

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-carbomethoxythiophene.

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.

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

The Absorption Spectra of *p*-Phenylazophenyl β -D-Glycosides and Related Compounds¹

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 Hiller² noted the appearance of a car-

bonyl adsorption band for glucose and arabinose in 50% sulfuric acid which disappeared on alkalinizing the solution. These results are at variance with earlier reports³ 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.

No.	Compounds	Ultraviolet				Visible			
		Minimum $m\mu$	Log ϵ	Maximum $m\mu$	Log ϵ	Minimum $m\mu$	Log ϵ	Maximum $m\mu$	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	<i>p</i> -phenylazophenol	272	3.58	350	4.43	None		430	3.22
15	<i>p</i> -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	<i>p</i> -(4-Methoxyphenylazo)-phenol	270	3.50	360	4.43	None			Smearred
20	C β -D-glucoside D	295	3.84	340	4.32	405	2.85	435	2.92
21	<i>p</i> -(3-Nitrophenylazo)-phenol	295	3.70	358	4.37	None			Smearred

(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).

traviolet absorption in acidic solution, but develop bands around 268 and 320 $m\mu$ in alkaline solution. A recent report⁴ that each monosaccharide has its own characteristic infrared spectrum and that the spectra of anomeric glycosides differ is also at variance with earlier reports⁵ that there are no pronounced differences in the infrared spectra of carbohydrates.

In 1947 Hurd and Zelinski⁶ prepared a series of *p*-phenylazophenyl β -D-glycosides, orange, crystalline compounds of the general formula $p\text{-GIO-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_5$. This work extended the limited number of known⁷ carbohydrate derivatives having a strong chromophoric group in the visible spectral regions. In connection with future studies on rotatory dispersion, we have measured the visible and ultraviolet spectra of thirteen sim-

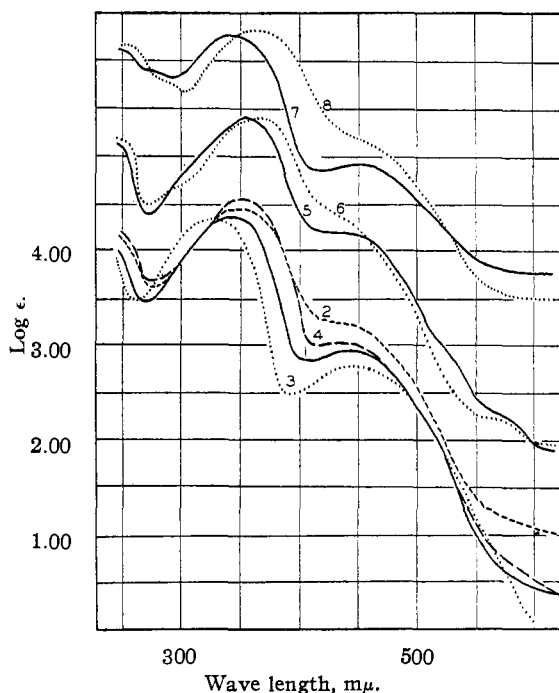


Fig. 1.—Absorption spectra of *p*-phenylazophenyl β -D-glucoside and related compounds: 1, *p*-phenylazophenyl β -D-glucoside; 2, *p*-phenylazophenol; 3, *p*-phenylazophenyl acetate; 4, methyl *p*-phenylazophenyl ether; 5, *p*-(4-methoxyphenylazo)-phenyl tetraacetyl- β -D-glucoside; 6, *p*-(4-methoxyphenylazo)-phenol; 7, *p*-(3-nitrophenylazo)-phenyl tetraacetyl- β -D-glucoside; 8, *p*-(3-nitrophenylazo)-phenol. Curves 5, 6 and 7, 8 are plotted with the ordinate axis beginning, respectively, one and two units above the labelled axis.

(4) Kuhn, reported before the Division of Sugar Chemistry and Technology, Portland, Oregon, September, 1948.

(5) Rogers and Williams, *THIS JOURNAL*, **60**, 2619 (1938); Barr and Chrisman, *J. Chem. Phys.*, **8**, 51 (1940).

(6) Hurd and Zelinski, *THIS JOURNAL*, **69**, 243 (1947).

(7) Hurd and Bonner, *J. Org. Chem.*, **11**, 50 (1946); Coleman, *et al.*, *THIS JOURNAL*, **64**, 1501 (1942); **65**, 1588 (1943); **67**, 381 (1945); Reich, *Compt. rend.*, **208**, 589, 748 (1939); *Biochem. J.*, **33**, 1000 (1939); Heflerich, Lang and Schmitz-Hillebrecht, *J. prakt. Chem.*, **138**, 275 (1933).

ple and nuclear substituted *p*-phenylazophenyl β -D-glycosides, and compared these spectra with those of the chromophoric aglycones and other related compounds.

As seen in Table I, the anticipated independence of absorption spectra on both gross and stereochemical structure in this series is striking. The spectral curves of all thirteen carbohydrates, including a pentose, two hexoses and three disaccharides, both acylated and non-acylated, proved identical almost within experimental error. Curve 1 of Fig. 1 is prototypical of all obtained. While the positions of the maxima and minima were practically identical, slightly greater differences in extinction values were noted, and these seemed to follow definite trends. Table I shows $\log \epsilon$ values for ultraviolet minima slightly higher for acylated than for unacylated glycosides, while $\log \epsilon$ for ultraviolet maxima and visible minima seem slightly lower for the acylated samples. No consistent trend is apparent in the visible maxima. These trends are very slight, and their validity can be established only with further work.

For comparison, we have also measured the spectra of *p*-phenylazophenol, the chromophoric aglycone, of *p*-phenylazophenyl acetate, and of methyl *p*-phenylazophenyl ether. These are shown in curves 2, 3 and 4 of Fig. 1. The most striking difference comes with the free phenol, where the entire curve is shifted to longer wave lengths and the sharp differentiation between the two peaks is softened. Similar results were obtained with *p*-phenylazophenol in slightly acid solution where possible ionization of the phenol should be suppressed. By contrast, with *p*-phenylazophenyl acetate the entire curve is shifted to shorter wave lengths, and the peak differentiation is accentuated.

The introduction of *p*-methoxy and *m*-nitro groups into the second nucleus of the aglycone bring about minor changes in the positions and shapes of the curves, as seen in Fig. 1. It is interesting to note that the shift of the curve for the free dyestuff to longer wave lengths and the suppression of peak differentiation follows the previous observation on the unsubstituted analogs.

Experimental Part

Materials.—Samples numbered 2 through 13 and sample 18 in Table I were those prepared by Hurd and Zelinski.⁶ Samples 1 and 20 were prepared by Hurd and Bonner.⁷ Samples 14 and 15 were prepared by coupling benzenediazonium chloride with phenol and recrystallizing the product from dilute ethanol, m.p. 154.5–155.5°. Sample 21 was prepared by coupling diazotized *m*-nitroaniline with phenol and recrystallizing from dilute ethanol, m.p. 147–148°. Sample 17 was prepared by methylation of sample 14 with methyl sulfate and alkali after the method of Colombano,⁸ m.p. 53.5°.

Measurements.—All absorption spectra were measured at intervals of 5 $m\mu$ with a Model DU Beckman Quartz Spectrophotometer. Measurements from 240 to 400 $m\mu$ used the hydrogen lamp light source, and measurements from 400 $m\mu$ on used the tungsten light. The ultraviolet

(8) Colombano, *Gazz. chim. ital.*, **37**, II, 474 (1907).

photo cell was used from 240 to 400 $m\mu$, and the visible cell above 400 $m\mu$. For the most part spectra in the visible region were measured in 10^{-3} molar solution and ultraviolet spectra in 10^{-4} molar solution. In certain cases, notably samples 14, 18, 19 and 21, it was necessary to use 10^{-4} molar solutions for measurements in the visible. Run 15 was 10^{-3} molar in dye and 10^{-2} molar in hydrochloric acid for visible measurements, and this solution was diluted 1 to 10 for ultraviolet measurements. All solutions were made with Commercial Solvents Gold Shield ethanol.

Summary

Absorption spectra for a series of acylated and

unacylated *p*-phenylazophenyl β -D-glycosides have been measured. No significant differences depending on either gross or stereochemical structure were found. Spectra of two substituted *p*-phenylazophenyl tetraacetyl- β -D-glucosides have been measured and compared with those of the unsubstituted analogs. Spectra of all of the above glycosides have been compared with those of the parent dyestuffs and several other related compounds.

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[CONTRIBUTION FROM THE ANALYTICAL AND PHYSICAL CHEMICAL DIVISION, NORTHERN REGIONAL RESEARCH LABORATORY¹]

Liquid-Vapor Equilibrium of Ethanol-Toluene Solutions

BY CARL B. KRETSCHMER AND RICHARD WIEBE

In continuation of this Laboratory's program of determining the physical properties of ethanol-hydrocarbon mixtures,² measurements have been made of the total and partial vapor pressures of ethanol-toluene solutions. The general purpose of the program is to select a representative member of each of the principal classes of hydrocarbons present in gasoline and to study their behavior in mixtures with ethanol.

The apparatus and methods described previously² were used unchanged except for a modification of the condensate trap and vaporizer as shown in Fig. 1. Any tendency toward stratification in the trap was prevented by means of the magnetic stirrer. The flash boiler of the type suggested and fully discussed by Jones, Schoenborn and Colburn³ simplified the operation of the still.

Density Measurements.—Commercially purified toluene was treated with concd. sulfuric acid until the isatin test⁴ for thiophene and methylthiophenes was negative, washed free of acid, and fractionated in the column previously described.² A melting point determination on the sample of toluene selected gave the value -95.048° , indicating an impurity content of 0.14 mole per cent.^{4a} The physical constants, *b. p.* $110.64 \pm 0.02^\circ$, d^{25}_4 0.86219, n^{25}_D 1.4940 are in good agreement with those reported by the National Bureau of Standards⁵ for toluene containing 0.10% impurity. Moisture was excluded by keeping the toluene un-

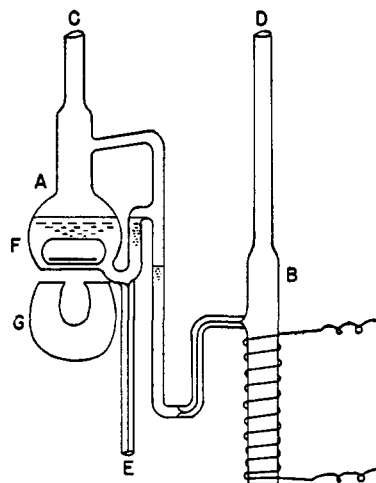


Fig. 1.—Condensate trap and vaporizer: A, trap; B, vaporizer; C, from condenser; D, to saturator; E, sampling line; F, nail in glass capsule; G, rotating magnet, 60 r.p.m.

der its own vapor pressure in a flask sealed to a vacuum manifold through a silicone-lubricated stopcock, and samples were taken by condensing vapor in bulbs attached to the manifold. The ethanol was purified as described previously.² Experimentally determined densities of ethanol-toluene solutions at 25° are given in Table I. As shown in column 4, the change in volume on mixing is positive at low ethanol concentrations but negative over the remainder of the range. The data are in qualitative agreement with those of Washburn and Lightbody,⁶ and the discrepancies may be accounted for by the fact that their solutions were made up by volume which is subject to greater errors than when made up by weight as was done in this work.

Vapor Pressure of Ethanol.—Vapor pressures of ethanol were measured at 10° intervals be-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Carl B. Kretschmer, Janina Nowakowska and Richard Wiebe, *THIS JOURNAL*, **70**, 1785 (1948).

(3) C. A. Jones, E. M. Schoenborn and A. P. Colburn, *Ind. Eng. Chem.*, **35**, 666 (1943).

(4) H. N. Holmes and N. Beeman, *ibid.*, **26**, 172 (1934).

(4a) Calculated using freezing point for zero per cent. impurity and cryoscopic constants listed by API Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table No. 5z, dated Aug. 31, 1945.

(5) A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini, *J. Research Nat. Bur. Standards*, **36**, 129 (1946).

(6) E. R. Washburn and A. Lightbody, *J. Phys. Chem.*, **34**, 2701, (1930).