Studies of Thio Acids. IV.[1]   Dipole Moments of Methyl Thiostearate, Thiostearic Acid and Thioacetic Acid[*1]

By Yoshio Hirabayashi

The acyl-thiol structure, RCO·SH, of aliphatic thio acids previously studied, e. g., thioacetic acid[2,3] and thiostearic acid,[4] has been confirmed by infrared absorption and other physical data. Furthermore, their molecular structures have been elucidated by the bond-length measurements[5] of electron diffraction. However, no study of the dipole moments of thio acids and their esters has yet been reported.

In this paper, the dipole moments of thiostearic acid, methyl thiostearate, and thioacetic acid (each of which has the thiol form) are measured, and some discussion on their molecular structures will be presented.

Experimental[*2] and Results

Materials.—The samples used in the present investigation were prepared according to the procedure previously described and were carefully purified. They are :

Thiostearic acid :[4] m. p. 39.8—40.3°C ; neutralisation value 186.0 ; S, 10.60%.

Methyl thiostearate :[1] m. p. 50.3—50.8°C ; S, 10.14%.

Thioacetic acid[1] : b. p. 88.0—88.5°C ; S, 41.80%.

All the solvents, n-hexane, benzene, and dioxane, used for the measurement of dipole moments were purified according to the methods given in " Organic Solvents. "[6]

Measurement.—The densities, d, and the dielectric constants, ε, of solutions of various concentrations were measured with a picnometer and an apparatus which consists of a fixed-frequency (3 Mc.) crystal oscillator and a variable-frequency oscillator with a cell (ca. 45 pF in capacity) for the measurement of the dielectric constant. The tuning points of the variable-frequency oscillator with the fixed-frequency oscillator were determined by a Lissajous' figure on a cathode-ray oscilloscope. The frequency used for the measurements was 1 Mc., and all measurements were made at 30.0°C.

The specific solute polarization, $p_{2\infty}$, (at an infinite dilution) was calculated by the following

TABLE I. Dipole Moments of Methyl Thiostearate, Thiostearic Acid and Thioacetic Acid

Solvent	ε_∞	d_∞ (g./cc.)	a	b (g./cc.)	$p_{2\infty}$ (cc./g.)	$P_{2\infty}$ (cc.)	μ (D)
Methyl thiostearate							
H	1.9059	0.6737	0.586	0.180	0.4212	132.5	1.30
B	2.2628	0.8685	0.501	0.008	0.4331	136.2	1.37
D	2.2903	1.0228	0.532	−0.188	0.4325	136.1	1.37
Thiostearic acid							
H	1.9057	0.6735	1.17	0.181	0.5937	178.4	2.06
B	2.2630	0.8685	1.47	0.009	0.6170	185.4	2.14
D	2.2924	1.0229	1.82	−0.189	0.6385	191.9	2.21
Thioacetic acid							
H	1.8920	0.6756	4.07	0.217	1.4238	109.8	2.12
B	2.2615	0.8683	6.20	0.137	1.4666	113.1	2.16
D	2.1950	1.0220	8.66	0.058	1.7072	131.7	2.36

H : n-Hexane, B : Benzene, D : Dioxane

R'_D (cc.) : Methyl thiostearate, 98.3 ; Thiostearic acid, 93.4 ; Thioacetic acid, 19.1

[*1] Presented at the Symposium held under the auspices of the Japan Oil Chemists' Society and the Tokai Branch of the Chemical Society of Japan, Nagoya, November, 1960.

1) Part III of this series : Y. Hirabayashi and T. Mazume, This Bulletin, 38, 171 (1965).

2) N. Sheppard, Trans. Faraday Soc., 45, 693 (1949).

3) W. W. Crouch, J. Am. Chem. Soc., 74, 2926 (1952).

4) Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, 37, 1002 (1964).

5) W. Gordy, J. Chem. Phys., 14, 560 (1946).

[*2] All melting points and boiling points are uncorrected.

6) A. Weissberger and E. S. Proskauer, " Organic Solvents " (Techniques of Organic Chemistry VII), Inter-, science Publishers, New York (1955).

formula, derived from Halverstadt-Kumler's method :[7]

$$p_{2\infty}=\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\cdot\frac{1}{d_\infty}\left[1+\frac{3a}{(\varepsilon_\infty-1)(\varepsilon_\infty+2)}-\frac{b}{d_\infty}\right]$$

$$\varepsilon=\varepsilon_\infty+aw,\quad d=d_\infty+bw$$

where ε_∞ and d_∞ are extrapolated values, at the concentration of 0, for ε and d respectively. The values of a and b are the coefficients of the linear expansion of the dielectric constant and the density of the solution with respect to the weight fraction of the solute, w, respectively.

The dipole moment, μ, is then given by the following equation :

$$\mu=0.0128\ [(P_{2\infty}-R'_D)\cdot T]^{1/2}$$

where $P_{2\infty}=M_2\cdot p_{2\infty}$ is the solute molar polarization at an infinite dilution, M_2 is the molecular weight of the solute, and T is the absolute temperature. The sum of the electronic (P_E) and atomic (P_A) polarization was assumed to be equal to the molar refraction, R'_D, for the sodium D line calculated by adding the bond refractions[8] of the constituent atoms and bonds.
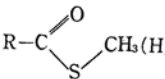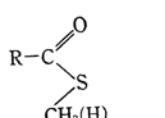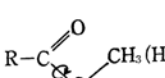
The results are shown in Table I.

Discussion

The molecular structures of methyl thiostearate, thiostearic acid, and thioacetic acid may now be discussed on the basis of the dipole moments obtained by the above measurements.

Three models for the spacial configurations of thio acids and their methyl esters have been selected and are shown as I, II, and III of Table II. In configurations I and II, the

TABLE II. RESULTANT MOMENTS OF THIO
ACID AND ITS ESTER

| Configuration | Resultant moment | |
	Ester	Acid
I R–C(=O)(S–CH₃(H))	1.1_8	1.6_4
II R–C(=O)(S)(CH₃(H))	3.5_8	2.9_5
III R–C(=O)(⊗S)(CH₃(H))	2.3_4	2.2_9

C–C, C=O, C–S, and S–C$_{CH_3}$ or S–H bonds are all coplanar, and the S–C$_{CH_3}$ or S–H bond is fixed on the same side as the C=O bond in

configuration I, while it is on the opposite side in configuration II. Configuration III corresponds to the case of free rotation about the C–S bond (the C–C(=O)(S) group being assumed to be coplanar). The moments calculated by using the bond moments derived from the textbook of Smyth[9] and from the following valence angles are given in Table II for each configuration : H–C, 0.4 ; H–S, 0.68 ; C–S, 0.9 ; C=O, 2.3 D ; the moment of $C_{17}H_{35}$–C or CH_3– C is assumed to be 0.4 D. The valence angles, $\angle C$–C=O $(=125°)$, $\angle C$–C–S $(=110°)$, and $\angle O=$ C–S$(=125°)$, are assumed to be the same as those of CH_3COSH,[10] and the valence angles, $\angle C$–S–C$_{CH_3}(=105°)$ and $\angle C$–S–H$(=100°)$, are set equal to the values of R–S–R[11] and R–SH[12] respectively.

Methyl Thiostearate.—The dipole moments (μ) measured in the solvents were 1.30 D(H), 1.37 D(B), and 1.37 D(D). The orientation polarization is not very large ; the observed values, therefore, depend relatively upon the assumed values of the P_E+P_A. When the sum of the P_E and P_A is assumed to be equal to the 1.05 R'_D or 1.10 R'_D, the observed values become as follows :

$$\mu'\ (\text{for } 1.05\ R'_D) : 1.21\ D(H)\ ;\ 1.28\ D(B)\ ;$$
$$1.28\ D(D)$$

$$\mu''\ (\text{for } 1.10\ R'_D) : 1.10\ D(H)\ ;\ 1.18\ D(B)\ ;$$
$$1.18\ D(D)$$

Although these data are still insufficient to enable us to discriminate whether the solvent effect is positive or negative, the order of this effect may be estimated by the following values, which are obtained when a plot of μ, μ', or μ'' versus $(\varepsilon_\infty-1)^2$, or $(\varepsilon_\infty-1)/(\varepsilon_\infty+2)$ is extrapolated to $\varepsilon_\infty=1$:

For $(\varepsilon_\infty-1)^2$: $\mu_e=1.22$ D, $\mu'_e=1.13$ D,
$$\mu''_e=1.02\ D$$

For $(\varepsilon_\infty-1)/(\varepsilon_\infty+2)$: $\mu_{e'}=1.06$ D,
$$\mu'_{e'}=0.95\ D,\ \mu''_{e'}=0.83\ D$$

As a result, the dipole moment of this molecule is found to be 1.1 ± 0.3 D.

On the other hand, since the induction effect is left out of consideration for the calculated values given in Table II, the moments induced at each bond by the C=O dipole should, of course, be taken into consideration. While

7) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

8) A. I. Vogel, W. C. Cresswell, G. H. Jeffery and J. Liecester, *J. Chem. Soc.*, **1952**, 514.

9) C. P. Smyth, "Dielectric Behavior and Structure," McGraw Hill, New York (1955), p. 224.

10) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950) ; W. Gordy, *J. Chem. Phys.*, **14**, 560 (1946).

11) L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2407 (1936).

12) R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955).

the quantitative values of these induced moments are not known at present, the calculated values given in Table II may not be grossly in error (possibly to within 20%) for the moments corresponding to configuration I since an intramolecular compensation of this effect seems to occur; the values for configurations II and III, on the other hand, will become somewhat larger than the values given in Table II, since no intramolecular compensation of this effect seems to occur with them.

On the basis of the above consideration of the observed and the calculated values, configuration I seems to be the most probable of the three possible configurations for methyl thiostearate. Furthermore, though it is still unknown whether or not the S–C$_{CH_3}$ bond is fixed in the C$\begin{smallmatrix}O\\\\S\end{smallmatrix}$ plane in configuration I, it seems reasonable, from a consideration of its resonance structures and of its electrostatic potential, to assume that the S–C$_{CH_3}$ bond is fixed in the C$\begin{smallmatrix}O\\\\S\end{smallmatrix}$ plane as in configuration I.

Thiostearic Acid and Thioacetic Acid.—Thiostearic acid is considerably stable and remains almost unchanged in solvents at room temperature. On the other hand, an authentic sample of thioacetic acid is rapidly changed with a decrease in its sulfur content. Even when much care was taken in the treatment of the latter, some change in the quality was inevitable.

The dipole moments measured were 2.06 D (H), 2.14 D (B), and 2.21 D (D) for thiostearic acid, and 2.12 D (H), 2.16 D (B), and 2.36 D (D) for thioacetic acid. In carboxylic acids, the dipole moments measured in benzene or hexane have sometimes been different from those in dioxane, and it is known that two molecules of carboxylic acids associate in benzene or hexane by hydrogen bonds.[13] For thio acids, however, the presence of only a slight solvent effect in the observed dipole moments suggests that such association by hydrogen bonds does not take place to any appreciable extent.

In the case of thio acids, for which the orientation polarizations are large, the decreases in the observed values are only 0.1 D for thiostearic acid, and about 0.02 D for thioacetic acid, when the sum of P_E and P_A is assumed to be equal to 1.10 R'_D. Furthermore, by a treatment similar to that used in the case of methyl thiostearate, the following values are obtained:

For thiostearic acid: $\mu_e = 1.95$ D; $\mu_{e'} = 1.82$ D

For thioacetic acid: $\mu_e = 1.96$ D; $\mu_{e'} = 1.82$ D

The dipole moments are thus found to be 1.9 ± 0.2 D for both molecules.

The obtained values are somewhat too large and too small respectively for the C$\begin{smallmatrix}O\\\\S-H\end{smallmatrix}$ group to be planar with configurations I and II.

As for the structures of thio acids, either of the following four cases appears reasonable judging from their observed values: A. configuration I; B. a configuration in which the S–H bond is located at a certain angle to the C$\begin{smallmatrix}O\\\\S\end{smallmatrix}$ plane from configuration I;[*3] C. the coexistence of configurations I and II; D. configuration III. However, the free rotation (D) is not probable in view of its electrostatic potential and in view of the fact that its resonance structures are similar to those of the ester. The other three structures (A, B, C) may be suitable; it seems difficult at present to determine which of the three is the most reasonable.

Summary

The dipole moments of methyl thiostearate, thiostearic acid, and thioacetic acid have been measured in n-hexane, benzene, and dioxane solutions at 30°C. The values obtained are; methyl thiostearate, 1.3$_0$ D (n-hexane), 1.3$_7$ D (benzene), 1.3$_7$ D (dioxane); thiostearic acid, 2.0$_6$ D (n-hexane), 2.1$_4$ D (benzene), 2.2$_1$D (dioxane); thioacetic acid, 2.1$_2$ D (n-hexane), 2.1$_6$ D (benzene), 2.3$_6$ D (dioxane). On the basis of the above results, a planar configuration similar to the cis configuration of carboxylic ester is considered to be the most probable structure of methyl thiostearate; three probable alternative configurations have been suggested for the structure of thio acid.

13) G. Briegreb, *Z. physik. Chem.* (B), **10**, 205 (1930).

*3 For the configuration in which the S–H bond is fixed on the plane perpendicular to the C$\begin{smallmatrix}O\\\\S\end{smallmatrix}$ plane, the resultant moment should be 2.3$_9$D.