Journal of Undergraduate Chemistry Research, **2026**, 25 (4), 122

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

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Abstract

The structures of substituted 1-thiophenols and substituted cyclohexa-2,4- and -2,5-diene-1-thiones and the parent molecules have been determined theoretically using density functional computational methods at the ωB97X-D/6-311++G level of theory. The substituents chosen were the chloro-, cyano-, fluoro-, nitro-, trifluoromethyl-, dimethylamino-, methoxy-, and methyl-groups; only molecules each containing a single substituent were investigated. Few of the substituted molecules have been previously investigated either experimentally or computationally, but, as expected, the six-membered ring in all of the molecules was found to be planar. Only small differences from the average carbon-carbon bond lengths were noted in the rings regardless of the substituent; the substituents also optimized as expected.**

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Keywords: density functional theory, ωB97X-D, thione-enethiol tautomerism, keto-enol tautomerism, substituted thiophenols, substituted cyclohexa-2,4- and -2,5-dienethiones

Received: September 3, 2026 Accepted: September 7, 2026 Revision Received: October 12, 2026 Published: October 26, 2026

Introduction

Thiophenol (**PhSH**) is, theoretically, the enethiol analog of both cyclohexa-2,4- and -2,5-diene-1-thione (**Chd^{24}=S** and **Chd^{25}=S**, respectively). Thus, these diene-thione molecules could potentially undergo the sulfur-equivalent of a keto-enol interconversion, *i.e.*, a thioketo-enethiol tautomerism reaction, with **PhSH**. (The keto-enol tautomerism of phenol has been computationally investigated.[1])

Experimentally, **PhSH** is well-known, while **Chd^{24}=S** and **Chd^{25}=S** have only been isolated and characterized in low temperature matrices; their properties have been calculated at the B3LYP/aug-cc-pVTZ level of theory.[2] Further, **Chd^{25}=S** has been detected in the Galactic Center molecular cloud G+0.693-0.027, both demonstrating the presence of this new sulfur-bearing species in space and helping to determine the types of sulfur-containing molecules that may exist in space.[3] The excited state properties of **Chd^{24}=S** and **Chd^{25}=S** have also been calculated using comparative multi-reference configuration interaction methods.[4] In addition, **Chd^{24}=S** has been computationally predicted[5] to be an intermediate in one of the theoretical thermal decomposition channels of thiophenol. As part of a study of antioxidant activity, the properties of thiophenol and some substituted thiophenols have been computationally investigated.[6] (As a reference point, the calculated structures of the planar parent molecules are depicted in Fig. 1.)

The thioketo-enethiol equilibrium (or interconversion, if an equilibrium is not established) has been experimentally observed in some molecules. For example, in low temperature matrices, thiourea, containing a thione moiety and two amine groups, has been photochemically converted to the thiol tautomers (both *syn* and *anti*) through low-temperature hydrogen tunneling, with the experimental results confirmed through computational means.[7] Some mercapto-pyridines and -pyrimidines have also been shown to undergo a thioketo-enethiol equilibrium, ultimately producing a symmetrical disulfide, maintaining the aromatic character of the mercapto-pyridines and -pyrimidines.[8]

Other examples, including synthetic studies, are known.[9] However, experimental and computational evidence indicates that the unsubstituted cyclohexadienethiones are stable only in low temperature matrices,[2] and apparently have not been detected experimentally as the result of the thioketo-enethiol tautomerism. Still, questions remain as to whether an appropriately-substituted cyclohexa-2,4- or -2,5-diene-1-thione could exist in an equilibrium with the parent substituted-thiophenol, and if so, whether these systems might be able to be detected (perhaps through nuclear magnetic resonance spectroscopy?[10]). Also, if successful synthetic methods were developed for the cyclohexadienethiones, would an equilibrium with the analogous thiophenol be established, or would the molecules immediately undergo tautomerization and convert, below the range of detection, to the corresponding substituted-thiophenol at temperatures higher than the matrix-isolation regime?

To address these questions, herein is reported the density functional computational investigation, at the ωB97X-D/6-311++G** level of theory, of mono-substituted thiophenols and the corresponding mono-substituted cyclohexa-2,4- and -2,5-diene-1-thiones isolated as if in the gas phase. The substituents chosen were the chloro-, cyano-, fluoro-, nitro-, trifluoromethyl-, dimethylamino-, methoxy-, and methyl-groups were electron-do-

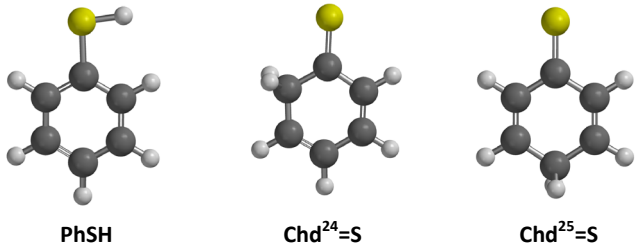


Figure 1. The calculated structures of thiophenol, PhSH, cyclohexa-2,4-diene-1-thione, Chd^{24}=S, and cyclohexa-2,5-diene-1-thione, Chd^{25}=S at the density functional ωB97X-D/6-311++G** level of theory. (The superscript numbers indicate the locations of the C=C double bonds ithe cyclohexadienethiones; atom numbering, for consistency, always begins with number one at the carbon attached to the sulfur and continues clockwise.)Light gray atoms, hydrogen; dark gray, carbon; and yellow, sulfur.

nating through resonance effects and the cyano-, nitro-, and trifluoromethyl-groups were electron-accepting through resonance effects.[10] In addition, most of these molecules, especially the mono-substituted cyclohexadienethiones, have not been experimentally (or computationally) investigated, making the calculated structures of the molecules of potential interest. While the structures and selected properties of these molecules are reported herein, an accompanying article, part II, of this investigation details the electronic energies of the thiophenols and the cyclohexa-2,4- and -2,5-diene-1-thiones and their substituted analogs and describes how these electronic energies may define the potentials for thioketo-to-enethiol interconversions in the molecules.[13]

Computational methods

All computations were carried out with the *Spartan* program packages[14] at the ωB97X-D/6-311++G** level of density functional theory.[15] This method is reported to perform well for covalent systems.[16] While no attempt was made to determine whether this density functional method was the most appropriate for this investigation, a density functional theory method was employed[2] in an earlier study of one of these sulfur-containing molecules, *i.e.*, using the B3LYP/aug-cc-pVTZ method, as was the more recent use of the B3LYP/6-311++G(d,p) method,[6] also lending support to the use of a density functional method in this investigation.

Initial trial geometries (ITGs) for all molecules were derived from the prototypical thiophenol planar hexagonal ring structure or the planar ring of the cyclohexa-2,4- or -2,5-diene-1-thione with the addition of the appropriate substituent for each isomer. While each molecule had multiple substitution sites — thiophenol and cyclohexa-2,5-diene-1-thione, three each, and cyclohexa-2,4-diene-1-thione, five — and each site (including the saturated carbon site in the cyclohexadiene-1-thiones) was investigated with each substituent, only a single substituent per molecule was employed. If the substituent could potentially exhibit rotational variability, *i.e.*, for the trifluoromethyl-, dimethylamino-, methoxy-, and methyl-groups, additional ITGs were employed to investigate the possibility of potential rotational isomers for these substituents. The rotation of the -SH moiety was also investigated in a similar fashion. However, only the most stable of the optimized structures for each of the molecules is reported herein. When higher energy rotational conformers were calculated to exist on the relevant potential energy surfaces, such conformers generally were only a few kJ/mol higher in energy than the reported structures, but were eliminated for the sake of simplicity. For each optimized structure, the vibrational frequencies were also calculated to ascertain that no imaginary frequencies existed, thus indicating that a true computational minimum had been located.

Results and Discussion

Selected calculated properties, excluding electronic energies, of thiophenol, the substituted thiophenols, cyclohexa-2,4- and 2,5-diene-1-thione, and the substituted cyclohexa-2,4- and -2,5-diene-1-thiones are discussed below. The electronic energies are discussed in the second part of this investigation.[13]

Thiophenol and substituted-thiophenols

The structure of thiophenol (**PhSH**), as calculated in this in-

Table 1. Calculated properties of thiophenol and the substituted thiophenols

Thiophenol[a]	dipole	molecular orbital energy (eV)[b]			selected bond distances (pm)[c]							
	moment (D)	HOMO	LUMO	difference	C^1–C^2	C^2–C^3	C^3–C^4	C^4–C^5	C^5–C^6	C^6–C^1	C^1–S	X–Y
PhSH	1.27	-8.15	1.01	9.16	139.4	138.8	139.0	139.0	138.8	139.4	178.0	
2-Cl-C_6H_4SH	1.55	-8.35	0.94	9.41	139.7	139.0	138.5	139.0	138.5	139.9	177.1	175.1^{CCl}
3-Cl-C_6H_4SH	0.70	-8.41	0.89	9.30	139.3	138.8	138.6	139.0	138.7	139.5	177.5	174.8^{CCl}
4-Cl-C_6H_4SH	1.40	-8.24	0.86	9.10	139.4	138.8	138.7	138.7	138.7	139.5	177.7	174.7^{CCl}
2-CN-C_6H_4SH	4.05	-8.68	-0.07	8.61	140.5	139.9	138.2	139.3	138.5	139.7	176.7	143.1$^{C\text{-}CN}$,115.3^{CN}
3-CN-C_6H_4SH	3.57	-8.74	-0.09	8.65	139.1	139.5	139.4	138.7	138.8	139.6	177.5	143.5$^{C\text{-}CN}$,115.1^{CN}
4-CN-C_6H_4SH	4.36	-8.69	-0.02	8.67	139.6	138.5	139.6	139.7	138.4	139.7	177.0	143.2$^{C\text{-}CN}$,115.2^{CN}
2-F-C_6H_4SH	1.51	-8.31	0.98	9.29	139.0	138.1	138.9	139.0	138.8	139.6	177.1	134.9^{CF}
3-F-C_6H_4SH	2.39	-8.39	0.94	9.33	139.4	138.2	138.3	138.9	138.9	139.5	177.5	134.4^{CF}
4-F-C_6H_4SH	0.97	-9.17	0.83	10.00	139.4	138.8	138.3	138.3	138.9	139.3	179.4	134.4^{CF}
2-NO_2-C_6H_4SH	5.53	-8.77	-0.93	7.84	140.2	139.3	138.0	139.2	138.2	140.4	176.8	146.7^{CN},121.6^{NO}
3-NO_2-C_6H_4SH	3.65	-8.80	-1.01	7.79	139.1	138.5	138.4	138.8	138.7	139.7	177.4	147.8^{CN},121.4^{NO}
4-NO_2-C_6H_4SH	4.52	-8.91	-0.94	7.97	139.7	138.5	138.6	138.7	138.4	139.7	177.2	147.1^{CH},121.5^{NO}
2-CF_3-C_6H_4SH	2.50	-8.55	0.50	9.05	140.4	139.3	138.5	138.8	138.5	139.7	177.6	150.6$^{C\text{-}CF}$,134.6^{CF}
3-CF_3-C_6H_4SH	1.88	-8.59	0.48	9.07	139.2	139.0	138.9	138.8	138.7	139.5	177.5	150.5$^{C\text{-}CF}$,134.4^{CF}
4-CF_3-C_6H_4SH	2.60	-8.65	0.52	9.17	139.5	138.6	139.0	139.0	138.5	139.6	177.3	150.1$^{C\text{-}CF}$,134.5^{CF}
2-NMe_2-C_6H_4SH	2.19	-7.80	1.01	8.81	140.7	139.4	138.9	138.8	138.8	139.3	177.4	142.6^{CN},145.6$^{N\text{-}Me}$
3-NMe_2-C_6H_4SH	2.29	-7.37	0.97	8.34	139.0	140.6	140.8	138.5	138.8	139.2	178.2	138.4^{CN},144.8$^{N\text{-}Me}$
4-NMe_2-C_6H_4SH	3.80	-7.46	0.91	8.37	139.1	138.6	140.7	140.8	138.5	139.2	179.0	138.3^{CN},144.8$^{N\text{-}Me}$
2-OMe-C_6H_4SH	2.82	-7.78	0.97	8.75	140.5	139.1	139.2	138.5	139.0	138.9	177.4	135.9^{CO},141.1$^{O\text{-}Me}$
3-OMe-C_6H_4SH	2.39	-8.04	1.00	9.04	138.6	139.7	139.1	139.4	138.3	139.9	177.7	135.6^{CO},141.1$^{O\text{-}Me}$
4-OMe-C_6H_4SH	2.58	-8.32	0.96	9.28	139.7	138.2	139.7	139.3	139.3	138.8	179.1	135.4^{CO},141.1$^{O\text{-}Me}$
2-Me-C_6H_4SH	0.82	-8.07	1.03	9.10	140.3	139.3	138.8	138.8	138.8	139.4	178.1	150.4$^{C\text{-}Me}$
3-Me-C_6H_4SH	1.27	-8.05	1.03	9.08	139.5	139.2	139.5	138.8	138.9	139.3	177.8	150.6$^{C\text{-}Me}$
4-Me-C_6H_4SH	1.81	-8.10	0.99	9.09	139.5	138.6	139.6	139.2	139.1	139.1	178.4	150.6$^{C\text{-}}$

[a]**Ph** = C_6H_5 and **Me** = CH_3. [b]HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital; the molecular orbital energy difference is $E_{LUMO} - E_{HOMO}$.
[c]The structural properties of the molecules investigated for their antioxidant activities,[6] which again corresponded well (generally within ± 0.4 pm) with those calculated herein, were reported for PhSH, 4-F-C_6H_4SH, 4-NO_2-C_6H_4SH, 2-CF_3-C_6H_4SH, 4-OMe-C_6H_4SH, and 4-Me-C_6H_4SH.

vestigation and depicted in Fig. 1, agreed well (generally within ± 0.4 pm) with the reports[2,5,6] of previous computational studies. Thiophenol has also been studied experimentally using microwave spectroscopy coupled with quantum chemical calculations to aid in the elucidation of the experimental results.[17] Both those experimental and calculated data compare well with the values reported herein, and the experimental data strongly suggested, unsurprisingly, that the molecule is planar, as was found computationally herein. The experimental microwave spectroscopic data[17] used a fixed mean C–C distance of 139.6 pm in the determination of the structure of **PhSH**; the mean C–C distance calculated herein was 139.1 pm, with a range from 138.8 pm to 139.4 pm. Selected calculated data for **PhSH**, and for the substituted thiophenols, are listed in Table 1.

While no experimental data exists on the structure of the chlorothiophenols, the structures of **2-Cl-C_6H_4SH**, **3-Cl-C_6H_4SH**, and **4-Cl-C_6H_4SH** (and the other possible polychlorothiophenol molecules from mono- through penta-chlorothiophenol) have been calculated.[18] Similar experimental microwave spectroscopic results, again coupled with and supported by quantum chemical calculations, for 4-fluoro-thiophenol (**4-F-C_6H_4SH**) have also been reported.[19] More recently, the physicochemical properties of some substituted thiophenols were investigated[6] at the B3LYP/6-311++G(d,p) level of theory as part of an investigation of antioxidant activity, specifically through analyses of the ionization potentials and electron affinities of the molecules. The structural properties of the molecules investigated for their antioxidant activities,[6] which again corresponded well (generally within ±0.4 pm) with those calculated herein, were reported for **PhSH**, **4-F-C_6H_4SH**, **4-NO_2-C_6H_4SH**, **2-CF_3-C_6H_4SH**, **4-OMe-C_6H_4SH**, and **4-Me-C_6H_4SH**.

In this investigation, the substituted thiophenols exhibited planar rings with no deviation from planarity for any of the atoms directly attached to the aromatic ring, as expected. The presence of substituents did little to change the C–C distances in the aromatic ring: In **PhSH**, the calculated C–C bond distances ranged from 138.8 pm to 139.4 pm. The longest calculated C–C bond distance for a substituted thiophenol was 140.8 pm in **3-** and **4-NMe_2-C_6H_4SH**, each with the electron-donating, by resonance effects, dimethylamino-group.[11] For the shortest calculated C–C

Table 2. Calculated properties of the parent and the substituted cyclohexa-2,4-diene-1-thiones

cyclohexadiene-1-thione[c]	dipole moment (D)	molecular orbital energies (eV)[a] HOMO	LUMO	difference	selected bond distances (pm)[b] C^1–C^2	C^2–C^3	C^3–C^4	C^4–C^5	C^5–C^6	C^6–C^1	C^1=S	X–Y
Chd^{24}=S	4.10	-8.08	-1.05	7.03	144.8	135.0	145.2	133.7	149.4	151.3	164.3	
2-Cl-Chd^{24}=S	4.64	-8.24	-1.30	6.94	145.9	135.1	144.8	133.6	149.0	151.6	163.6	173.8^{CCl}
3-Cl-Chd^{24}=S	3.78	-8.26	-1.25	7.01	144.5	135.0	145.3	133.5	149.2	151.3	164.4	173.6^{CCl}
4-Cl-Chd^{24}=S	2.05	-8.36	-1.34	7.02	145.0	134.7	145.2	133.2	149.5	151.2	164.0	174.6^{CCl}
5-Cl-Chd^{24}=S	3.18	-8.31	-1.32	6.99	144.6	135.0	145.0	133.5	149.4	151.6	164.1	173.9^{CCl}
6-Cl-Chd^{24}=S	3.70	-8.59	-1.71	6.88	144.9	134.8	145.4	133.6	149.2	151.8	163.2	183.3^{CCl}
2-CN-Chd^{24}=S	7.07	-8.55	-1.68	6.87	146.1	135.8	144.5	133.7	149.1	151.1	163.5	143.4$^{C\text{-}CN}$,115.1^{CN}
3-CN-Chd^{24}=S	4.29	-8.68	-1.94	6.74	144.9	135.5	146.0	133.4	149.4	151.1	163.8	143.4$^{C\text{-}CN}$,115.2^{CN}
4-CN-Chd^{24}=S	1.34	-8.62	-1.64	6.98	145.2	134.5	146.1	134.2	148.9	151.3	163.8	143.4$^{C\text{-}CN}$,115.1^{CN}
5-CN-Chd^{24}=S	3.62	-8.63	-1.82	6.81	145.1	134.8	144.9	134.2	150.4	151.3	163.8	142.9$^{C\text{-}CN}$,115.2^{CN}
6-CN-Chd^{24}=S	5.71	-8.71	-1.67	7.04	144.7	134.8	145.4	133.3	151.1	153.8	163.3	146.7$^{C\text{-}CN}$,114.9^{CN}
2-F-Chd^{24}=S	4.66	-8.29	-1.28	7.01	144.9	134.6	144.9	133.7	149.2	151.3	163.7	133.4^{CF}
3-F-Chd^{24}=S	4.12	-8.18	-1.07	7.11	144.0	134.6	144.7	133.5	149.4	151.6	164.6	133.4^{CF}
4-F-Chd^{24}=S	1.99	-8.35	-1.33	7.02	145.1	134.7	144.6	132.8	149.6	151.5	164.3	134.5^{CF}
5-F-Chd^{24}=S	3.20	-8.29	-1.23	7.06	144.5	135.2	144.9	133.2	148.5	151.6	164.2	133.7^{CF}
6-F-Chd^{24}=S	4.52	-8.40	-1.40	7.00	145.4	134.8	145.7	133.5	149.7	151.9	163.0	137.7^{CF}
2-NO_2-Chd^{24}=S	6.64	-8.65	-1.66	6.99	145.4	134.6	144.7	133.8	149.3	151.2	163.1	147.5^{CN},121.2^{NO}
3-NO_2-Chd^{24}=S	4.34	-8.79	-2.21	6.58	145.2	134.4	144.8	133.5	149.4	151.2	163.7	148.5^{CN},121.4^{NO}
4-NO_2-Chd^{24}=S	1.48	-8.67	-1.71	6.96	145.2	134.6	144.9	133.3	148.9	151.4	163.7	147.6^{CN},121.4^{NO}
5-NO_2-Chd^{24}=S	3.81	-8.73	-2.13	6.60	145.4	134.7	145.0	133.4	149.0	151.4	163.7	146.9^{CN},121.6^{NO}
6-NO_2-Chd^{24}=S	5.09	-8.86	-1.94	6.92	144.7	134.6	145.6	133.4	150.1	152.2	163.1	154.1^{CN},121.2^{NO}
2-CF_3-Chd^{24}=S	5.51	-8.39	-1.42	6.97	146.3	135.3	144.7	133.6	148.9	153.4	163.6	151.4$^{C\text{-}CF}$,134.2^{CF}
3-CF_3-Chd^{24}=S	3.37	-8.54	-1.58	6.96	145.2	134.6	145.6	133.4	149.4	151.2	163.9	150.7$^{C\text{-}CF}$,134.2^{CF}
4-CF_3-Chd^{24}=S	1.28	-8.48	-1.45	7.03	145.1	134.6	145.6	133.5	149.1	151.3	163.9	150.0$^{C\text{-}CF}$,134.3^{CF}
5-CF_3-Chd^{24}=S	3.07	-8.50	-1.55	6.95	145.1	134.7	145.3	133.5	149.9	151.3	163.8	150.0$^{C\text{-}CF}$,134.4^{CF}
6-CF_3-Chd^{24}=S	3.87	-8.57	-1.51	7.06	145.0	134.7	145.4	133.4	150.5	152.5	163.3	154.1$^{C\text{-}CF}$,133.9^{CF}
2-NMe_2-Chd^{24}=S	3.35	-7.45	-0.78	6.67	147.6	136.5	144.7	133.6	149.1	150.9	164.0	139.3^{CN},145.0$^{N\text{-}Me}$
3-NMe_2-Chd^{24}=S	7.93	-7.19	-0.28	6.91	141.7	138.3	146.6	133.4	148.8	151.1	166.3	135.8^{CN},145.4$^{N\text{-}Me}$
4-NMe_2-Chd^{24}=S	5.04	-7.78	-0.88	6.90	144.8	134.7	146.2	134.6	149.6	150.7	164.3	140.7^{CN},145.1$^{N\text{-}Me}$
5-NMe_2-Chd^{24}=S	7.35	-7.14	-0.52	6.62	142.2	136.4	142.4	137.0	150.6	151.7	165.5	136.1^{CN},145.2$^{N\text{-}Me}$
6-NMe_2-Chd^{24}=S	2.98	-7.85	-1.20	6.65	145.0	134.8	145.6	133.5	150.5	153.2	164.0	147.0^{CN},145.2$^{N\text{-}Me}$
2-OMe-Chd^{24}=S	4.20	-7.84	-0.85	6.99	146.8	135.8	145.0	133.5	149.1	151.2	163.6	134.2^{CO},140.9$^{O\text{-}Me}$
3-OMe-Chd^{24}=S	4.48	-7.77	-0.58	7.19	143.2	136.4	14,5.6	133.3	149.2	151.3	165.2	133.6^{CO},141.9$^{O\text{-}Me}$
4-OMe-Chd^{24}=S	4.66	-8.08	-0.99	7.09	144.9	134.6	145.5	134.0	149.8	151.1	164.3	135.4^{CO},141.1$^{O\text{-}Me}$
5-OMe-Chd^{24}=S	6.07	-7.84	-0.82	7.02	143.8	135.5	144.1	134.9	149.6	151.4	164.7	133.8^{CO},141.7$^{O\text{-}Me}$
6-OMe-Chd^{24}=S	4.12	-8.16	-1.22	6.94	145.1	134.9	145.3	133.5	150.5	153.2	163.6	139.8^{CO},141.4$^{O\text{-}Me}$
2-Me-Chd^{24}=S	3.72	-8.01	-0.97	7.04	146.0	135.6	144.9	133.6	148.9	151.3	164.6	150.0$^{C\text{-}Me}$
3-Me-Chd^{24}=S	4.72	-7.92	-0.85	7.07	144.3	135.5	146.0	133.5	149.3	151.2	164.7	149.8$^{C\text{-}Me}$
4-Me-Chd^{24}=S	4.48	-8.03	-0.97	7.06	144.7	134.9	145.9	133.9	149.4	151.0	164.4	150.2$^{C\text{-}Me}$
5-Me-Chd^{24}=S	4.53	-7.99	-0.96	7.03	144.4	135.1	144.8	134.1	150.0	151.2	164.4	149.7$^{C\text{-}Me}$
6-Me-Chd^{24}=S	3.91	-8.09	-1.03	7.06	144.7	135.0	145.0	133.7	149.7	151.6	164.3	155.0$^{C\text{-}Me}$

[a]HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital; the molecular orbital energy difference is $E_{LUMO} - E_{HOMO}$.
[b]For consistency, the carbon atom attached to the sulfur atom is always labelled as "1", regardless of priority(see Fig. 1).
[c]The superscript numbers in the molecule designations in this column indicate the locations of the C=C double bonds in the cyclohexa-**2,4**-diene-1-thiones (Chd^{24}=S).
[d]The superscripts in this column indicate the atoms involved in the bond, with the first superscript representing the "X" and the second superscript the "Y".
Mean bond lengths have been reported where appropriate.

bond distance, **2-NO_2-C_6H_4SH** exhibited a C–C bond distance of 138.0 pm; the nitro-group is considered to be electron-withdrawing by both field and resonance effects.[11] From these data, the electron-withdrawing groups by resonance generally appeared to shorten the C–C distances in the ring, while electron-donating groups by resonance lengthened the distances, although the differences were minimal.

The structures of the mono-substituted thiophenols and the mono-substituted cyclohexa-2,4- and -2,5-diene-1-thiones are depicted in Fig. 2–9, arranged by substituent: Fig. 2, chloro-; Fig. 3, cyano-; Fig. 4, fluoro-; Fig. 5, nitro-; Fig. 6, trifluoromethyl-; Fig. 7, dimethylamino-; Fig. 8, methoxy-; and Fig. 9, methyl-sub-

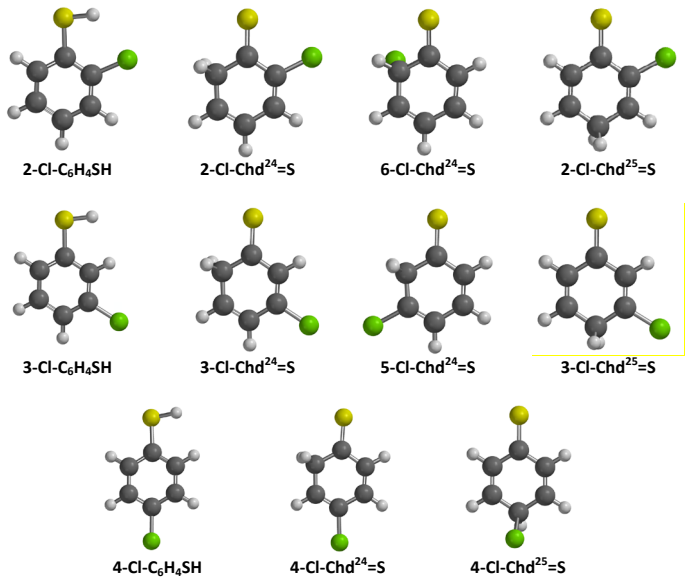


Figure 2. The chloro-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and green, chlorine. See Fig. 1 for the numbering convention used herein.

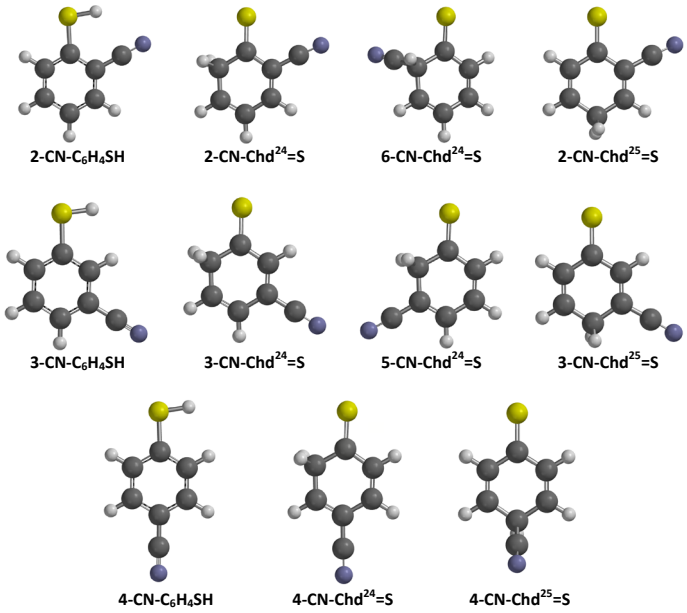


Figure 3. The cyano-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and blue, nitrogen. See Fig. 1 for the numbering convention used herein.

Table 3. Calculated properties of the parent and the substituted cyclohexa-2,5-diene-1-thiones

cyclohexadiene-1-thione[c]	dipole moment (D)	molecular orbital energies (eV)[a] HOMO	LUMO	difference	selected bond distances (pm)[b] C^1–C^2	C^2–C^3	C^3–C^4	C^4–C^5	C^5–C^6	C^6–C^1	C^1=S	X–Y
Chd^{25}=S	4.97	-8.07	-0.92	7.15	146.2	133.8	149.0	149.0	133.8	146.2	164.4	
2-Cl-Chd^{25}=S	5.37	-8.24	-1.16	7.08	147.4	133.8	148.8	148.6	133.6	149.4	163.7	174.0^{CCl}
3-Cl-Chd^{25}=S	4.16	-8.30	-1.18	7.12	146.0	133.6	149.0	149.2	133.6	146.3	164.3	174.0^{CCl}
4-Cl-Chd^{25}=S	2.70	-8.53	-1.60	6.93	146.3	133.6	146.3	146.3	133.6	146.3	163.8	182.7^{CCl}
2-CN-Chd^{25}=S	7.35	-8.55	-1.45	7.10	147.6	134.5	148.5	148.9	133.7	146.1	163.5	143.7$^{C\text{-}CN}$,115.1^{CN}
3-CN-Chd^{25}=S	4.19	-8.66	-1.75	6.91	146.3	134.3	149.9	148.9	133.7	146.0	164.1	143.2$^{C\text{-}CN}$,115.2^{CN}
4-CN-Chd^{25}=S	2.84	-8.65	-1.54	7.11	146.4	133.4	150.4	150.5	133.4	146.4	163.8	147.0$^{C\text{-}CN}$,114.9^{CN}
2-F-Chd^{25}=S	5.44	-8.29	-1.17	7.12	146.4	133.4	148.8	148.8	133.8	146.2	163.8	133.5^{CF}
3-F-Chd^{25}=S	4.38	-8.25	-1.06	7.19	145.5	133.3	148.2	149.3	133.6	146.6	164.3	133.8^{CF}
4-F-Chd^{25}=S	2.25	-8.56	-1.54	7.02	146.6	133.5	149.2	149.2	133.5	146.6	163.7	140.0^{CF}
2-NO_2-Chd^{25}=S	7.09	-8.67	-1.53	7.14	146.6	133.2	148.6	149.0	133.7	146.3	163.4	147.7^{CN},121.2^{NO}
3-NO_2-Chd^{25}=S	4.14	-8.78	-2.09	6.69	146.5	133.4	148.5	149.1	133.8	146.0	163.9	147.7^{CN},121.4^{NO}
4-NO_2-Chd^{25}=S	2.46	-8.76	-1.77	6.99	146.5	133.4	149.0	149.6	133.4	146.5	163.6	153.6^{CN},121.0^{NO}
2-CF_3-Chd^{25}=S	6.03	-8.38	-1.28	7.10	147.7	134.0	148.5	148.7	133.6	146.5	163.9	151.6$^{C\text{-}CF}$,134.2^{CF}
3-CF_3-Chd^{25}=S	3.64	-8.53	-1.46	7.07	146.5	133.6	149.4	148.9	133.7	145.9	164.0	150.4$^{C\text{-}CF}$,134.3^{CF}
4-CF_3-Chd^{25}=S	2.65	-8.51	-1.43	7.08	146.3	133.5	149.8	149.8	133.5	146.3	163.9	152.8$^{C\text{-}CF}$,134.1^{CF}
2-NMe_2-Chd^{25}=S	4.52	-7.81	-0.79	7.02	148.6	135.0	148.7	148.3	133.6	146.2	164.5	140.3^{CN},145.2$^{N\text{-}Me}$
3-NMe_2-Chd^{25}=S	8.01	-7.46	-0.31	7.15	143.3	136.8	150.3	149.2	133.2	146.6	165.8	136.6^{CN},145.2$^{N\text{-}Me}$
4-NMe_2-Chd^{25}=S	4.42	-8.17	-1.08	7.09	146.2	133.6	149.8	150.4	133.7	146.3	164.2	146.5^{CN},145.3$^{N\text{-}Me}$
2-OMe-Chd^{25}=S	5.28	-7.91	-0.81	7.10	147.8	134.6	149.0	148.5	133.7	146.0	164.0	134.4^{CO},140.8$^{O\text{-}Me}$
3-OMe-Chd^{25}=S	5.08	-7.86	-0.64	7.22	144.7	135.1	149.2	149.1	133.5	146.5	165.0	133.8^{CO},141.9$^{O\text{-}Me}$
4-OMe-Chd^{25}=S	2.72	-8.35	-1.30	7.05	146.4	133.6	150.0	150.1	133.6	146.4	164.0	141.6^{CO},141.5$^{O\text{-}Me}$
2-Me-Chd^{25}=S	4.63	-8.00	-0.85	7.15	147.5	134.4	148.8	148.6	133.7	146.2	164.7	150.1$^{C\text{-}Me}$
3-Me-Chd^{25}=S	5.42	-7.96	-0.82	7.14	145.7	134.3	149.7	149.0	133.6	146.2	164.6	149.8$^{C\text{-}Me}$
4-Me-Chd^{25}=S	5.01	-8.07	-0.94	7.13	146.1	133.8	149.4	149.4	133.8	146.1	164.3	154.2$^{C\text{-}Me}$

[a] HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital; the molecular orbital energy difference is $E_{LUMO} - E_{HOMO}$.
[b] For consistency, the carbon atom attached to the sulfur atom is always labelled as "1", regardless of priority(see Fig. 1).
[c] The superscript numbers in the molecule designations in this column indicate the locations of the C=C double bonds in the cyclohexa-**2,5**-diene-1-thiones (Chd^{25}=S).
[d] The superscripts in this column indicate the atoms involved in the bond, with the first superscript representing the "X" and the second superscript the "Y". Mean bond lengths have been reported where appropriate.

stituents. (The parent, unsubstituted molecules, **PhSH**, **Chd^{24}=S**, and **Chd^{25}=S**, are depicted in Fig. 1.) Note, in the figures, that the lowest energy conformation of the thiol group in each of the thiophenols, with the exceptions of **4-F-C$_6$H$_4$SH**, **4-NMe$_2$-C$_6$H$_4$SH**, **4-OMe-C$_6$H$_4$SH**, and **4-Me-C$_6$H$_4$SH**, has the S–H group lying in the plane of the ring. While the reasons for these exceptions are not understood, the energy differences between the S–H rotamers was small in each case in which the higher-energy perpendicular (or planar) S–H rotamer could be optimized (on the order of ~1.5 kJ/mol). In addition, for the nitro-thiophenols, the nitro-group lies in the plane of the ring for each of the three isomers, potentially allowing electronic interactions to occur between the aromatic ring and the nitro-group. A joint experimental and computational determination of the structure of nitrobenzene also shows the nitro-group to be in the plane of the ring.[20]

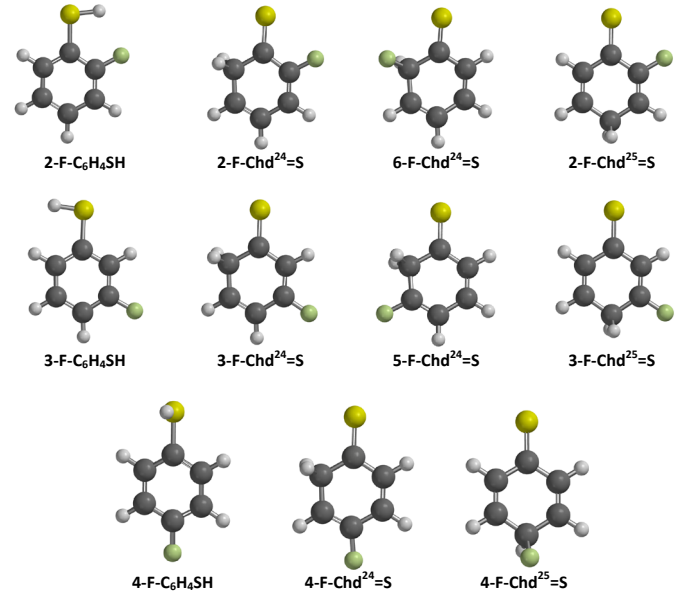


Figure 4. The fluoro-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and light yellow-green, fluorine. See Fig. 1 for the numbering convention used herein.

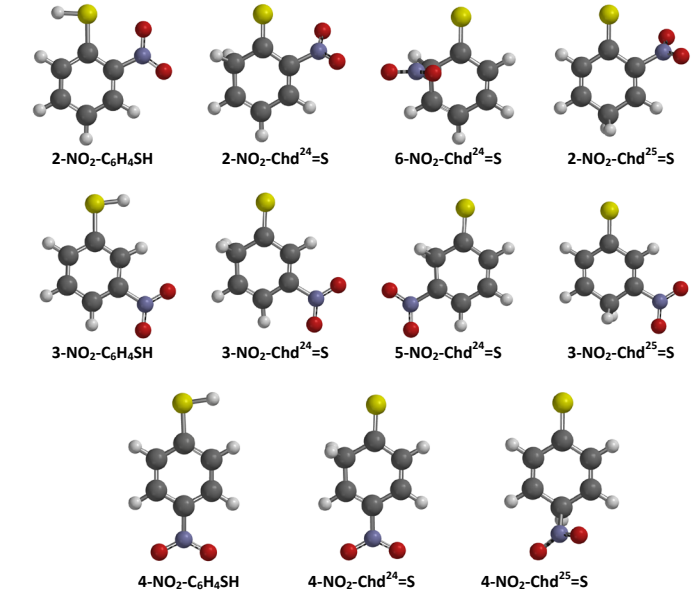


Figure 5. The nitro-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; blue, nitrogen; and red, oxygen. See Fig. 1 for the numbering convention used herein.

Molecular orbital energy differences were smallest for the nitro-substituted thiophenols, which also exhibited the most negative *lowest unoccupied* molecular orbital energies. Such molecular orbital energies indicated that these molecules — **2-**, **3-**, **4-CN-C$_6$H$_4$SH** and **2-**, **3-**, **4-NO$_2$-C$_6$H$_4$SH** — may be able to be readily reduced to anionic systems. For those molecules with the least negative *highest occupied* molecular orbital energies — **2-**, **3-**, **4-NMe$_2$-C$_6$H$_4$SH** and **2-OMe-C$_6$H$_4$SH** — indicated that these molecules may be the most readily oxidized to cationic systems. Such results may be of interest in synthetic studies if these molecules can be synthesized and may have applications in such reactions as electrophilic aromatic substitutions.[21]

Cyclohexa-2-4- and -2-5-diene-1-thione and substituted-cyclohexa-2-4- and -2-5-diene-1-thiones

The cyclohexa-2-4- and -2-5-cyclohexadiene-1-thiones and the mono-substituted analogs all optimized as planar ring systems

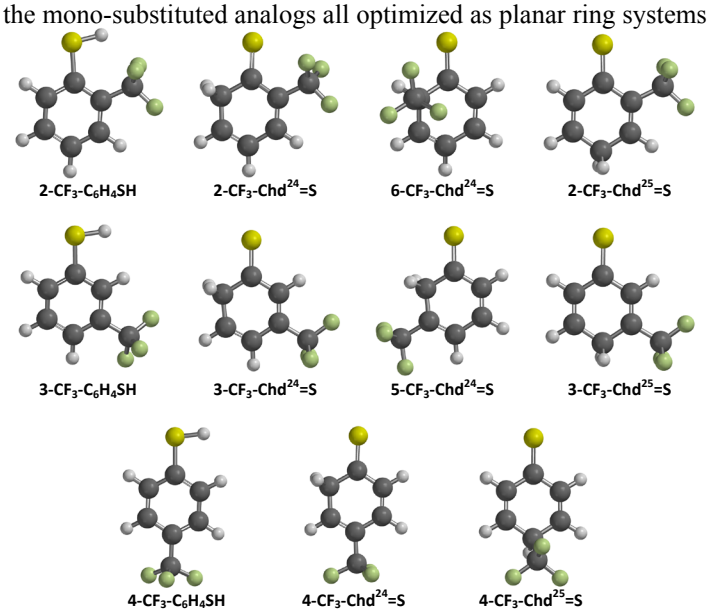


Figure 6. The trifluoromethyl-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and light yellow-green, fluorine. See Fig. 1 for the numbering convention used herein.

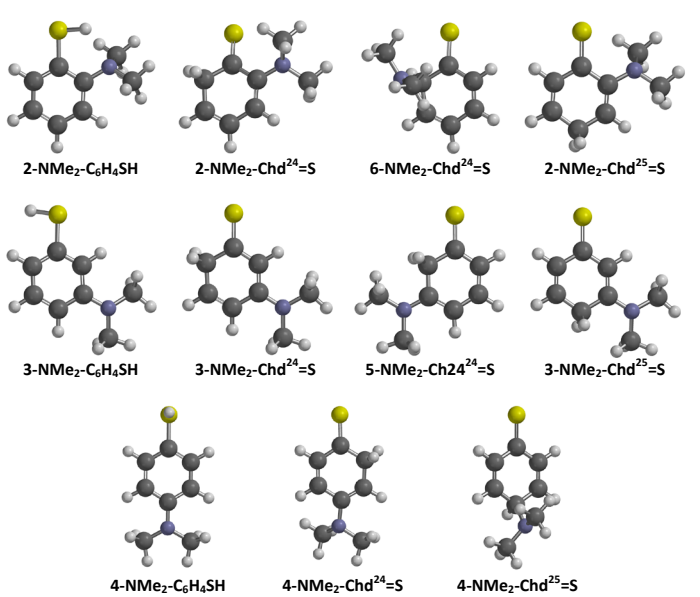


Figure 7. The dimethylamino-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and blue, nitrogen. See Fig. 1 for the numbering convention used herein.

exhibiting shorter C=C sp^2-sp^2 double bonds and longer C–C sp^2-sp^3 single bonds, as expected; relevant data are listed in Table 2 for the cyclohexa-2-4-cyclohexadiene-1-thiones (**Chd^{24}=S**) and in Table 3 for the cyclohexa-2-5-cyclohexadiene-1-thiones (**Chd^{25}=S**). The cyclohexa-2-4-cyclohexadiene-1-thiones form conjugated π-systems[22] with the thione and the carbon–carbon double bonds, while the cyclohexa-2-5-cyclohexadiene-1-thiones form cross-conjugated[23] π-systems with the thione moiety positioned between the two carbon-carbon double bonds.

As was found with the substituted thiophenols, the structures of the substituted cyclohexa-2,4- and -2,5-diene-1-thiones exhibit no unexpected bond distances; alternating C–C single bonds and C=C double bonds exhibit bond distances indicative of conjugated[22] and cross-conjugated[23] systems. The nitro-groups, with the exceptions of **2-NO$_2$-Chd^{24}=S** and **2-NO$_2$-Chd^{25}=S** (and of course, **6-NO$_2$-Chd^{24}=S** and **3-NO$_2$-Chd^{25}=S**, as these two molecules have

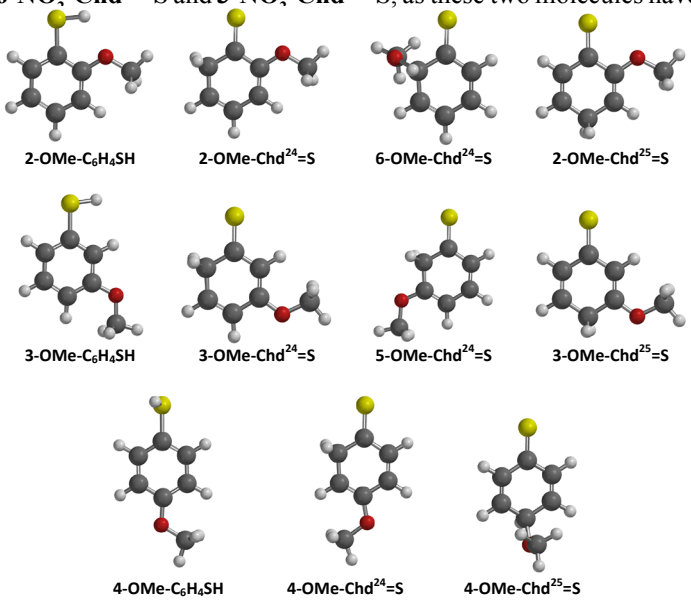


Figure 8. The methoxy-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; yellow, sulfur; and red, oxygen. See Fig. 1 for the numbering convention used herein.

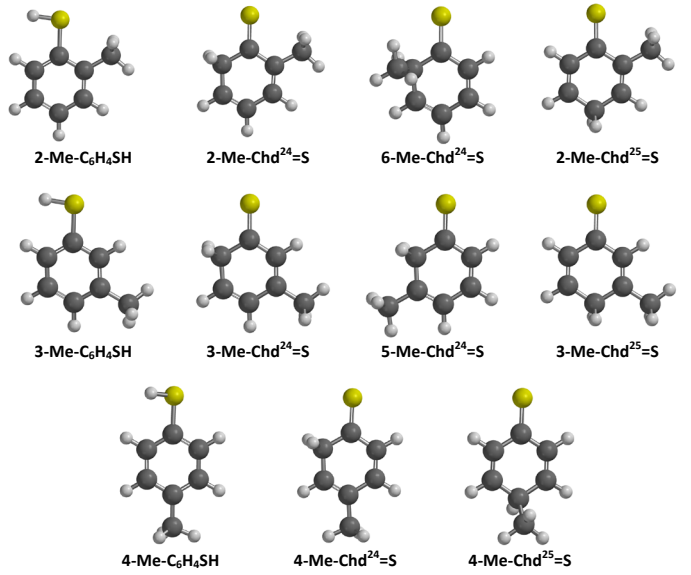


Figure 9. The methyl-substituted-thiophenols and -cyclohexadiene-1-thiones. Light gray atoms, hydrogen; dark gray, carbon; and yellow, sulfur. See Fig. 1 for the numbering convention used herein.

the nitro-group attached to the saturated carbon center) were again calculated to remain in the same plane as the cyclic C=C double bonds. In **2-NO$_2$-Chd^{24}=S** and **2-NO$_2$-Chd^{25}=S**, steric factors may prevent the nitro-groups from lying in the plane of the ring.

Conclusions

The structures of the thiophenol and cyclohexa-2,4- and -2,5-diene-1-thione parent molecules, and the analogs of these molecules each containing a single substituent, have been theoretically determined using the ωB97X-D/6-311++G** level of density functional theory. Beyond the unsubstituted molecules, either a single chloro-, cyano-, fluoro-, nitro-, trifluoromethyl-, dimethylamino-, methoxy-, or methyl-substituent was attached to each molecule in each possible position. These structures, as calculated, each exhibited a planar central six-membered ring with little change in bond lengths ascribable to the substituent, whether formally electron-donating or electron-withdrawing by field or resonance effects. However, few of these molecules have been the subject of either experimental or computational investigations; this study presents a broad body of information for other researchers.

The second part of this investigation[13] details the effect of the substituents on the potential for substituted-cyclohexa-2,4- and -2,5-diene-1-thiones to exist in a thioketo-enethiol equilibrium with the corresponding substituted-thiophenol.

Supplementary Information

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

Acknowledgements

The National Science Foundation's Course, Curriculum, and Laboratory Improvement Program, Adaptation and Implementation Section (NSF-9950344), is acknowledged for generous support for the initial purchase of computers and computational chemistry software, upon which all of this work is based. Matching funds and additional support were received at various times from the Department of Chemistry, the College of Natural Resources and Sciences, the Office for Research and Graduate Studies, the Office of the Vice-President for Academic Affairs, the Office of the President, and the Sponsored Programs Foundation of Humboldt State University (now California State Polytechnic University, Humboldt).

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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