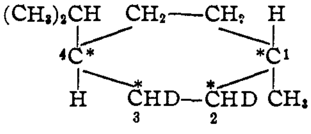
It is evident that in these experiments (which were carried out twice from *l*-menthol), the reduction of *trans* 2-menthene with deuterium gas in the presence of Raney nickel led to optically active 2,3-dideutero-*trans*-menthane.

Discussion

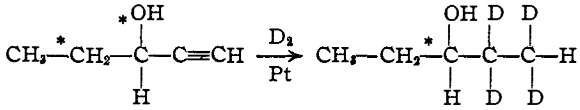
We believe that the optical activity of the 2,3-dideutero-*trans*-menthane, which has been prepared, is due to the asymmetric introduction of deuterium into the molecule and not to the presence of traces of impurities. In support of this conclusion, the following points seem particularly significant: (1) Hydrogenation of one-half of the *same solution* from which optically active 2,3-dideutero-*trans*-menthane was obtained, resulted in an optically inactive *trans*-menthane. (2) Rather drastic treatment of the 2,3-dideutero-*trans*-menthane with such reagents as hydrogen and nickel, alkaline potassium permanganate, sulfuric acid, a nitrating mixture, and metallic sodium, changed none of the physical properties of the material.

The origin of optical activity in 2,3-dideutero-*trans*-menthane has not yet been established. There are four asymmetric carbon atoms in the molecule (VI), and they are of two kinds: Carbon atoms 1 and 4 belong to that class indicated by the general formula (I).



VI

Carbon atoms 2 and 3 are asymmetric because of the direct comparison of hydrogen and deuterium atoms attached to the asymmetric center (II). It is probable, however, that the measurable optical activity is due to carbon atoms 2 and 3. McGrew and Adams,[5] for example. were able to resolve 1-pentyn-3-ol (VIII), but on reduction with deuterium, no optical activity could be detected. Consequently, we would expect the contribution of carbon atoms 1 and 4 toward optical activity to be very small.



$$\mathrm{CH_3\overset{*}{-}CH_2-\overset{*}{\underset{H}{\overset{OH}{C}}}-C{\equiv}CH \xrightarrow[\text{Pt}]{\text{D}_2} CH_3-CH_2\overset{*}{-}\underset{H}{\overset{OH}{C}}-\underset{D}{\overset{D}{C}}-\underset{D}{\overset{D}{C}}-H}$$

VII (no detectable activity)

Acknowledgment.—The authors are indebted to Mrs. J. L. Johnson for the determination and interpretation of the infrared absorption curves which are shown in the paper.

Summary

The reduction of *trans* 2-menthene in diethylcarbitol solution with deuterium in the presence of Raney nickel produces optically active 2,3-dideutero-*trans*-menthane, $[\alpha]^{25}\mathrm{D}$ $-0.09 \pm 0.01°$ (l = 2, no solvent). The sole cause of asymmetry in this molecule is the replacement of hydrogen atoms by deuterium atoms.

Urbana, Illinois Received December 6, 1948

[Contribution No. 706 from the Department of Chemistry, University of Pittsburgh]

Electric Moments and Structure of Substituted Thiophenes. II. Certain Thiotolene Derivatives[1,2]

By Ram Keswani and Henry Freiser

This work, dealing with the thiotolenes and some of the derivatives of 2-thiotolene, is part of an extensive program for the determination of the electric moments of substituted thiophenes. Since it was found helpful in the case of the halogenated thiophenes[1] to make comparisons with the corresponding halogenated benzenes, a similar procedure is used here to help explain the results of electric moment measurements of the methylthiophenes, 2-thenyl chloride, 2-thiophenealdehyde, 2-acetylthiophene, and 2-carbethoxythiophene.

Experimental

Purification of Materials.—All of the materials studied were liquids and were purified by careful fractionation[3] through a three-foot glass helices-packed column as described previously.[1] A summary of their physical properties is presented in Table I. The benzene used is Jones and Laughlin reagent-grade. The thiotolenes and 2-acetylthiophene were 99 mole % grade obtained from the Socony-Vacuum Company. The 2-carbethoxythiophene was obtained by the esterification of thiophenic acid formed by the action of alkali hypochlorite on 2-acetylthiophene. The 2-thiophene-aldehyde was prepared from 2-thenyl chloride according to the directions of Dunn, *et al.*,[4] while

Table I

Physical Properties of Compounds

	B. p., °C.	*P*. mm.	d^{20}_4, g./ml.	$n^{20}\mathrm{D}$	*MR*D, cc./mole
2-Methylthiophene	112.1-.3	747.2	1.0095	1.5118_5	29.2
3-Methylthiophene	114.2	741.6	1.0109	1.5126_0	29.2
2-Thenyl chloride	84.5	30	1.1950	1.5552_5	35.6
2-Thiophene-aldehyde	89-90	20	1.2143	1.5838_0	30.9
2-Acetylthiophene	208.0	740	1.1606	1.5606_0	35.2
2-Carbethoxythiophene	81.7	6	1.1749	1.5174_5	40.3

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[1] For paper I, see This Journal, 71, 218 (1949).

[2] Part of this work is abstracted from a thesis submitted by Ram Keswani to the University of Pittsburgh in partial fulfillment of the requirements for the Master of Science degree, February, 1949.

[3] The acetylthiophene was purified first by fractional crystallization.

[4] Dunn, Waugh and Dittmer, This Journal, 68, 2118 (1946).

the latter compound was obtained by the method of Blicke and Burckhalter.[5] The last three compounds were prepared under the direction of Dr. M. F. Dull.

Measurements and Calculations.—The procedure has been described previously.[1] The measurements are summarized in Table II where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction, f_2, of the substance indicated are given along with the molar polarization, P_2. The table also includes the polarization, P_∞, obtained by extrapolation to $f_2 = 0$ of the P_2 values and the dipole moment, $\mu_{\text{obs.}}$, calculated therefrom in the usual manner. When the P_2 values showed no trend with concentration, the average value was taken as P_∞.

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS AND ELECTRIC MOMENTS AT 30°

f_2	ϵ	d	P_2	$P_{2\infty}$	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$
		2-Methylthiophene				
0.00000	2.2627	0.86823	...	38.2	0.67	0.57
.01420	2.2700	.87006	37.2			
.02059	2.2740	.87087	37.3			
.02801	2.2807	.87183	39.0			
.03066	2.2816	.87216	38.7			
		3-Methylthiophene				
0.01679	2.2768	0.87059	41.7	42.8	0.82	0.83
.02151	2.2841	.87125	43.9			
.02580	2.2869	.87185	43.1			
.03090	2.2907	.87256	42.6			
		2-Thenyl Chloride				
0.01602	2.3509	0.99718	88.6	85.8	1.58	1.58
.02923	2.4175	.90282	84.1			
.04083	2.4810	.91653	84.8			
		2-Thiophenealdehyde				
0.009071	2.4178	0.87138	272.4	284	3.55	2.86
.009077	2.4186	.87168	273.5			
.01652	2.5451	.87397	266.3			
.02173	2.6285	.87577	258.1			
		2-Acetylthiophene				
0.00890	2.4030	0.87149	259.1	264.0	3.37	2.86
.01002	2.4205	.87189	258.0			
.01364	2.4775	.87321	255.4			
.01648	2.5251	.87424	255.6			
		2-Carbethoxythiophene				
0.00645	2.2971	0.87101	118.8	114.0	1.91	2.07
.01242	2.3329	.87359	123.0			
.01543	2.3523	.87475	125.4			
.01865	2.3745	.87627	127.5			

Discussion of Results

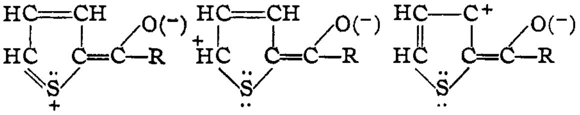
For purposes of comparison, electric moment values were calculated on the basis of vector addition using the group moment values obtained in the corresponding benzene derivatives ($\mu_{\text{C—CH}_3} = 0.34$,[6] $\mu_{\text{C—CH}_2\text{Cl}} = 1.82$,[7] $\mu_{\text{C—CHO}} = 2.77$,[8] $\mu_{\text{C—COCH}_3} = 2.77$,[8] and $\mu_{\text{C—COOC}_2\text{H}_5} = 1.9$[9]) assuming free rotation of the group about the bond to the nuclear carbon and the thiophene moment value of 0.53.[1] These values, $\mu_{\text{calc.}}$, are included in Table II.

While the observed value of the moment of 3-methylthiophene is in exact agreement with the calculated value, that of the 2-methyl derivative is 0.10 debye unit higher. This may be attributed to the possibility that structures involving hyperconjugation between the 2-methyl group and the thiophene nucleus have greater polarity than analogous structures encountered in toluene.

The excellent agreement encountered in the case of the 3-methyl derivative indicates the similarity between the 3-position in thiophene and the *meta* position of disubstituted benzenes.

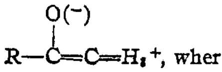
The exact agreement of calculated and observed moment values of 2-thenyl chloride shows the resemblance of this compound to benzyl chloride.

The argument that the thiophene nucleus can participate in certain resonance structures with substituents in the 2-position which are more polar than those of the benzene nucleus in analogous derivatives gains further weight in the results of the measurements of thiophene aldehyde and acetylthiophene. Positive deviations in the moments of these compounds of 0.69 and 0.51 unit, respectively, have been encountered. These deviations may also be attributed to the greater contributions of structures such as



where R = H or CH_3

in the ground state of these thiophene derivatives than those of corresponding structures in benzaldehyde and acetophenone. It is of interest to note that while the moments of benzaldehyde and acetophenone are identical,[8] the moment of the thiophene aldehyde is significantly larger than that of acetylthiophene. In the cases of both the methyl ketones, structures such as



$$\text{R—}\overset{\text{O}^{(-)}}{\overset{|}{\text{C}}}\text{=C=H}_3{}^+, \text{ where R} = \text{C}_4\text{H}_3\text{S or C}_6\text{H}_5$$

tend to reduce the contributions of structures as shown above. While in the benzene derivatives the reduced importance of structures involving the benzene nucleus is exactly compensated by the structures involving the hyperconjugation of the methyl group, these latter structures do not make up for the contribution of the more strongly polar structures involving the resonance of the thiophene nucleus.

Lastly, the observed moment value of 2-carbethoxythiophene is 0.16 unit lower than the calculated value. This deviation can be explained on the basis of mutual inductance effects as discussed in the case of the 2-halothiophenes.[1] While resonance structures for this compound similar to those shown above for the thiophene-

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(5) Blicke and Burckhalter, THIS JOURNAL, **64**, 447 (1942).

(6) LeFevre and LeFevre, *J. Chem. Soc.*, 957 (1935).

(7) Parts, *Z. physik. Chem.*, **B12**, 323 (1931).

(8) Goebel and Wenzke, THIS JOURNAL, **59**, 2301 (1937).

(9) Bergmann and Weizmann, *ibid.*, **57**, 1755 (1935).

aldehyde and ketone derivatives would lead one to expect a higher moment for the ester, electrostatic repulsion of the sulfur atom in the nucleus and the ethoxide group of the substituent would tend to interfere with complete freedom of rotation and thus cause a decrease in the over-all moment. Since the agreement between the observed and calculated moment values is fair, either the resonance and electrostatic repulsion effects largely counterbalance one another or they are not of sufficient magnitude to affect the moment. It would be of importance in this regard to learn the atomic spacings in this molecule from electron or X-ray diffraction experiments.

Summary

1. Dielectric constants and densities at 30° are reported for benzene solutions of 2- and 3-methylthiophene, 2-thenyl chloride, 2-thiophene-aldehyde, 2-acetylthiophene and 2-carbethoxythiophene.

2. The electric moments for these compounds have been found to be 0.67, 0.82, 1.58, 3.55, 3.37 and 1.91, respectively.

3. The general resemblance of the structure of substituted thiophenes to those of the corresponding benzene derivatives is observed. The 3-position in thiophene is likened to the *meta* position of disubstituted benzene. Resonance structures of some 2-substituted thiophenes involving the nucleus are more polar than corresponding structures in benzene derivatives.

PITTSBURGH 13, PENNA. RECEIVED JANUARY 7, 1949

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF DE PAUL UNIVERSITY AND STANFORD UNIVERSITY]

The Absorption Spectra of *p*-Phenylazophenyl β-D-Glycosides and Related Compounds[1]

BY ROBERT P. ZELINSKI AND WILLIAM A. BONNER

Despite a large literature on the absorption spectra of organic compounds, there are relatively few papers on the spectra of carbohydrates. Recently Pacsu and Hiller[2] noted the appearance of a carbonyl adsorption band for glucose and arabinose in 50% sulfuric acid which disappeared on alkalizing the solution. These results are at variance with earlier reports[3] that aldoses show no selective ul-

TABLE I

PARAMETERS OF ABSORPTION SPECTRA CURVES FOR *p*-PHENYLAZOPHENYL β-D-GLYCOSIDES AND RELATED SUBSTANCES

A, *p*-Phenylazophenyl; B, *p*-(4-methoxyphenylazo)-phenyl; C, *p*-(3-nitrophenylazo)-phenyl; D, tetraacetate; E. tetrapropionate; F, triacetate; G, tripropionate; H, heptaacetate; I, heptapropionate; J, in acidified ethanol.

		Ultraviolet				Visible			
		Minimum		Maximum		Minimum		Maximum	
No.	Compounds	mμ	Log ε	mμ	Log ε	mμ	Log ε	mμ	Log ε
1	A β-D-glucoside	265	3.43	340	4.35	400	2.82	436	2.92
2	A β-D-glucoside D	265	3.36	338	4.35	395	2.70	436	2.92
3	A β-D-glucoside E	265	3.55	332	4.35	400	2.80	436	2.95
4	A β-D-galactoside	265	3.48	339	4.39	400	2.88	435	2.96
5	A β-D-galactoside D	265	3.55	336	4.35	400	2.82	438	2.93
6	A β-D-galactoside E	265	3.52	335	4.37	395	2.75	437	2.97
7	A β-D-xyloside	265	3.48	338	4.41	400	2.85	436	2.97
8	A β-D-xyloside F	264	3.49	335	4.38	398	2.75	435	2.92
9	A β-D-xyloside G	265	3.53	335	4.37	396	2.78	436	2.97
10	A β-D-lactoside	265	3.44	338	4.35	400	2.80	435	2.92
11	A β-D-lactoside I	265	3.58	335	4.34	398	2.76	436	2.92
12	A β-D-maltoside I	263	3.57	338	4.37	398	2.77	436	2.93
13	A β-D-cellobioside H	265	3.47	340	4.44	400	2.80	438	2.93
14	*p*-phenylazophenol	272	3.58	350	4.43	None		430	3.22
15	*p*-phenylazophenol J	270	3.62	345	4.55	None		430	3.20
16	A acetate	258	3.48	325	4.34	390	2.48	440	2.80
17	A methyl ether	270	3.68	343	4.56	410	2.97	430	3.00
18	B β-D-glucoside D	272	3.38	350	4.47	None		440	3.27
19	*p*-(4-Methoxylphenylazo)-phenol	270	3.50	360	4.43	None		Smeared	
20	C β-D-glucoside D	295	3.84	340	4.32	405	2.85	435	2.92
21	*p*-(3-Nitrophenylazo)-phenol	295	3.70	358	4.37	None		Smeared	

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[1] Presented before the Division of Sugar Chemistry and Technology of The American Chemical Society, Portland, Oregon, September, 1948.

[2] Pacsu and Hiller, THIS JOURNAL, **70**, 523 (1948).

[3] Gabryelski, Marchlewski, *et al.*, *Bull. intern. acad. polonaise*, **1929A**, 317; **1933A**, 87, 397, 409; *C. A.*, **24**, 3711; **27**, 4481; **28**, 3305; *Bull. soc. chim.*, **45**, 591 (1929); *Biochem. Z.*, **250**, 385; **261**, 393; **262**, 248; **265**, 50 (1933); **300**, 42 (1938).