[Contribution from the Research Department, Standard Oil Company (Indiana)]

Monomolecular Films of 1,3,4-Thiadiazole-2,5-bis-α-mercaptostearic and -mercaptolauric Acids

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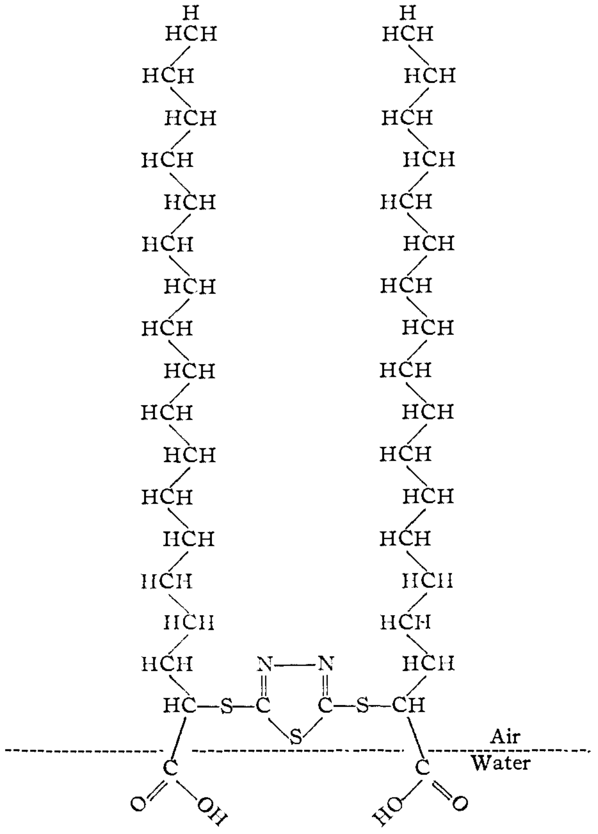
Pressure–area isotherms for two new compounds, 1,3,4-thiadiazole-2,5-bis-α-mercaptostearic acid and -mercaptolauric acid, indicate close packing of the thiadiazole ring between the vertically oriented fatty acid chains. The two isotherms almost coincide in the intermediate pressure range. The film of the thiadiazole mercaptostearic acid, like that of stearic acid, collapses abruptly at 42 dynes per cm.; that of the thiadiazole mercaptolauric acid collapses gradually near 23 dynes per cm. The behavior of an equimolar mixture of thiadiazole mercaptostearic acid and stearic acid further supports the suggested orientation.

Introduction

Film balance measurements of monomolecular films give pressure–area isotherms that are sensitive to small differences in molecular geometry, orientation and packing.[1,2] They can be used to characterize most organic compounds with twelve or more carbon atoms and a polar group. Monolayer properties provide a sound basis for interpreting the physical behavior of compounds and mixtures.

Individual compounds of simple structure have been extensively studied, but little has been done with complex materials of known structure, alone or in mixtures. The present study helps bridge this gap by dealing with two complex molecules: 1,3,4-thiadiazole-2,5-bis-α-mercaptostearic acid (TS) and 1,3,4-thiadiazole-2,5-bis-α-mercaptolauric acid (TL). Film properties of these new compounds have been compared with those of stearic acid, a simple fatty acid structure. An equimolar mixture of TS and stearic acid was also studied to determine the compatibility of the two structures in adsorbed films and to elucidate further the structure and orientation of TS.



1,3,4-Thiadiazole-2,5-bis-α-mercaptostearic acid

Fig. 1.—Molecular orientation.

Experimental

The complex molecules were synthesized by condensing a substituted diazole with appropriate bromo acids. 2,5-Dimercapto-1,3,4-thiadiazole was prepared according to the method of Busch[3] and crystallized from ethanol under nitrogen to give colorless crystals melting at 168° with decomposition. Purchased α-bromostearic and α-bromolauric acids were used as received.

1,3,4-Thiadiazole-2,5-bis-α-mercaptostearic acid (TS) was prepared by treating a suspension of 45 g. (0.3 mole) of 2,5-dimercapto-1,3,4-thiadiazole in 300 ml. of ethanol with a solution of 33.6 g. (0.6 mole) of potassium hydroxide in 150 ml. of ethanol. In succession were added, at 20°, 218.1 g. (0.6 mole) of α-bromostearic acid and 33.6 g. of potassium hydroxide in 200 ml. of ethanol. The mixture was refluxed 3 hours, cooled to 20°, acidified with 65 ml. of concentrated hydrochloric acid, filtered, and evaporated to dryness under vacuum. The residue was extracted with 1000 ml. of warm *n*-heptane. The solution was filtered and evaporated to dryness under vacuum. Finally, the residue was crystallized twice from a 50:50 mixture of hexane and benzene. The product, 206.7 g. (96%), was a light-buff solid melting at 81°.

Anal. Calcd. for $C_{38}H_{70}O_4S_3N_2$: S, 13.46; N, 3.92; neut. equiv., 357. Found: S, 13.22; N, 3.86; neut. equiv., 353.

1,3,4-Thiadiazole-2,5-bis-α-mercaptolauric acid (TL) was similarly obtained from α-bromolauric acid and dimercaptothiadiazole in 91% yield. It was crystallized from *n*-heptane as a white solid melting at 86–87°.

Anal. Calcd. for $C_{26}H_{46}O_4S_3N_2$: S, 17.64; N, 5.13; neut. equiv., 273. Found: S, 17.42; N, 4.93; neut. equiv., 264.

Stearic acid of m.p. 69.61° was specially prepared by the Research Division of Armour and Company. The volatile solvent used in the monolayer experiments was C.P. benzene distilled twice to remove non-volatile impurities; film experiments on the redistilled benzene alone showed that remaining impurities were negligible. The deionized water used had a conductivity of about 0.5 micromho and a *p*H of 6.

The apparatus is a Cenco Hydrophil Balance of the Langmuir–Adam–Harkins type, modified to improve the reliability of the measurements.[4] Before each experiment, the trough, barriers, float and platinum foils were thoroughly cleaned and coated with high melting paraffin wax dissolved in hot *n*-hexane. The coated trough was filled with deionized water to about 2.5 mm. above the edge. After the film was spread, ten minutes were allowed for the solvent to evaporate. Surface pressures were read as the

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[1] N. K. Adam, "The Physics and Chemistry of Surfaces," Third Edition, Oxford University Press, Oxford, England, 1941.

[2] W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952.

[3] M. Busch, *Ber.*, **27**, 2518 (1894).

[4] H. E. Ries, Jr., and H. D. Cook, *J. Colloid Sci.*, **9**, 535 (1954).

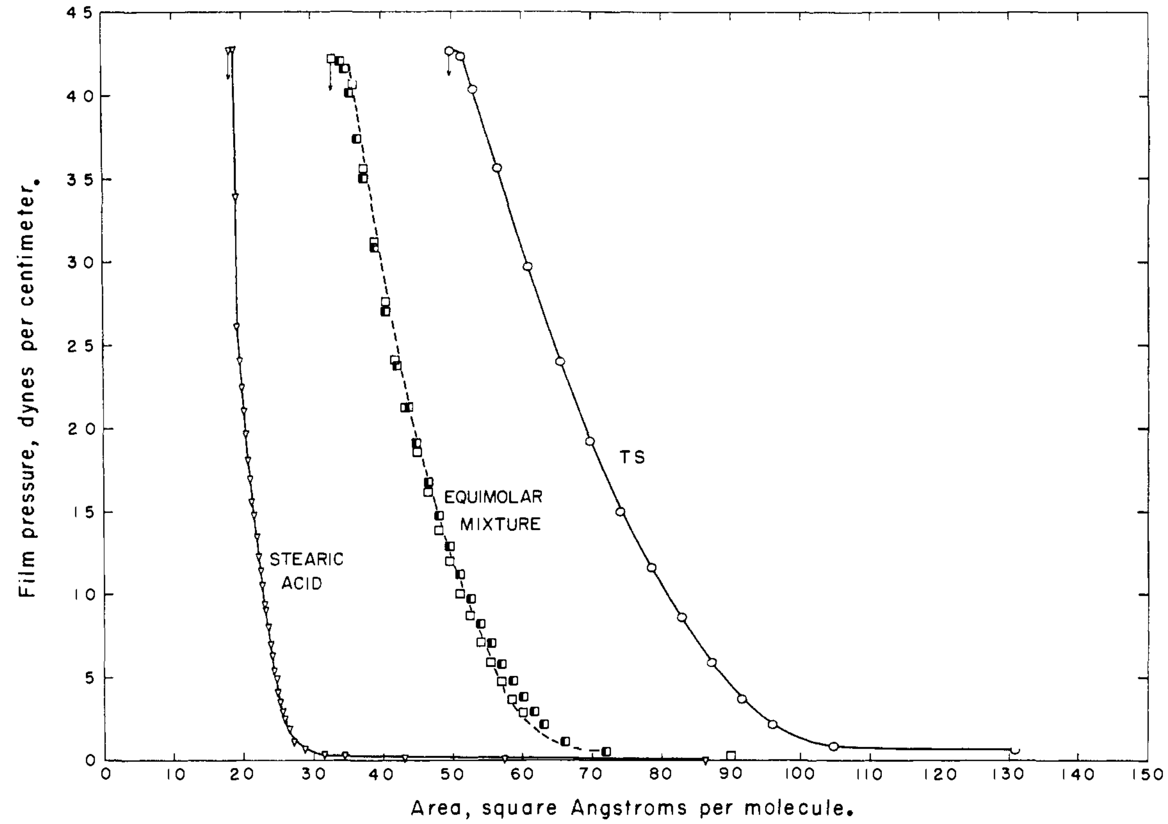

Fig. 2.—Pressure–area isotherms for stearic acid, TS, and an equimolar mixture. For the mixture, the points are experimental and the curve is the calculated average.

film area was reduced in small decrements until the film collapsed. Intervals of two minutes were usually allowed between readings; one-minute intervals were used for extremely small decrements. A pressure–area isotherm was plotted from these data. During a single experiment the temperature was held to 0.2°, although different experiments were conducted at 21 to 24°; in this range, temperature had little effect on the films studied.

Discussion

Repeated determinations of the isotherms agreed closely. Rigid or solid-like films usually collapse abruptly; mobile or liquid-like films gradually approach a constant pressure. Although abrupt collapse is a "weakest link" phenomenon and should be difficult to duplicate, good reproducibility was obtained.

Monolayer Properties.—Area, compressibility and collapse pressure are shown in Table I. Areas were obtained by extrapolating to zero pressure the steepest part of the isotherm, usually near collapse. Film compressibility is the change in area with pressure

$$\frac{a_0 - a_1}{a_0 f_1}$$

where a_0 is the extrapolated area at zero pressure and a_1 is a smaller area at pressure f_1. Collapse pressure is the maximum film pressure. These data reflect the long chain fatty acid structure of the three compounds studied. TS, shown schematically in Fig. 1, consists of two stearic acid structures connected by a thiadiazole ring. In TL, the two hydrocarbon chains are much shorter. Stearic acid, with the simplest long chain structure, has an area that agrees well with earlier measurements[1,2,5] and with calculated values.[6,7]

TABLE I

MONOLAYER PROPERTIES

	Area,[a] Å.^{2} per molecule	Compressibility, $(a_0 - a_1)/a_0f_1$	Collapse pressure, dynes per cm.
Stearic acid	20.3	0.0019	42
1,3,4-Thiadiazole-2,5-bis-α-mercaptostearic acid (TS)	83	.0090	42
Equimolar mixture: stearic acid and TS	51	.0075	41
1,3,4-Thiadiazole-2,5-bis-α-mercaptolauric acid (TL)	91	.0120	23

[a] By extrapolation to zero pressure.

1,3,4-Thiadiazole-2,5-bis-α-mercaptostearic Acid (TS).—The isotherms plotted in Fig. 2 show the strong film properties of TS. Extrapolation to zero pressure gives an area of 83 Å.^{2} per molecule, which is consistent with the orientation in Fig. 1. At collapse, the observed 52 Å.^{2} per molecule seems reasonable from studies of molecular models and represents the tightest packing possible in the monolayer.

The isotherms for TS and for stearic acid are

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(5) E. F. Porter, THIS JOURNAL, **59**, 1883 (1937).

(6) J. J. Kipling and A. D. Norris, *J. Colloid Sci.*, **8**, 547 (1953).

(7) M. J. Vold, *ibid.*, **7**, 196 (1952).

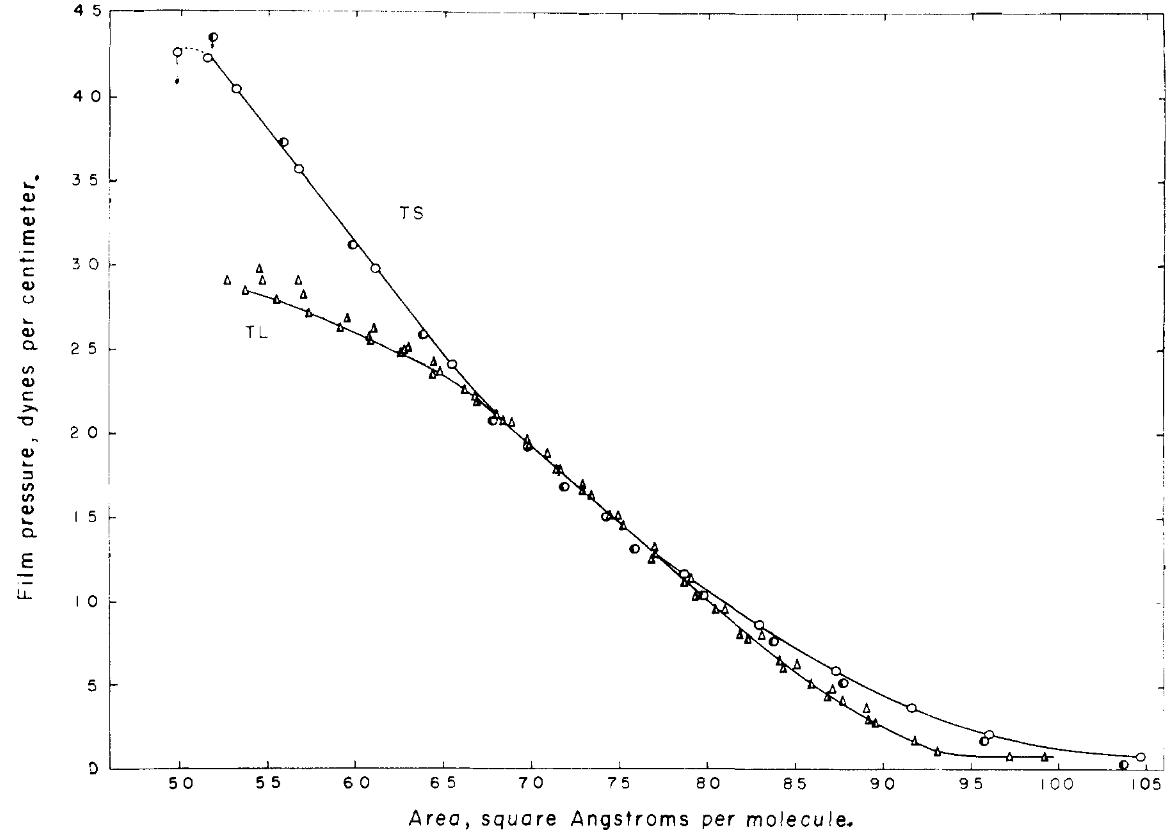

Fig. 3.—Pressure–area isotherms for TS and TL.

generally similar. The collapse pressure for TS, 42 dynes per cm., is identical to that for stearic acid and is unexpectedly high for a bulky structure. At high pressures, both films are extremely rigid, as shown by observations with lycopodium powder.[4] The stearic acid structures in the TS molecule must dominate at the final stage of compression. Possibly the dimercaptothiadiazole group functions as part of a large polar aggregate and increases the polarity at the end of the molecule. However, the much greater compressibility of the TS film shows that, before the final stage of compression, TS does not pack nearly so tightly as stearic acid.

The isotherms for an equimolar mixture of TS and stearic acid, included in Fig. 2, are strikingly similar to those for the two components. An extrapolated area per average molecule, 51 Å.^{2}, is almost identical to the calculated average for the components, 52 Å.^{2} The calculated average isotherm based on simple additivity agrees well with the experimental isotherm. Furthermore, the collapse pressure of the mixture, 41 dynes per cm., is within experimental error of that for the components. The film compressibility, 0.0075, lies between those for the components but is closer to that for TS. The compatibility of the two compounds is further supported by the smooth contour of the isotherm for the mixture.

An equimolar mixture of stearic acid and tri-*p*-cresyl phosphate gave entirely different results[4]—an isotherm displaced far to the right of the calculated average and composed of two distinct contours representing the independent behavior of the two components.

1,3,4-Thiadiazole-2,5-bis-α-mercaptolauric Acid (TL).—Lauric acid gives a weaker film than does stearic acid.[2] The thiadiazole derivatives also show the effect of chain length. The extrapolated area of TL, 91 Å.^{2}, is greater than that for TS. Films of TL are more compressible, and examination with lycopodium powder indicates much less rigidity. As shown in Fig. 3, collapse of the TL film occurs at a pressure about half that for TS and takes place gradually, whereas the TS film collapses abruptly. Weaker cohesion of the shorter chains is clearly indicated. Nevertheless, isotherms for the two compounds almost coincide at intermediate pressures of 10 to 20 dynes per cm. In this region, the packing properties are similar and the longer stearic acid chains do not pack tightly enough to exhibit greater cohesive forces.

Conclusion

In a sense, the TS molecule is an intramolecular mixture of two long straight chains and a ring structure. In the monolayer, large portions of the chains are free to cohere intramolecularly, but they probably pack better with chains of neighboring molecules. If, at collapse, the two stearic acid structures, each having an area of 18.5 Å.^{2}, are subtracted from the 52 Å.^{2} for TS, only 15 Å.^{2} remains for the thiadiazole ring. This small area reflects the compactness of the structure at the polar end of the molecule.

In the mixture, close packing of the two chains of TS with the adjacent long chains of stearic acid is undoubtedly responsible for the compatibility. Stearic acid probably neither aids nor hinders packing of TS molecules. The thiadiazole ring is sufficiently small or hidden that it does not interfere.

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WHITING, INDIANA

[CONTRIBUTION FROM THE VENABLE LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra and the Dissociation Constants of the Monochloroquinolines and the Monomethylquinolines

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The ultraviolet absorption spectra of all seven of the monochloroquinolines and the 2-, 3-, 4-, 6-, 7- and 8-monomethylquinolines have been determined in 95% ethanol, 10% ethanol and 10% ethanol that is 0.01 molar in hydrochloric acid. The changes in intensity and the shifts in wave lengths of the maxima of the monochloroquinolines have been correlated with molecular dimensions. The shifts in the wave lengths for the methylquinolines cannot be associated with the dimensions of the molecules as was the case with the haloquinolines studied. The dissociation constants of the monochloro- and monomethylquinolines have also been determined from spectral data. Possible reasons, based on electron densities at the nitrogen atom, as influenced by the various substituents, are given for the order of basic strengths.

The data presented in this paper are the results of a continuation of the work done previously in this Laboratory on the ultraviolet absorption spectra of the monosubstituted quinolines.[1-3]

It has been shown in one of these papers[3] that the spectral shifts of the monobromo- and monofluoroquinolines can be correlated with molecular dimensions. In the present work the spectra of the chloroquinolines and the methylquinolines have been determined in 95% ethanol, 10% ethanol and 10% ethanol that is 0.01 molar in hydrochloric acid.

The dissociation constants of the chloroquinolines and the methylquinolines were also determined from spectral measurements.

Discussion

The shifts of wave length and the changes in the molar extinction coefficients for the two near ultraviolet absorption peaks of the chloroquinolines follow the same generalizations as those given in a previous paper for the other haloquinolines.[3] From Table I it can be seen that the greater changes in the longer wave length peak, the B band, come about when the chlorine is in the 2-, 3-, 6- or 7-position. Substitution in the 4-, 5- or 8-position produces the greater changes in the shorter wave length peak, the E_2 band. These displacements are explained if one associates the great extension of the molecule with the longer wave length peak and the smaller extension with the next shorter wave length peak. Substitution which will increase the length of the field in which the oscillating electron is free to move will lower the energy of that electron. The wave length of the peak arising from this transition will be shifted to longer wave lengths. For a clearer picture reference[3] should be consulted.

TABLE I

SPECTRAL DATA OF THE CHLOROQUINOLINES IN 10% ETHANOL

Compound	B Band λ_{max}, Å.	B Band ϵ_{max}	B Band $\Delta\lambda$	E_2 Band λ_{max}, Å.	E_2 Band ϵ_{max}	E_2 Band $\Delta\lambda$
2-Chloroquinoline	3180	4610	50	2820	3320	60
3-Chloroquinoline	3230	3560	100	2830	3060	70
4-Chloroquinoline	3160	2850	30	2890	4900	130
5-Chloroquinoline	3170	3170	40	2920	4640	160
6-Chloroquinoline	3190	3500	60	2760	3650	0
7-Chloroquinoline	3190	3670	60	2790	3560	30
8-Chloroquinoline	3150	2990	20	2920	4500	160
Quinoline	3130	3410		2760	3590	

In the study of light absorption in the methylquinoline series one must recognize the possibility of hyperconjugation of the methyl group. Mulliken *et al.*,[4] and Coulson[5] give the structure of the methyl group as $\text{—C}\equiv\text{H}_3$ where the three hydrogens are treated as a group. The molecular orbitals of this group of hydrogens give an unsymmetrical distribution of electron density above and below the plane of the ring system with a node in the plane. This cloud resembles the π-electron configuration and may interact with the ring. Hyperconjugation leads one to expect a lowering of the energy necessary for the electronic transitions in quinoline resulting in bathochromic shifts. The data in Table II show that there is a red shift for the two absorption

TABLE II

SPECTRAL DATA OF THE METHYLQUINOLINES IN 10% ETHANOL

Compound	B Band λ_{max}, Å.	B Band ϵ_{max}	B Band $\Delta\lambda$	E_2 Band λ_{max}, Å.	E_2 Band ϵ_{max}	E_2 Band $\Delta\lambda$
2-Methylquinoline	3150	3860	20	2790	3200	30
3-Methylquinoline	3180	3120	50	2860	3350	100
4-Methylquinoline	3130	2730	0	2830	4530	70
6-Methylquinoline	3170	2330	40	2850	2340	90
7-Methylquinoline	3180	2400	50	2920	2170	160
8-Methylquinoline	3140	2650	10	2920	3750	160

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[1] W. K. Miller, S. B. Knight and A. Roe, THIS JOURNAL, **72**, 1629 (1950).

[2] W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 4763 (1950).

[3] S. B. Knight, R. H. Wallick and J. Bowen, *ibid.*, **76**, 3780 (1954).

[4] R. S. Mulliken, C. A. Rieke and W. G. Brown, *ibid.*, **63**, 4 (1941).

[5] C. A. Coulson, *Quart. Rev.*, **1**, 144 (1947).