SPECTROSCOPIC ANALYSIS OF
THE PRODUCTS FROM THE REACTION OF
o-CHLOROBENZYLIDENEMALONONITRILE (CS)
AND 2-DIETHYLMINOETHYL MERCAPTAN (DEAEM)

by

Irwin Master
Ronald J. Piffath
Samuel Sass

June 1972
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SPECTROSCOPIC ANALYSIS OF THE PRODUCTS FROM THE REACTION OF O-CHLOROBNZYLDENEMALONONITRILE (CS) AND 2-DIETHYLAMINOETHYL MERCAPTAN (DEAEM)

This work was started in June 1965 and completed in March 1968.

Irwin Master
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EATR 4622

NA

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Ultraviolet, infrared, and Raman spectra have been determined for the products of the reaction of o-chlorobenzylidenemalononitrile (CS) and 2-diethylaminoethyl mercaptan (DEAEM). Structures for two of the products, CS(DEAEM)₂ and (CS)₂DEAEM, are given, and their spectral characteristics are discussed. Reactions were followed in the ultraviolet by observing the changes occurring in the spectrum with time. Possible reaction mechanisms are discussed for the formation of the product CS(DEAEM)₂. The order of addition to CS in the case of the product CS(DEAEM)₂, as observed by ultraviolet, is first, the addition to the double bond, and second, addition to the nitrile.

**KEYWORDS**

- o-Chlorobenzylidenemalononitrile
- Infrared spectra
- CS
- Raman spectra
- 2-Diethylaminoethyl mercaptan
- Benzylidenemalononitriles
- DEAEM
- NaCN
- Reaction products
- NaHSO₃
- (CS)₂DEAEM
- Pentanethiol
- Structure determination
- Ultraviolet spectra
SPECTROSCOPIC ANALYSIS OF THE PRODUCTS FROM THE REACTION OF o-CHLOROBENZYLIDENEMALONONITRILE (CS) AND 2-DIETHYLAMINOETHYL MERCAPTAN (DEAEM)

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Irwin Master
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Chemical Research Division

June 1972

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Task 1B562602AD1002

DEPARTMENT OF THE ARMY
EDGWOOD ARSENAL
Chemical Laboratory
Edgewood Arsenal, Maryland 21010
FOREWORD

This work was conducted under Task 1B562602AD1002, Analytical Studies. The experimental data are contained essentially in notebooks 7326, 7396, and 7706 and in dated and signed spectra. The experimental work was started in June 1965 and completed in March 1968.

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DIGEST

Ultraviolet, infrared, and Raman spectra have been determined for the products of the reaction of CS (o-chlorobenzylidenedimalononitrile) and 2-diethylaminoethyl mercaptan (DEAEM). Structures for two of the products, CS(DEAEM)$_2$ and (CS)$_2$DEAEM, are given, and their spectral characteristics are discussed. Reactions were followed in the ultraviolet by observing the changes occurring in the spectrum with time. Possible reaction mechanisms are discussed for the formation of the product CS(DEAEM)$_2$. The order of addition of DEAEM to CS in the case of the product CS(DEAEM)$_2$, as observed by ultraviolet, is first, the addition to the double bond, and second, addition to the nitrile.
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SPECTROSCOPIC ANALYSIS OF THE PRODUCTS FROM THE
REACTION OF \( \alpha \)-CHLOROBENZYLIDENEMALONONITRILE (CS)
AND 2-DIETHYLAMINOETHYL MERCAPTAN (DEAEM)

I. INTRODUCTION.

The addition of mercaptan to active double bonds has been the basis for an analytical method\(^1\) for acrylonitrile and \(\alpha,\beta\)-unsaturated carbonyl compounds. This addition is base catalyzed and results generally in the addition of one molecule of mercaptan, as in the case of acrylonitriles.\(^1\) However, Fesiak, Holmes, and Reesor\(^2\) reported the addition of more than one molecule of mercaptan in the base-catalyzed reaction with CS (\(\alpha\)-chlorobenzylidene-2-malononitrile) and related benzylidenemalononitriles. Holmes has reported on the spectral\(^3,4\) and polarographic\(^4\) analysis of some benzylidenemalononitriles and related compounds and on their rates of reaction with amines. Weir and Hyne have investigated the base-catalyzed dimerizations of several alkylidenemalononitriles\(^5\) and the base-catalyzed condensations of the systems \(\phi CH_2C=\text{C(CN)}_2\), \(\phi HC=\text{C(CN)}_2\), and \(\text{CH}_3\text{HC}C=\text{C(CN)}_2\).\(^6\) Proton nuclear magnetic resonance spectral evidence was presented in support of the suggested cyclic structures of the dimerization and condensation products. The infrared\(^7,8\) and Raman\(^8\) spectra for a large number of benzylidenemalononitriles and related compounds have also been determined. Fesiak, Holmes, and Reesor\(^9\) studied the reaction of mercaptan with benzylidenemalononitriles in the presence of piperidine and proposed a reaction scheme. Tarantino and Sass\(^1\) have made extensive studies on the reaction between benzylidenemalononitriles and 2-diethylaminoethyl mercaptan (DEAEM), using polarography to obtain reaction rates and reaction mechanisms. DEAEM was used because the molecule contains both the amine and mercaptan moieties and thus would simulate the protein-thiol present in vivo.


\(^{6}\)Weir, M. R. S., and Hyne, J. B. Some Base-Catalyzed Condensations of Systems of the Form \( R_1R_2C=\text{C(CN)}_2 \). Can. J. Chem. 43, 772 (1965).


Tarantino and Sass\textsuperscript{10} have reported that the products formed in the reaction of CS and DEAEM depended on the concentration of the reactants. They reported the following conclusions based on various reactant ratios: (1) in a 1:1 reaction mixture, DEAEM added to the $\alpha$-$\beta$-double bond of CS produced initially a monothioether (CS-DEAEM); (2) with CS in excess, the same product formed. After long standing (hours to days), a product formed in both reaction mixtures that had the empirical formula (CS)$_2$DEAEM. (3) With DEAEM in excess, a product formed having the empirical formula CS(DEAEM)$_2$, through addition of the DEAEM first to the $\alpha$-$\beta$-double bond and then to a nitrile of CS. This report describes the results of the ultraviolet (UV), infrared (IR), and Raman spectroscopic studies of the reaction products of CS and DEAEM, namely CS(DEAEM)$_2$ and (CS)$_2$DEAEM.

II. EXPERIMENTATION.

A. Reagents.

1. 2-Diethylaminocetyl mercaptan (DEAEM). Purification is given by Tarantino and Sass.\textsuperscript{10}

2. $\alpha$-Chlorobenzylidenemalononitrile (CS), 99%.

3. Methanol, reagent grade, Allied Chemical.

4. Sodium cyanide, reagent grade, Mallinckrodt.

5. Sodium bisulfite, reagent grade, J. T. Baker.

6. 1-Pentanethiol, reagent grade, Eastman Organic Chemicals.

7. Chloroform, infrared quality, Matheson Coleman and Bell.

B. Instrumentation.

1. Ultraviolet Spectra and Procedure.

   Ultraviolet spectra were determined on a Cary 14 recording spectrophotometer\textsuperscript{*} using 1.0-, 0.2-, and 0.1-cm silica cells. The UV spectra of specific compounds were run on approximately $5 \times 10^{-4}$ M methanol, chloroform, and methylene chloride solutions.

   Reactions were followed, in the UV, by adding the particular reagent to a solution of CS, placing the reaction solution as quickly as possible into a cell, and then scanning the spectrum several times over a period of time.

2. Infrared Spectra.

   Infrared spectra were determined on a Perkin-Elmer 521 grating spectrophotometer. Solid samples were run as potassium bromide pellets using infrared quality KBr (Harshaw Chemical Company, Cleveland, Ohio). Spectra also were recorded for chloroform solutions. Liquids were run as capillary films between KBr windows. Deuterium studies were performed with $D_2O$, 99.5 mol % min (Matheson Coleman and Bell). A few drops of $D_2O$ were added to a solution of the sample in chloroform. After shaking and phase separation, the chloroform layer was removed; then the infrared spectrum was run against a blank composed of chloroform containing a few drops of $D_2O$.

\textsuperscript{*}Cary Instruments, Monrovia, California.

Raman spectra were recorded on a Cary 81 spectrophotometer* equipped with a 50-mW Spectra-Physics model 125 CW He/Ne gas laser source,** using the 6328Å laser line for excitation and the 180° viewing technique.

The Raman solid sample holder rod has a concave conical face, and the sample is held in position by compaction. The sample holder rod, conical end down, was placed in a vial containing the powdered sample. The rod was tamped down gently several times into the powder, with rotation, causing the sample to be compacted into the conical hole. The excess sample was wiped off the outside surface of the rod; the rod was clamped in the solid sample holder and placed in the sample compartment of the instrument.

Raman spectra of liquid samples were obtained with a fused silica capillary cell 6 cm in length, 1-mm OD and 0.6-mm ID, with a window at one end and a capacity of 25 µl. The cell, while in its holder, was filled with a 0.25-ml hypodermic syringe with a 27-gage by 10-cm-long blunt hypodermic needle. A small drop of glycerol was applied to the open end of the cell to prevent evaporation of volatile samples. Another drop of glycerol was applied to the window end of the cell to improve optical efficiency. The sample holder and cell were then placed in the sample compartment of the spectrophotometer.

III. RESULTS AND DISCUSSION.

The ultraviolet, infrared, and Raman spectra of the products from the reaction of CS and DEAEM are reproduced in the appendix.

A. Ultraviolet Spectral Data.

Spectra were obtained on two isolated solid products from the reaction of CS with DEAEM. One was a product empirically representing 2 CS to 1 DEAEM, and the other 1 CS to 2 DEAEM. In addition, spectra were obtained for the reaction products as they formed in solution. As these products were not isolated from solution, their spectral data, λmax and εmax, were taken at maximum absorption and are given in table I. In addition to the spectra of the reaction products of CS with DEAEM, spectra also were obtained for the products of the reaction of CS with pentanethiol, sodium cyanide, and sodium bisulfite and the subsequent reaction of these latter products with DEAEM.

The mechanism for the formation of the product in the reaction of two moles of mercaptan with benzylideneamalononitriles has been postulated10 as follows:

*ibid.

**Spectra-Physics, Inc, Mountain View, California.
Table 1. UV Spectral Maxima of CS and CS Analogs and Their Reaction Products With Various Nucleophiles

<table>
<thead>
<tr>
<th>Original compound</th>
<th>Reactant</th>
<th>Spectral maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$</td>
</tr>
<tr>
<td>CS(DEAEM)$_2$</td>
<td></td>
<td>$nm$</td>
</tr>
<tr>
<td>(CS)$_2$DEAEM</td>
<td></td>
<td>292</td>
</tr>
<tr>
<td>CS</td>
<td>DEAEM in excess</td>
<td>299</td>
</tr>
<tr>
<td>CS</td>
<td>NaCN</td>
<td>299</td>
</tr>
<tr>
<td>CS·HCN</td>
<td>DEAEM</td>
<td>268</td>
</tr>
<tr>
<td>CS</td>
<td>NaHSO$_3$</td>
<td>299</td>
</tr>
<tr>
<td>CS·HSO$_3$</td>
<td>DEAEM</td>
<td>277</td>
</tr>
<tr>
<td>CS</td>
<td>C$<em>5$H$</em>{11}$SH(large excess)</td>
<td>299</td>
</tr>
<tr>
<td>CS·C$<em>2$H$</em>{11}$SH</td>
<td>DEAEM</td>
<td>298*</td>
</tr>
<tr>
<td>H$_2$C-CN</td>
<td>DEAEM</td>
<td>258</td>
</tr>
<tr>
<td>H$_2$C-CN</td>
<td>DEAEM</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Br-CN·C-CN</td>
<td>DEAEM</td>
<td>306</td>
</tr>
<tr>
<td>Cl·CH$_2$Br-CN·C-CN</td>
<td>DEAEM</td>
<td>312</td>
</tr>
<tr>
<td>Br·CH$_2$Br-CN·C-CN</td>
<td>DEAEM</td>
<td>311</td>
</tr>
</tbody>
</table>

*90% of CS reacted.
Table I. Continued

<table>
<thead>
<tr>
<th>Original compound</th>
<th>Reactant</th>
<th>Spectral maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$</td>
</tr>
<tr>
<td>$\text{O}_2\text{N--H}$</td>
<td>DEAEM</td>
<td>$305$</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>NaCN</td>
<td>$289$</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>DEAEM</td>
<td>$258$</td>
</tr>
</tbody>
</table>

The IR data, which will be discussed later, are consistent with the structure of the final product (I), and the rates of addition have been followed polarographically. The spectrum, in solution, of the final reaction product of CS with a five- or tenfold excess of DEAEM is the same as for I, namely CS(DEAEM)$_2$. Attempts to stop the reaction after the addition of one mole of DEAEM to CS were unsuccessful because the initial reaction is too fast, leading rapidly to an equilibrium mixture of mono- and diadduct.

One way to isolate or simulate the equivalent addition of the second mole of DEAEM to CS or an analog is to add the DEAEM after the elimination of the double bond. The double bond is absent or has been eliminated in a compound such as benzylmalononitrile and in the reaction products of CS with sodium cyanide, sodium bisulfite, and pentanethiol. Each of these compounds showed a UV spectrum like that of an isolated phenyl group (250- to 270-nm region) before reaction with DFAEM. But on the addition of DEAEM to the solution, an intense peak developed in the 280- to 290-nm region with an $\epsilon_{\text{max}}$ around 15,000. These experiments indicate that the order of addition, as observed by UV, is initially to the double bond, followed by a further addition to the nitrile. These results are in agreement with the mechanism given above. Addition of DEAEM only to the nitrile, however, would result in a nonconjugated product that would absorb weakly in the UV, having a structure:

\[
\begin{align*}
\text{H} & \quad \text{C=NH} \\
\text{C=CN} & \quad \text{SR}
\end{align*}
\]

The high intensity described above requires conjugation, and this is produced by the proton shift resulting in the structure:
α,β-Unsaturated nitriles have their main peak around 215 nm, \( \varepsilon_{\text{max}} 10,000 \). The large bathochromic shift in the CS-DEAEM products must be caused by the amine and sulfide groups. Spectra of enamines conjugated to nitriles have been reported with intense bands above 250 nm in compounds II \(^{13} \) and III. \(^{14,15} \)

\[
\begin{align*}
\text{II} & \quad \lambda_{\text{max}} 289 \text{ nm} \\
& \quad \varepsilon_{\text{max}} 17,500 \\
\text{III} & \quad \lambda_{\text{max}} 258 \text{ nm} \\
& \quad \varepsilon_{\text{max}} 19,000
\end{align*}
\]

The exact contribution of the sulfide group is not known, but increases in peak intensities occur in α,β-unsaturated sulfides. Allyl sulfide \(^{16} \) has a \( \lambda_{\text{max}} \) at 221 nm and \( \varepsilon_{\text{max}} \) of 2000, whereas methyl vinyl sulfide \(^{17} \) has a \( \lambda_{\text{max}} \) at 240 (sh) and 225 nm with \( \varepsilon_{\text{max}} \) of 10,000 and 15.850 respectively.

The variation in the \( \lambda_{\text{max}} \) of the different reaction products of CS with DEAEM must be a result of the influence of the remaining group, even if it is not conjugated to the chromophore.

These experiments also indicate that the double bond is not necessary for the reaction that produces the chromophore, but only the

\[
\begin{align*}
\text{H} & \quad \text{C} \equiv \text{N} \\
\text{C} \equiv \text{N}
\end{align*}
\]

group is required. The UV and IR spectra do not indicate the presence of ketenimine before the reaction, as postulated by Holmes \(^3 \) and Tarantino and Sass \(^{16} \) but the ketenimine might be induced by the presence of DEAEM before its reaction to form the addition product.

B. Infrared and Raman Spectral Data for CS(DEAEM)\(_2\) and (CS)\(_2\)DEAEM.

As stated previously, two of the products formed in the reaction of CS and DEAEM have the empirical formulas CS(DEAEM)\(_2\) and (CS)\(_2\)DEAEM. The product CS(DEAEM)\(_2\) has structure I and is similar to the product (IV)* formed in the reaction of benzylidemalononitrile with phenyl mercaptan, and the product (V)** formed in the reaction of CS with phenyl mercaptan, as done in these laboratories. Infrared and Raman data for product I are listed in table II, and infrared data for products IV and V are listed in table III.

Products I, IV, and V all show an intense vC\(\equiv\)N band between 2200 and 2180 cm\(^{-1}\) and a strong band around 1540 cm\(^{-1}\) resulting from the olefinic C=C stretch. The attachment of a sulfur atom to the olefinic double bond, together with the conjugation of the olefinic double bond with the nitrile, usually lowers and intensifies the vC=C band.\(^1\) Two or three bands are observed in the NH stretching region. For product I in chloroform, the vNH bands occur at 3423 and 3270 cm\(^{-1}\) and shift to 2550 and 2440 cm\(^{-1}\) on deuteration. The 2900 cm\(^{-1}\) region also changes on deuteration, and a band appears at ca 2200 cm\(^{-1}\), which indicates that a vNH band also occurs in the CH stretching region (2900 cm\(^{-1}\)) and overlaps the normal CH stretching bands. The band is probably caused by an N–H (of the NH\(_2\) group) bonded to the N in the amine moiety of the mercaptan. This band does not occur in IV and V because the phenyl mercaptan does not contain an amine moiety; thus, this type of hydrogen bonding is precluded. The 1637 cm\(^{-1}\) band also shifts on deuteration, indicating that this band is a result of the \(\delta\)NH\(_2\). The low nitrile stretching band observed for products I, IV, and V is caused by the presence of the unsaturated \(\beta\)-amino group and can be explained in terms of the enamionitrile structure (H\(_2\)N–C=C–C=\(\equiv\)N), which absorbs strongly at 2210 to 2185 cm\(^{-1}\) due to resonance (\(\geq\)N=CH=CH=C\(\equiv\)N).\(^1\)

*Anal for I as C\(_2\)\(_2\)H\(_3\)N\(_5\)S\(_3\)Cl. Calcd: C, 58.06; H, 7.8; N, 12.3; S, 14.1; Cl, 7.79. Found: C, 58.10; H, 7.6; N, 12.6; S, 14.4; Cl, 7.78.

**Anal for (CS)\(_2\)DEAEM as C\(_{26}\)H\(_{35}\)N\(_5\)S\(_2\)C\(_1\). Calcd: C, 61.2; H, 4.9; N, 13.7; S, 6.3; Cl, 13.9. Found: C, 60.6; H, 4.8; N, 14.0; S, 6.4; Cl, 13.9.

The IR and Raman spectral data for (CS)\(_2\)DEAEM are listed in table IV. No NH stretching band is observed in the normal area for (CS)\(_2\)DEAEM. A broad band occurs in the range 3300 to 2000 cm\(^{-1}\) in KBr and CHCl\(_3\), having its center at ca 2660 cm\(^{-1}\). A strong band occurs at 2198 cm\(^{-1}\) in CHCl\(_3\) (2195 cm\(^{-1}\) in KBr and 2192 cm\(^{-1}\) in the Raman) and is assigned to a vC\(\equiv\)N.

---

*Sample isolated by R. Proper, Organic Chemistry Department. Anal. 9912.
**Sample obtained from Suffield Experimental Station, Ralston, Alberta.
Table II. Infrared and Raman Data for CS(DEAEM)₂

<table>
<thead>
<tr>
<th>IR (KBr)</th>
<th>Raman (solid)</th>
<th>IR (CHCl₃)*</th>
<th>Assignment</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>3230 W</td>
<td>-</td>
<td>3423 VW</td>
<td>µNH₂</td>
</tr>
<tr>
<td>ca 3190 W</td>
<td>-</td>
<td>ca 3270 VW</td>
<td></td>
</tr>
<tr>
<td>ca 2900 B</td>
<td>-</td>
<td>ca 2900 B</td>
<td></td>
</tr>
<tr>
<td>ca 3068 VVW</td>
<td>3068 VVW</td>
<td>-</td>
<td>µCH aromatic</td>
</tr>
<tr>
<td>ca 3055 VVW</td>
<td>3059 VVW</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2973 MS</td>
<td>2964 VW</td>
<td>2976 S</td>
<td></td>
</tr>
<tr>
<td>2936 M</td>
<td>ca 2935 VVW</td>
<td>2938 M</td>
<td></td>
</tr>
<tr>
<td>2923 M</td>
<td>2923 W</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2876 W</td>
<td>2868 VVW</td>
<td>2879 VW</td>
<td></td>
</tr>
<tr>
<td>2831 MS</td>
<td>ca 2835 VVW</td>
<td>2823 M</td>
<td></td>
</tr>
<tr>
<td>2808 W</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2180 S</td>
<td>2176 S</td>
<td>2186 MS</td>
<td>µC=πN (conjugated)</td>
</tr>
<tr>
<td>ca 1668 W</td>
<td>-</td>
<td>ca 1637 W</td>
<td>δNH₂</td>
</tr>
<tr>
<td>1590 VVW</td>
<td>1591 M</td>
<td>1592 VVW</td>
<td></td>
</tr>
<tr>
<td>1571 VW</td>
<td>1574 W</td>
<td>ca 1571 sh</td>
<td>Aromatic ring C=C</td>
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<tr>
<td>1534 S</td>
<td>1538 MS</td>
<td>1540 S</td>
<td>µC=C olefinic (conjugated)</td>
</tr>
<tr>
<td>1469 sh</td>
<td>-</td>
<td>1467 M</td>
<td></td>
</tr>
<tr>
<td>1463 M</td>
<td>1459 W</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1450 W</td>
<td>1453 W</td>
<td>14.5 W</td>
<td></td>
</tr>
<tr>
<td>1438 W</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>1426 sh</td>
<td>1427 VW</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1406 W</td>
<td>1406 VVW</td>
<td>1407 VW</td>
<td></td>
</tr>
<tr>
<td>1380 M</td>
<td>1378 VW</td>
<td>1388 W</td>
<td></td>
</tr>
<tr>
<td>1374 W</td>
<td>-</td>
<td>1377 W</td>
<td></td>
</tr>
<tr>
<td>1288 M</td>
<td>1289 VW</td>
<td>1291 W</td>
<td>Vibrations of the mercaptan moiety</td>
</tr>
<tr>
<td>1194 M</td>
<td>1202 VW</td>
<td>1191 W</td>
<td></td>
</tr>
<tr>
<td>1180 sh</td>
<td>1181 MS</td>
<td>-</td>
<td>βCH ortho substitution</td>
</tr>
<tr>
<td>1030 M</td>
<td>1032 MS</td>
<td>1032 W</td>
<td>γCH ortho substitution</td>
</tr>
<tr>
<td>753 M</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>748 M</td>
<td>744 M</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>666 VVW</td>
<td>668 MS</td>
<td>-</td>
<td>µC-S</td>
</tr>
</tbody>
</table>

*The product CS(DEAEM)₂ appears to dissociate in CHCl₃ as bands appear at 2235 and 1592 cm⁻¹. The bands probably are caused by CS.
Because of its intensity and low position, the nitrile band must be conjugated and similar to the type found in CS(DEAEM)$_2$, namely a β-amino unsaturated nitrile. A very weak band occurs at ca 2253 cm$^{-1}$ in CHCl$_3$ and KBr and at 2249 cm$^{-1}$ (W) in the Raman. This band can be assigned to a saturated nitrile. A strong band occurs at ca 1545 cm$^{-1}$ (KBr), 1537 cm$^{-1}$ (Raman), which is assigned to a conjugated olefinic $\nu$C=C. A sulfur atom is probably attached to the C=C group, as this together with conjugation usually lowers and intensifies the $\nu$C=C.$^{18}$ The broad band observed between 3300 and 2000 cm$^{-1}$ did not change in intensity on dilution in CHCl$_3$, but the band center (2660 cm$^{-1}$) shifted to the 2000 cm$^{-1}$ area on deuteration. A change also occurred in the 1550 cm$^{-1}$ area on deuteration. This would indicate an NH group that is intramolecularly hydrogen bonded. The hydrogen bond is also quite strong judging from its low position, perhaps because of a N H $\ldots$ N hydrogen bond.

Table III. Infrared Data for Products IV and V in KBr

<table>
<thead>
<tr>
<th></th>
<th>IV</th>
<th>V</th>
<th>Assignment</th>
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<td>$cm^{-1}$</td>
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<tr>
<td>3465 W</td>
<td>3464 MS</td>
<td>$\nu$NH$_2$</td>
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<tr>
<td>3324 M</td>
<td>3362 S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3219 W</td>
<td>3187 VW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ca 3070 sh</td>
<td>ca 3073 sh</td>
<td>$\nu$CH aromatic</td>
<td></td>
</tr>
<tr>
<td>ca 3060 VW</td>
<td>3062 W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ca 3030 VVW</td>
<td>-</td>
<td></td>
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</tr>
<tr>
<td>ca 3020 sh</td>
<td>3019 VVV</td>
<td></td>
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<tr>
<td>2191 MS</td>
<td>2188 MS</td>
<td>$\delta$NH$_2$</td>
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</tr>
<tr>
<td>1622 S</td>
<td>1605 S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ca 1600 sh</td>
<td>-</td>
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</tr>
<tr>
<td>ca 1590 inf</td>
<td>1582 VW</td>
<td>Aromatic ring C=C</td>
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<td>1571 VW</td>
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<td>1473 W</td>
<td>1471 MS</td>
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<td>1439 MS</td>
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<td>1560 M</td>
<td>-</td>
<td>$\nu$C=C olefinic (conjugated)</td>
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<td>1545 sh</td>
<td>1544 S</td>
<td></td>
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<td>1306 M</td>
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<td>-</td>
<td>1054 sh</td>
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<tr>
<td>-</td>
<td>1048 W</td>
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<td></td>
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<td>1024 W</td>
<td>1026 M</td>
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<td>1002 W</td>
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<td>IR, KBr</td>
<td>IR, CHCl₃</td>
<td>Raman (solid)</td>
<td>Assignment</td>
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<tr>
<td>ca 3067 VW</td>
<td>ca 3064 VW</td>
<td>ca 3065 VW</td>
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<tr>
<td>ca 3020 VVW</td>
<td>ca 3025 VW</td>
<td>-</td>
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<td>ca 2978 M</td>
<td>ca 2980 M</td>
<td>ca 2976 VVW</td>
<td>ν₁_CH₂</td>
</tr>
<tr>
<td>ca 2940 W</td>
<td>ca 2941 W</td>
<td>ca 2935 VVW</td>
<td>ν₂_CH₃</td>
</tr>
<tr>
<td>ca 2880 VW</td>
<td>ca 2880 VW</td>
<td>-</td>
<td>ν₃_CH₂</td>
</tr>
<tr>
<td>ca 2832 VW</td>
<td>ca 2836 W</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ca 2660 B</td>
<td>ca 2660 B</td>
<td>-</td>
<td>νNH bonded; shifts to 2000 cm⁻¹ area on deuteration</td>
</tr>
<tr>
<td>ca 2250 VVW</td>
<td>ca 2253 VVW</td>
<td>2249 VVW</td>
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<td>2195 S</td>
<td>2198 S</td>
<td>2192 S</td>
<td>νC=N conjugated</td>
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<td>ca 1590 inf</td>
<td>ca 1591 sh</td>
<td>1596 W</td>
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<td>-</td>
<td>-</td>
<td>1588 W</td>
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</tr>
<tr>
<td>ca 1577 sh</td>
<td>1577 sh</td>
<td>1566 W</td>
<td></td>
</tr>
<tr>
<td>1545 S</td>
<td>1548 S</td>
<td>1537 M</td>
<td>δCH₃, CH₂</td>
</tr>
<tr>
<td>1474 M</td>
<td>1475 M</td>
<td>-</td>
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<tr>
<td>1450 sh</td>
<td>1450 M</td>
<td>1454 W</td>
<td>Aromatic ring C=C</td>
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<td>1440 M</td>
<td>1440 sh</td>
<td>-</td>
<td>δS–CH₂?</td>
</tr>
<tr>
<td>1409 W</td>
<td>1410 W</td>
<td>1406</td>
<td>δ₀_CH₃?</td>
</tr>
<tr>
<td>1378 W</td>
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<td>1376 VVW</td>
<td></td>
</tr>
<tr>
<td>1285 M</td>
<td>1284 M</td>
<td>1285 W</td>
<td>ωS–CH₂?</td>
</tr>
<tr>
<td>1190 W</td>
<td>1190 W</td>
<td>1188 M</td>
<td>βCH ortho-sub(s) (?)</td>
</tr>
<tr>
<td>-</td>
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<td>1039 M</td>
<td>βCH ortho-sub(s)</td>
</tr>
<tr>
<td>755 MS</td>
<td>-</td>
<td>-</td>
<td>γCH ortho-sub(s)</td>
</tr>
<tr>
<td>667 VW</td>
<td>-</td>
<td>667 M</td>
<td>νC–S</td>
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<tr>
<td>653 sh</td>
<td>-</td>
<td>654 M</td>
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</table>
The hydrochloride salt of (CS)$_2$DEAEM analyzed as C$_{26}$H$_{26}$N$_5$SCl$_3$ (Calcd: C, 57.10; H, 4.8; N, 12.8; S, 5.9; Cl, 19.4. Found: C, 57.17; H, 4.6; N, 12.8; S, 5.6; Cl, 19.3), showed bands at 2600 cm$^{-1}$ resulting from the υNH$^+$ and a band at ca 3130 cm$^{-1}$ (KBr) resulting from υNH. The υNH of the salt occurs higher than that of the free base (ca 2660 cm$^{-1}$), indicating a weaker hydrogen bond in the salt. A N–H...N hydrogen bond would be quite strong, thus its lower position in the free base. In the salt, the tertiary nitrogen of the amino-mercaptan moiety would become blocked on salt formation, preventing the formation of the intramolecular N–H...N hydrogen bond. This would result in a weaker hydrogen bond (possibly intermolecular) as indicated by the higher frequency for the υNH in the salt than in the free base. The υC≡N of the hydrochloride salt occurs at 2196 cm$^{-1}$ (MS) and 2250 cm$^{-1}$ (VVW) in KBr and at 2193 cm$^{-1}$ (S) and 2250 cm$^{-1}$ (W) in the Raman. The lower υC≡N band is probably caused by an enaminonitrile moiety, whereas the higher υC≡N band would indicate a saturated nitrile moiety based on its position and intensity. Kitson and Griffith have shown that saturated nitriles have their nitrile stretching band at 2250 ± 10 cm$^{-1}$. After the above data for both the free base and the hydrochloride salt of (CS)$_2$DEAEM were considered, structures VI and VII appear to best fit the infrared and Raman spectral data.

VI, Free Base of (CS)$_2$DEAEM

VII, HCl Salt of (CS)$_2$DEAEM

The UV bands for (CS)$_2$DEAEM are given in table I. The main peak at 285 nm, $\varepsilon_{\text{max}}$ 15,000, can be attributed to the enamine structure conjugated to the nitrile. The peaks at 277 and 270 nm may be only "shoulders" on the main peak caused by the isolated phenyl groups. The isolated chloro-phenyl group has $\lambda_{\text{max}}$ at 275, 268, and 263 nm. Using baseline techniques, the $\varepsilon_{\text{max}}$ at 277 and 270 nm were calculated to be about 500, which is what one would expect. The UV spectrum is consistent with the postulated structure (VI).

As stated previously, no indication of the ketenimine moiety, ≥C–C=N–, could be found in the ultraviolet or infrared spectra of the reaction products of CS and DEAEM. Ketenimines trisubstituted with aliphatic or aromatic groups absorb strongly at 2050 to 2000 cm$^{-1}$. No infrared band was ever observed in this region to indicate the presence of the ketenimine moiety. When CS and DEAEM were mixed together in various ratios in chloroform, and the reaction followed in the infrared, a band appeared at ca 2200 cm$^{-1}$ or slightly below, indicating the presence of the enaminonitrile moiety, H$_2$N C≡C–C≡N. No band was observed in the 2050 to 2000 cm$^{-1}$ region.


IV. CONCLUSIONS.

In the reaction of CS with diethylaminoethyl mercaptan (DEAEM), two products were formed having the empirical formulas \( \text{CS(DEAEM)}_2 \) and \( (\text{CS})_2\text{DEAEM} \). The former product formed with DEAEM in excess, and the latter product formed in a 1:1 reactant mixture after long standing. Structures have been postulated for both products based on their ultraviolet, infrared, and Raman spectra. The order of addition of DEAEM to CS in the case of the product \( \text{CS(DEAEM)}_2 \), as observed by ultraviolet, was first, addition to the double bond and second, addition to the nitrile.
LITERATURE CITED


Figure A-1. o-Chlorobenzylidene malononitrile (CS), 199 µg/ml, 0.1 cm, in Methanol

In figures A-1 through A-25:
- - - - absorbance 0 to 1
- - - - - - - absorbance 1 to 2
Figure A-2. 2-Diethylaminoethyl Mercaptan (DEAEM), 1500 µg/ml, 0.1 cm, in Methanol.

Figure A-3. CS + DEAEM in Excess, 19.7 µg/ml, 1.0 cm, in Methanol.
Figure A-4. CS(DEAEM)$_2$, 192 µg/ml, 0.1 cm, in Methanol

Figure A-5. (CS)$_2$DEAEM, 92 µg/ml, 0.2 cm, in Methanol
Figure A-6. CS + NaCN, 95.6 μg/ml, 1.0 cm, in Methanol-Water

Figure A-7. CS + NaCN + DEAEM, 99.4 μg/ml CS, 0.2 cm.
in Methanol-1% Acetic acid
Figure A-8. CS + NaHSO₃, 88.9 μg/ml CS, 0.2 cm, in Methanol-1% Acetic acid

Figure A-9. CS + NaHSO₃ + DEAEM, 88.9 μg/ml CS, 0.2 cm, in Methanol-1% Acetic acid
Figure A-10. CS + C_4H_11SH (1-Pentanethiol), 109.2 μg/ml CS, 0.2 cm, in Methanol

Figure A-11. CS + C_3H_11SH + DEAEM, 109.2 μg/ml CS, 0.2 cm, in Methanol

Appendix
Figure A-12. Benzylmalononitrile, 403 µg/ml, 1.0 cm, in Methanol

Figure A-13. Benzylmalononitrile + DEAEM, 18.5 µg/ml, 1.0 cm, in Methanol
Figure A-14. Malonitrile + DEAEM, 38.0 µg/ml, 0.2 cm. in Methanol

Figure A-15. β-(Bromomethyl)benzylidenemalononitrile, 266 µg/ml, 0.1 cm. in Methanol
Figure A-16. β-(Bromomethyl)benzylidenemalononitrile + DEAEM, 266 μg/ml, 0.1 cm, in Methanol

Figure A-17. β-(Bromomethyl)-4-Chlorobenzylidenemalononitrile, 282 μg/ml, 0.1 cm, in Methanol
Figure A-18. \(\beta\text-(Bromomethyl)-4\text-\text{Chlorobenzylidene}\text{malononitrile + DEAEM,}\)
282 \(\mu\text{g/ml}, 0.1\text{ cm, in Methanol}\)

Figure A-19. \(\beta\text-(Bromomethyl)-4\text-\text{Bromobenzylidene}\text{malononitrile,}\)
328 \(\mu\text{g/ml, 0.1 cm, in Methanol}\)
Figure A-20. β-(Bromomethyl)-4-Bromobenzylidenemalononitrile + DEAEM, 328 µg/ml, 0.1 cm, in Methanol

Figure A-21. 4-Nitrobenzylidenemalononitrile, 84.4 µg/ml, 0.2 cm, in Methanol
Figure A-22. 4-Nitrobenzylidenemalononitrile + DEAEM, 84.4 μg/ml, 0.2 cm, in Methanol

Figure A-23. β-Methylbenzylidenemalononitrile, 101.5 μg/ml, 0.2 cm, in Methanol
Figure A-24. β-Methylbenzylidenemalononitrile + NaCN,
90.8 µg/ml, 0.2 cm, in Methanol

Figure A-25. β-Methylbenzylidenemalononitrile + NaCN + DEAEM,
90.8 µg/ml, 0.2 cm, in Methanol-1% Acetic acid
Figure A-26. o-Chlorobenzylidemalononitrile (CS)

a. Infrared spectrum in KBr.
b. Raman spectrum, solid—sens. 1.7 x 10, S.W. 5 cm⁻¹, pen 0.5 sec, scan 1 cm⁻¹/sec.
Figure A-27. 2-Diethylaminoethyl Mercaptan (DEAEM)

a. Infrared spectrum—liquid, capillary film.
b. Infrared spectrum in chloroform, 0.265 M, 0.104-mm cell.
c. Raman spectrum, liquid—sens. 1.4 X 200, S.W. 5 cm⁻¹, pen 5 sec, scan 1 cm⁻¹/sec.

Appendix 35
Figure A-28. 2-Diethylaminoethyl Mercaptan Hydrochloride

a. Infrared spectrum in KBr.
b. Raman spectrum, solid—sens. 2 x 500, S.W. 5 cm⁻¹, pen 20 sec, scan 1 cm⁻¹/sec.
Figure A-29. Compound (IV)

a. Infrared spectrum in KBr.
b. Infrared spectrum in chloroform, 0.192-mm cell.
Figure A-31. Compound (I)–(CS(DeAEM))$_2$

a. Infrared spectrum in KBr.
b. Infrared spectrum in chloroform, 0.126 M, 0.154-mm cell.
Appendix 4

Figure A-31. Continued

Appendix
Figure A-32. Compound (VI) – (CS)$_2$DEAEM

a. Infrared spectrum in KBr.
b. Infrared spectrum in chloroform, 0.192-mm cell.
Figure A.33. Compound (VII) \((\text{CS})_2\), DEAEM+HCl Infrared Spectrum in KBr.