This is much less than the observed difference of 23 cal deg^{-1} mol^{-1}. The remaining difference must result from variations between chloride–water and perchlorate–water interactions.

A comparison, Figure 9, of the concentration dependence of $\bar{C}_{p1}$ for solutions of rare earth chlorides with solutions of perchlorates shows a divergence up to about 2*m*. In the case of the perchlorates, there is a slight tendency for the heavier rare earths to exhibit an upturn. This tendency is much more pronounced for the chlorides. Although it is generally believed that the complexes formed in these concentrated solutions are probably outer sphere, it is known from the stoichiometric ratio of water to ions that these outer sphere complexes must interact with each other. The upturns are probably related to these interactions. It would therefore be very helpful if we knew the formation constants for these complexes and understood how they interact.

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NEW COMPOUND SECTION

Tetrachlorobenzenethiols

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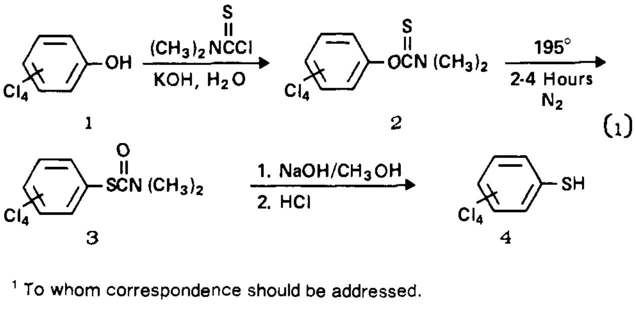
An unequivocal synthesis of the three isomeric tetrachlorobenzenethiols is described, and infrared and NMR spectral data for these compounds are presented.

Although the synthesis of the isomeric tetrachlorobenzenethiols from pentahalobenzenes has previously been reported (*1*, *3*), positive structure identification has only been established for 2,3,5,6-tetrachlorobenzenethiol. In this paper we would like to present an unequivocal synthesis of the three isomeric tetrachlorobenzenethiols and a summary of their infrared and NMR spectral properties.

The thiols were synthesized by the method of Newman and Karnes (*2*), which is outlined in Equation 1:



The phenols (**1**) were converted to the corresponding *O*-(tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamates (**2**, Table I) by reaction with dimethylthiocarbamoyl chloride in the presence of potassium hydroxide. The *O*-(tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamates were converted to the corresponding *S*-(tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamates (**3**) by thermal rearrangement in a nitrogen atmosphere at 195°. The progress of the rearrangement was conveniently followed by NMR, with the two singlets for the methyl groups of **2** disappearing and the broad singlet for the methyl groups of **3** appearing. The *S*-(tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamates were not isolated but were hydrolyzed directly with sodium hydroxide in refluxing methanol, followed by acidification with hydrochloric acid, to give the tetrachlorobenzenethiols (**4**, Table II). The infrared spectra of the three isomeric tetrachlorobenzenethiols are given in Figures 1–3 (deposited with the ACS Microfilm Depository Service).

The chemical shift (7.509 δ) of the aromatic proton of *O*-(2,3,4,6-tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamate and the chemical shift (7.507 δ) of the aromatic proton of *O*-(2,3,5,6-tetrachlorophenyl)-*N*,*N*-dimethylthiocarbamate are identical, indicating that these two protons are in identical environments and that the *N*,*N*-dimethylthiocarbamoyl group does not donate electron density to the aromatic ring system via resonance interaction. In the case of *O*-(2,3,4,5-tetrachlo-

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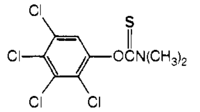
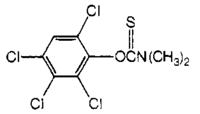
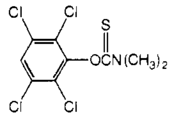
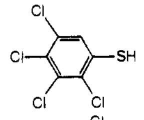
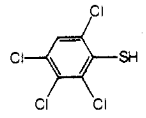
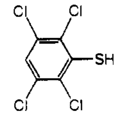
Table I. Isomeric O-(Tetrachlorophenyl)-N,N-dimethylthiocarbamates, 2[a]

Structure	Mp, °C	Yield, %	NMR data[b]	
			$N(CH_3)_2$	Arom H
	129–131	97	3.367 3.444	7.266
	157–158	90	3.401 3.469	7.509
	148–150	98	3.399 3.468	7.507

[a] All of the compounds gave elemental analyses within ±0.30 of the calculated values. [b] The NMR data are given in ppm (δ) downfield from TMS and are accurate to ±0.002 δ. The spectra were run with a 10% wt/vol solution of the compound in $CDCl_3$ and were recorded on a Varian XL-100 spectrometer equipped with a Digilab Fourier transform system.

Table II. Isomeric Tetrachlorobenzenethiols, 4

Structure	Mp, °C	Yield, %	NMR data[a]	
			SH	Arom H
	93–94	93	4.01	7.38
	112–113[b]	90	4.70	7.44
	105–107	82	4.90	7.37

[a] The NMR data are given in ppm (δ) downfield from TMS. The spectra were run with a 10% wt/vol solution of the thiol in $CDCl_3$ and were recorded on a Varian HA-100 spectrometer with TMS as an internal standard. [b] Literature (1), mp 101–102°. *Anal.* Calcd for $C_6H_2Cl_4S$: C, 29.06; H, 0.81; Cl, 57.20; S, 12.93. Found: C, 29.40; H, 0.96; Cl, 57.00; S, 13.10.

rophenyl)-*N,N*-dimethylthiocarbamate, the aromatic proton signal (7.266 δ) is shifted upfield (shielded) with respect to the other two isomers owing to inductive and anisotropic effects of the adjacent *N,N*-dimethylthiocarbamoyl group.

In contrast, the opposite situation exists for the tetrachlorobenzenethiols. The chemical shift (7.38 δ) of the aromatic proton of the 2,3,4,5-isomer and the chemical shift (7.37 δ) of the aromatic proton of the 2,3,5,6-isomer are virtually identical, indicating that these two protons are in nearly identical environments. Apparently, the thiol group donates electron density to the aromatic ring system via resonance interaction, causing an upfield shift of the aromatic proton signals in these two isomers in comparison to the aromatic proton signal (7.44 δ) of the 2,3,4,6-isomer.

Experimental

O-(Tetrachlorophenyl)-N,N-dimethylthiocarbamates (2). In a 1-l., 3-neck flask equipped with a mechanical stirrer, a thermometer, and an addition funnel were placed 14.2 grams of 85% potassium hydroxide, 250 ml of water, and 49.9 grams (0.215 mol) of the tetrachlorophenol (Aldrich Chemical Co., 98+% pure by gas chromatography). The reaction mixture was cooled to 10°, and a solution of 35.0 grams (0.283 mol) of dimethylthiocarbamoyl chloride in 80 ml of tetrahydrofuran was added dropwise, with stirring, at such a rate that the reaction temperature remained below 15°. After the addition was complete, the reaction mixture was made basic with sodium hydroxide solution, diluted with water, and filtered to remove the solid product. The solid was washed with water, air dried, and vacuum dried to give the *O*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamate as a white solid (Table I).

Tetrachlorobenzenethiols (4). In a 500-ml, single-neck flask fitted with a magnetic stirrer, a nitrogen inlet, and a calcium chloride drying tube were placed 59.60 grams (0.187 mol) of the *O*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamate. The material was melted and then heated, with stirring, at 195° for 2–4 hr. The flask was then allowed to cool to room temperature. The contents of the flask (the *S*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamate) were washed into a 1-l. flask with approximately 300 ml of methanol. To the methanol slurry, 14.5 grams (0.365 mol) of sodium hydroxide were added, and the reaction mixture was heated, under nitrogen, at reflux for 3 hr. The reaction mixture was allowed to cool and was then diluted to a volume of approximately 1 l. with water. The resulting solution was filtered and then acidified with dilute hydrochloric acid to precipitate the thiol. The resulting precipitate was filtered off, washed with water, air dried, vacuum dried, and recrystallized from absolute ethanol to give the tetrachlorobenzenethiol (**4**, Table II).

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Supplementary Material Available. Figures 1–3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JCED-75-443.