-2,5-diene-1-thiones

thiophenol[a]	electronic energy (eV)	cyclohexadiene-1-thione[c]	electronic energy (eV)	difference[b] (kJ/mol)
PhSH	-630.417139	**Chd^{25}=S**	-630.383283	88.89
2-Cl-C$_6$H$_4$SH	-1090.023319	**2-Cl-Chd^{25}=S**	-1089.985360	99.66
2-CN-C$_6$H$_4$SH	-722.647530	**2-CN-Chd^{25}=S**	-722.607295	105.64
2-F-C$_6$H$_4$SH	-729.658723	**2-F-Chd^{25}=S**	-729.620528	100.28
2-NO$_2$-C$_6$H$_4$SH	-834.907909	**2-NO$_2$-Chd^{25}=S**	-834.865862	110.39
2-CF$_3$-C$_6$H$_4$SH	-967.472348	**2-CF$_3$-Chd^{25}=S**	-967.434683	99.89
2-NMe$_2$-C$_6$H$_4$SH	-764.380781	**2-NMe$_2$-Chd^{25}=S**	-764.344199	96.05
2-OMe-C$_6$H$_4$SH	-744.938881	**2-OMe-Chd^{25}=S**	-744.900417	74.73
2-Me-C$_6$H$_4$SH	-669.733913	**2-Me-Chd^{25}=S**	-669.700552	87.59
3-Cl-C$_6$H$_4$SH	-1090.024303	**3-Cl-Chd^{25}=S**	-1089.992333	83.94
3-CN-C$_6$H$_4$SH	-722.646039	**3-CN-Chd^{25}=S**	-722.610613	93.01
3-F-C$_6$H$_4$SH	-729.658878	**3-F-Chd^{25}=S**	-729.627545	82.26
3-NO$_2$-C$_6$H$_4$SH	-834.912201	**3-NO$_2$-Chd^{25}=S**	-834.875928	95.23
3-CF$_3$-C$_6$H$_4$SH	-967.475642	**3-CF$_3$-Chd^{25}=S**	-967.441520	89.59
3-NMe$_2$-C$_6$H$_4$SH	-764.380885	**3-NMe$_2$-Chd^{25}=S**	-764.358261	59.40
3-OMe-C$_6$H$_4$SH	-744.937934	**3-OMe-Chd^{25}=S**	-744.913883	63.15
3-Me-C$_6$H$_4$SH	-669.733226	**3-Me-Chd^{25}=S**	-669.702844	79.77
4-Cl-C$_6$H$_4$SH	-1090.024048	**4-Cl-Chd^{25}=S**	-1089.986162	99.47
4-CN-C$_6$H$_4$SH	-722.647190	**4-CN-Chd^{25}=S**	-722.601381	120.27
4-F-C$_6$H$_4$SH	-729.658238	**4-F-Chd^{25}=S**	-729.616461	109.69
4-NO$_2$-C$_6$H$_4$SH	-834.913570	**4-NO$_2$-Chd^{25}=S**	-834.870718	112.51
4-CF$_3$-C$_6$H$_4$SH	-967.476486	**4-CF$_3$-Chd^{25}=S**	-967.439894	96.07
4-NMe$_2$-C$_6$H$_4$SH	-764.380871	**4-NMe$_2$-Chd^{25}=S**	-764.338105	112.28
4-OMe-C$_6$H$_4$SH	-744.937649	**4-OMe-Chd^{25}=S**	-744.893230	116.62
4-Me-C$_6$H$_4$SH	-669.732837	**4-Me-Chd^{25}=S**	-669.696749	94.75

[a] **Ph** = C_6H_5, **Me** = CH_3. [b] The difference is the electronic energy difference, $E_{Chd} - E_{PhSH}$, as the thiophenol was always found to be more stable (to exhibit a more negative calculated electronic energy) than the corresponding cyclohexadiene-1-thione; 1 a.u. = ~2625.5 kJ/mol. [c] The superscript numbers indicate the location of the C=C double bonds in the cyclohexa-2,5-diene-1-thiones (*i.e.*, **Chd^{25}**). When the cyclohexa-2,5-diene-1-thione is more stable than the corresponding cyclohexa-2,4-diene-1-thione, the molecule is highlighted in red.

The Boltzmann distribution equation provides a straightforward answer, even with the smallest of the energy differences — 59.40 kJ/mol with **3-NMe$_2$-C$_6$H$_4$SH** compared to **3-NMe$_2$-Chd^{25}=S** — NO! Apparently, the resonance energy in the benzenethiol vastly overcomes any potential equilibrium or tautomerism possibility, even with the most effective substituent. The potential for the experimental detection of a substituted-cyclohexadiene-1-thione is vanishingly small.

However, given the effect that **3-NMe$_2$-Chd^{25}=S** had on the calculated tautomeric energy difference, additional calculations were carried out on 2,3,4,5,6-penta(amino)-1-thiophenol (**1**) and 2,3,4,5,6-penta(amino)cyclohexa-2,5-diene-1-thione (**2**), illustrated in Fig.1. For the sake of computational time, simplicity, and the potentially extreme steric hindrance of five dimethylamino-groups on both of the six-membered rings, the unsubstituted amino-group was used in place of the dimethylamino-group. The energy difference between (**1**) and (**2**) was 54.4 kJ/mol, an insufficient change in the energy difference even with five substituents. Such a thiophenol would not undergo a tautomerization reaction based on results at this level of theory.

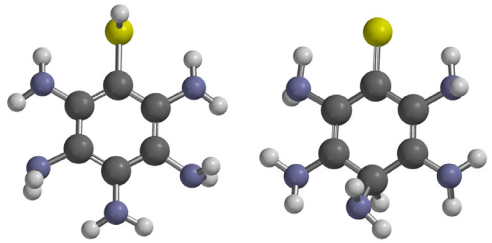
Conclusions

While the initial goal of this investigation was to examine the effect of electron withdrawing and electron donating substituents, the data indicated that such a simplistic thrust was not viable. In fact, the substitution position and the specific cyclohexadiene-1-thione that resulted from the thioketo-enethiol conversion (*i.e.*, the cyclohexa-2,4- *versus* the -2,5-dienethiones) were of exceptional importance in the analysis. No potential for the detection of a thione tautomer of the corresponding thiophenol could be found at the level of theory used in this investigation. However, both the energetic information described and discussed herein, and the structural information[1] in Part I of this investigation provide a broad range of material for potential research.

The aromatic character of the thiophenols involved in this investigation is obviously a major contributor to the stability of the thiophenols; destroying that aromatic character from arising by transferring the thiol hydrogen to any position on the ring is also the major contributor to the lack of stability of the cyclohexadienethiones. The conjugational stability (or cross-conjugational stability) of the cyclohexadienethiones simply cannot compete. That this result was expected even before the investigation began does not, however, minimize the results discovered. Now there is strong evidence to state that thiophenols will be very unlikely to engage in tautomerization, at least with single substituents. More work should be done with other, non-aromatic thiols that could engage in tautomerization, as well as work with the effect of hydrogen-bonding in the tautomerization reactions.

Supplementary Information

Supplementary information, including all output files, is available on request from the corresponding author, <rwz7001@humboldt.edu>.



(**1**) -907.215913 a.u. (**2**) -907.195204 a.u.

Figure 1. The calculated structures of 2,3,4,5,6-penta-amino-thiophenol (**1**), and 2,3,4,5,6-penta-amino-cyclohexa-2,5-diene-1-thione (**2**), with the calculated electronic energies (in atomic units, a.u.) also listed. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and blue, nitrogen.

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Artificial Intelligence Statement

The authors declare that no artificial intelligence program or "assistant" was used in any way during the course of this research or in the composition of this manuscript.

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