[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Rotatory Dispersions of Some *p*-Phenylazophenyl β-D-Glycosides[1]

BY WILLIAM A. BONNER

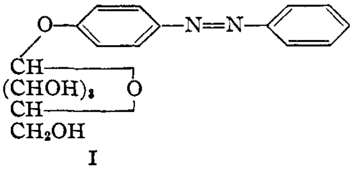
Measurements of rotatory dispersion shown by simple sugars and their derivatives have indicated that specific rotation varies with wave length in the visible spectrum according either to a simple Drude equation of the type

$$[\alpha]_\lambda = k/(\lambda^2 - \lambda_0^2) \qquad (1)$$

where *k* is the "rotation constant" and λ_0^2 the "dispersion constant," or to a more complex equation involving several terms similar to that in equation (1). In common with other optically active compounds, however, the simple or complex rotatory dispersions characteristic of measurements on sugars with visible light may become anomalous[2] in the ultraviolet regions as the wave length of the light approaches that corresponding to a specific absorption band in the molecule. It is known that the light absorbing group must be located in the close vicinity of the asymmetric center, and it is believed[2] that the asymmetric center imparts an induced dissymmetry to the chromophoric group which in turn contributes to the optical activity of the molecule, giving rise to anomalous dispersion when disturbed by light of the proper frequency. Thus the dispersion constant, λ_0^2, in equation (1) frequently corresponds to the wave length characteristic of an absorbing group near the asymmetric center.

There have been reported no experiments designed to test the possibility that absorbing groups further situated from an asymmetric center might also give rise to dispersion anomalies when coupled with the asymmetric center by appropriate conjugation. Experiments designed to test this possibility are reported in the present paper.

The absorption spectra of *p*-phenylazophenyl β-D-glycosides such as I have recently been measured.[3] Such spectra for a number of glycosides related to I have been found almost identical and, as was expected, quite similar to the spectra of the phenolic aglycone. Two distinct absorption bands were observed between 240 and 800 mμ: a relatively low intensity "R-band"[4] with a maximum around 436 mμ and a high intensity "K-band" with a maximum around 338 mμ. A third and more intense band below 240 mμ was also evident. It has been suggested[4] that the R-band in compounds such as I is due to the isolated azo linkage, and the K-band to the conjugated *p*-phenylazophenyl chromophore as a whole.



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To the extent that this interpretation of the spectra of azo compounds is valid, one would expect the optical activity of compounds such as I to be affected by the *p*-phenylazophenyl chromophore causing the K-band, since this chromophore had its origin close to the first center of optical activity. We have attempted to determine if the azo chromophore causing the R-band might also affect the optical activity. At long wave lengths where solutions of I are transparent such an effect might not be expected, but it seemed reasonable to look for anomalous dispersion when wave lengths in the vicinity of the R-band were employed. Electronic disturbances of the azo chromophore by light of the R-band wave lengths might interact through the conjugation of the benzene ring with the first asymmetric center in I thus causing anomalous effects.

A serious experimental difficulty has prevented us from observing the optical effects we desired to study. The molar extinction coefficients of compounds such as I were in the neighborhood of 24000 for the high intensity K-band and 890 for the low intensity R-band.[3] These extinctions were so high that, even at high dilution, it was impossible to make polarimetric readings with light even in the longer wave length regions of the R-band. As soon as the initial R-band wave lengths were approached (*i. e.*, in the vicinity of 540 mμ) the optical densities of our solutions became so great that accurate polarimetric measurements were impossible. Thus with compounds such as I we have been unable to test the effect of distant chromophores which are conjugated with centers of optical activity on the rotations caused by these optically active centers. This problem is being studied at the present time with compounds whose absorption bands are characterized by lower extinction coefficients.

We have, however, been able to study the rotatory dispersion of compounds such as I for wave lengths above their R-band region. Since difficulties due to strong light absorption were anticipated, *p*-phenylazophenyl β-D-glucoside and *p*-phenylazophenyl β-D-galactoside were employed in these studies because of their relatively high specific rotations.[5] The dispersions of these compounds were measured in dioxane in the region from 667 to 524 mμ. The observed dispersions and their close similarities are illustrated graphically

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[1] Presented before the Division of Sugar Chemistry, Portland, Oregon, September, 1948.

[2] Harris, Hirst, *et al.*, *J. Chem. Soc.*, 1403 (1935), 1658 (1936); Lowry, Wolfrom, *et al.*, *ibid.*, 696 (1933); 1179 (1935); Dimler and Link, THIS JOURNAL, **62**, 1216 (1940).

[3] Zelinski and Bonner, *ibid.*, **71**, 1791 (1949).

[4] Burawoy, *J. Chem. Soc.*, 1865 (1937).

[5] Hurd and Zelinski, THIS JOURNAL, **69**, 243 (1947).

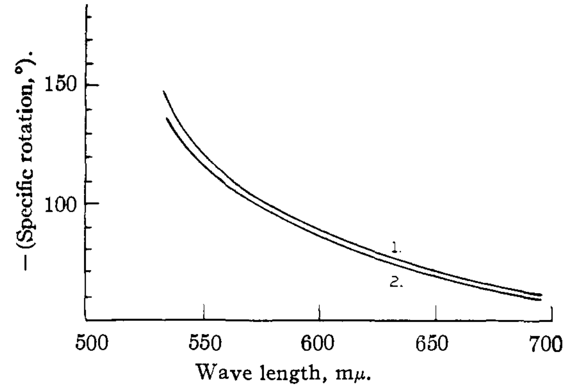

Fig. 1.—Rotatory dispersions of *p*-phenylazophenyl β-D-glucoside and β-D-galactoside, Ar = *p*-$C_6H_4N{=}NC_6H_4$-: 1, Ar β-D-glucoside; 2, Ar β-D-galactoside.

in Fig. 1. The curves in Fig. 1 can be expressed mathematically with fair accuracy by means of the simple Drude formula of equation (1). On plotting the reciprocal of the observed specific rotation against the square of the wave length (Fig. 2) the linear relation characteristic of simple dispersion was found very nearly to hold. The slopes of the lines in Fig. 2 give rotation constants of −21.90 and −21.05, respectively, for *p*-phenylazophenyl β-D-glucoside and β-D-galactoside. Now knowing k of equation (1) for each compound it is possible, by substituting a measured specific rotation and wave length into the equation, to evaluate λ_0^2 and thus λ_0. This dispersion constant was determined to be 339 mμ for the glucoside and 342 mμ for the galactoside. These values are in striking agreement with the 338 mμ measured spectrophotometrically[3] for the position of maxima of the high intensity K-bands in compounds of type I. It is thus quite apparent that the conjugated *p*-phenylazophenyl chromophore is the one which affects the optical activity of type I compounds in the transparent regions of their spectrum. This observation, incidentally, is in accord with Burawoy's assignment[4] of the two absorption bands to their respective chromophores in the molecule.

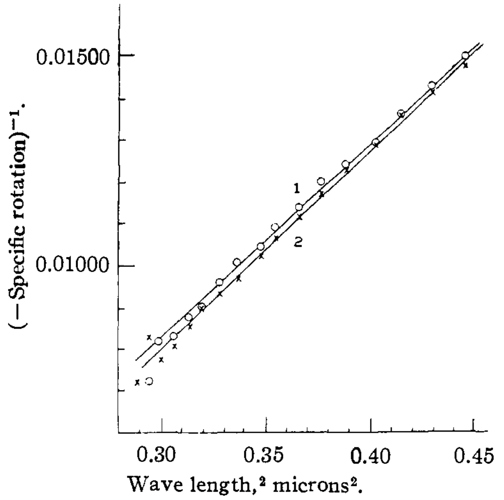

Fig. 2.—$1/[\alpha]$ *vs.* λ^2 for *p*-phenylazophenyl β-D-glucoside and β-D-galactoside: 1, Ar = *p*-$C_6H_4N{=}NC_6H_4$-: 1, Ar β-D-glucoside, O; 2, Ar β-D-galactoside, X.

As a further test of the simple dispersion observed in the transparent spectral regions we have used our values of k and λ_0 to calculate the specific rotation at each of our measured wave lengths. The calculated specific rotations, the observed specific rotations, and the average deviations from the means of the latter are recorded in Table I. With respect to the glucoside it is seen that the observed rotations agree with the calculated quite within the experimental error for longer wave lengths. From about 572 mμ downward, however, there seems to be a divergence in calculated and observed rotations which is beyond experimental error. This occurs in those very regions of the spectrum where the R-band absorption is just becoming evident and suggests that there is some interaction due to conjugation between the distant azo chromophore and the C-1 center of asymmetry as the electronic system of the azo chromophore becomes disturbed. It is most unfortunate that the high extinction coefficients characteristic of the absorption bands in our compounds prevented further polarimetric observation at the very point that this interesting divergence began to appear.

The agreement betwen observed and calculated specific rotations for the galactoside is not as satisfactory as in the case of the glucoside, due apparently to the fact that the dispersion of the galacto-

TABLE I

ROTARY DISPERSIONS OF SEVERAL *p*-PHENYLAZOPHENYL β-D-GLYCOSIDES

Wave length, mμ	Specific rotation, ° Glucoside Calcd.	Glucoside Observed	Galactoside Calcd.	Galactoside Observed	Acetylated galactoside Calcd.	Acetylated galactoside Observed
693			−58.0	−58.9[a]	+16.4	+13.2[b]
679			61.5	62.5	17.3	14.8[g]
667	−66.4	−66.6[a]	64.3	65.3	18.1	16.3[b]
655	69.9	70.0	67.5	68.1	19.0	18.2[g]
643	73.3	73.4	70.9	70.9	20.0	20.0
633	76.6	77.3	74.2	74.4	20.9	20.4
622	80.5	80.6	78.0	78.0	22.0	22.0
613	84.0	83.4	81.4	82.0	22.9	22.3
604	87.8	87.8[b]	84.9	85.4	23.9	25.0
595	91.7	91.7	88.9	89.4	25.0	25.8
589	94.5	95.5	91.6	93.4	25.8	25.0[b]
580	99.2	99.5	96.1	97.8	27.1	27.2[e]
572	103.2	104.4	100.1	101.6	28.2	31.8
565	107.2	110.6	104.1	105.5	29.3	33.3
559	110.6	113.9	107.2	110.5[e]	30.2	32.6
553	114.6	120.0[c]	111.2	116.0	31.4	36.4[h]
547	119.0	122.2	115.6	120.0[f]		
542[1]	122.2	138.1[d]	118.9	113.5		

Average deviation from mean value[2]: [a] 0.5 to 0.6; [b] 1.0 to 1.2; [c] 2.2; [d] 6.4; [e] 1.5 to 1.8; [f] 3.3; [g] 0.7 to 0.8; [h] 4.5.

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[1] Measurements below 542 mμ were subject to such large experimental errors due to the high optical density of the solutions that the data are of doubtful significance and, therefore, not included.

[2] The deviation for an unlettered figure is that of the first lettered figure appearing above it.

side is not strictly simple. This trend away from simple dispersion is even more evident in *p*-phenylazophenyl tetraacetyl-β-D-galactoside, where the discrepancies in rotation between those observed and those calculated by equation (1) are even greater. It is interesting to note in Table I that the negative rotation of the unacylated glycosides become more negative with decreasing wave length, whereas the positive rotation of the acetylated galactoside becomes more positive. No attempts were made to extend dispersion measurements to other *p*-phenylazophenyl β-D-glycosides because of the comparatively low specific rotations of the known members of this class[5] and the high extinction coefficients of their absorption bands.[3]

Experimental Part

Dispersion measurements were made with a Lippich–Landolt precision polarimeter no. 80 and spectroscope monochromator no. 85[6] manufactured and calibrated by O. C. Rudolph and Sons. Solutions of the *p*-phenylazophenyl β-D-glycoside (10^{-1} molar for the glucoside and galactoside and 5×10^{-2} molar for the acetylated galactoside) were made in commercial dioxane and placed in a 10-ml. 1-dcm. polarimeter tube. Measurements were made at room temperature (*ca.* 23°) with no thermostating. Readings were taken at wave lengths indicated in Table I. The half-shade angle of the polarimeter was kept at 5 on its scale during all readings, and the slit widths on the monochromator were varied between 0.3 and 0.6 mm. depending upon the amount of light which would traverse the solution. Measurements were made at the concentrations indicated until increasing optical densities with decreasing wave length made matching of the polarimeter field impossible. At this point the solutions were diluted to 50% of their initial concentration with dioxane. Readings were continued until dilution was again necessary. One or two dilutions were usually sufficient to obtain data as in Table I. The dilution technique could not be employed to permit lower wave length readings as the observed rotation rapidly decreased with each dilution until the experimental errors of measurement made the results meaningless for comparative purposes.

Summary

Rotatory dispersion measurements on *p*-phenylazophenyl β-D-glucoside, β-D-galactoside, and tetraacetyl-β-D-galactoside have been conducted in order to see if the isolated azo chromophore of the aglycone might cause anomalous dispersion by interacting with the asymmetric centers through the conjugation of the benzene ring. The high extinction coefficients characteristic of the absorption bands in the aglycone, however, prevented dispersion measurements as the wave length of the first absorption band was approached.

In the transparent regions of the spectrum the dispersion of the unacylated glycosides was very nearly simple. Divergencies from simple behavior of possible significance were observed as the first absorption band of the aglycone was approached.

The wave length of the active absorption band calculated from a simple Drude equation agreed very well with the wave length of the ultraviolet absorption band as measured spectrophotometrically, indicating that the isolated azo chromophore in the aglycone had no effect on the rotation in the visible regions of the spectrum.

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[6] Purchased with a grant kindly furnished by The Research Corporation, New York.

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Thermal Data on Organic Compounds. XXV. Some Heat Capacity, Entropy and Free Energy Data for Nine Hydrocarbons of High Molecular Weight

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In a series of investigations carried out at Stanford University between 1937 and 1944 heat capacity measurements were made upon twelve hydrocarbons of high molecular weight. From the data thus obtained the corresponding molal entropies were derived and in most instances the free energies of formation were also computed with the aid of available heats of combustion. Results for three of these hydrocarbons (11-*n*-decylheneicosane,[1] and *cis*- and *trans*-decahydronaphthalene[2]) have already been published in other connections. In the present paper we shall present similar results for the remaining nine compounds: *n*-hexadecane, *n*-octadecane, *n*-tetracosane, *n*-dotriacontane, ethylcyclohexane, *n*-heptylcyclohexane, *n*-dodecylcyclohexane, 11-cyclohexylheneicosane and 11-phenylheneicosane.

Materials

The hydrocarbon samples were the best obtainable at the time of these measurements, although more recently *n*-hexadecane and ethylcyclohexane have become available in much purer form. Most of the materials were also used in This Laboratory in determinations of the heats of combustion, in which work non-hydrocarbon impurities are especially serious. Accordingly, appropriate tests were run for ash content, the presence of halogens and in

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[1] F. B. Fischl, B. F. Naylor, C. W. Ziemer, G. S. Parks and J. G. Aston, THIS JOURNAL, **67**, 2075 (1945).

[2] G. S. Parks and J. A. Hatton, *ibid.*, **71**, 2773 (1949).