

**294. *The Analysis of Rotatory Dispersion: 1 : 2-Diphenylethanol.***

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The equilibrium method of analysis has been applied to the rotation-temperature curves of 1 : 2-diphenylethanol. The value of  $\Delta H$  so obtained is in agreement with that obtained by calorimetric measurements. The results show that, in certain cases, the experimental accuracy required for a successful analysis may be quite moderate.

GERRARD and KENYON<sup>1</sup> examined the rotatory dispersion of 1 : 2-diphenylethanol at different temperatures in the homogeneous state and in various solvents. Application of the equilibrium method of analysis<sup>2</sup> to these results for the homogeneous material is recorded below.

## ANALYSIS

Examination of the  $[\alpha]$ - $T$  curves for the different wavelengths suggests, in the light of the findings with 2 : 3-epoxypropyl phenyl ether,<sup>2</sup> that only one of these curves (that for 5461 Å) should be analysable by this method into the rotatory constant of two isomeric forms or conformations. This curve is, in fact, the only one in which all the points lie on a smooth line to within the accuracy previously thought to be required. The result obtained for this line is, therefore, the most probable ( $\Delta H = 5.85$  kcal./mole). The analysis for the other curves was carried out merely to see whether an analysis was possible. Reasonable solutions were obtained for all except that for 4358 Å. For  $\lambda$  6708 Å a straightforward solution was obtained from a smoothed

<sup>1</sup> Gerrard and Kenyon, *J.*, 1928, 2564.

<sup>2</sup> Hargreaves, *J.*, 1957, 1071.

curve even though two of the points lie off the curve by as much as  $0.5^\circ$ . In the case of 2:3-epoxypropyl phenyl ether curves of this kind were found to be useless. The difference in the sensitivity in the two cases lies in the form of the  $[\alpha]-T$  curve. In 2:3-epoxypropyl phenyl ether the change of  $d[\alpha]/dT$  with  $T$  is so small in the visible region, over the range of temperature covered, that certain terms in the solution are reduced nearly to zero, so that the expression becomes unusable. For homogeneous 1:2-diphenylethanol all the terms are of sufficient magnitude; even in this case, however, a smooth curve through the points for  $4358 \text{ \AA}$  does not yield a solution. It seems possible that these readings are in error as the slope of the  $[\alpha]-T$  curve is quite different from those for the other wavelengths. Although by suitable minor adjustments in the values taken, solutions from this line are also possible, as has been pointed out previously,<sup>3</sup> the justification of the method lies in the coherence of the values obtained directly from a smooth curve through the experimental points.

The temperatures in the earlier paper were recorded only to the nearest degree; the success of these solutions implies that in most cases the temperatures were more accurate than claimed.

Wavelength ( $\text{\AA}$ )	$[\alpha]_1$	$[\alpha]_2$	$[\alpha]_3$	$[\alpha]_4$	<i>a</i>	<i>b</i>	$\Delta H$	$\Delta S$
	$[\alpha]_1'$	$[\alpha]_2'$	$[\alpha]_3'$	$[\alpha]_4'$				
5461	{ 31.82°	20.40°	(13.05)°	6.51°	-5.47	111.2	5.85	19.1
	{ 31.82	20.40	16.57	(8.97)				
6708	{ 20.20	12.85	(7.83)	3.41	-4.69	61.17	6.02	19.1
	{ 20.20	12.85	10.32	(5.19)				
5893	{ 26.11	16.80	(10.40)	(4.90)	-3.64	64.08	6.95	22.4
	{ 26.11	16.80	13.39	(6.95)				
5780	{ 27.88	17.68	(11.25)	5.22	-8.56	160.2	4.71	16.7
	{ 27.88	17.68	14.38	(7.50)				
4358	No satisfactory solution.							

The Table gives values for the specific rotations used in solving, by the previous method,<sup>3</sup> the equilibrium relation,  $(b - [\alpha]_4^T)/([\alpha]_4^T - a) = \exp(-\Delta H/RT + \Delta S/R)$ . The values of  $[\alpha]$  used are those given by Gerrard and Kenyon,<sup>1</sup> those in parentheses being interpolated from a smooth curve through the experimental points. *a* and *b* are the rotatory constants of two forms A and B in the equilibrium  $B \rightleftharpoons A$ . The form B is that predominating at low temperatures. The experimental temperatures were given to the nearest degree (c). The temperatures ( $\kappa$ ) corresponding to the values of  $[\alpha]$  are:  $T_1$  333.16;  $T_2$  353.16;  $T_3$  372.92;  $T_4$  398.16;  $T_1'$  333.16;  $T_2'$  353.16;  $T_3'$  363.16;  $T_4'$  387.05.

#### DISCUSSION

The heats of dilution of 1:2-diphenylethanol in the solvents used for the dispersion measurements have been determined, and an attempt has been made to correlate the dispersion and thermochemical measurements.<sup>3</sup> The heat of dilution measures the algebraic sum of the changes in the heat content of the system during dilution due to the breaking and the formation of solute-solute, solvent-solvent, and solute-solvent "bonds." It also includes any heat exchange due to changes in conformational potential energy. Since the barrier which restricts free rotation about a single bond corresponds to about 3 kcal./mole, the energy differences between different energy troughs (or different conformations) will be less than this. The substitution of a methyl group for one of the hydrogen atoms in ethane raises<sup>4</sup> the energy barrier by about 0.5 kcal./mole. The differences in energy between different conformations may, therefore, be expected to be of this order, where no bonding exists, and may be neglected, to a first approximation, in comparison with energy changes due to the formation of bonds. In the dilution of 1:2-diphenylethanol with benzene, and possibly also with carbon tetrachloride and carbon disulphide, it is reasonable to assume that the observed heat changes are due solely to the rupture of solute-solute "bonds." In the attempt to explain the dispersion, a "tied" form of the molecule was proposed for the solution in ethanol and in the cold homogeneous state, this form being distinct from a free, non-hydrogen bonded form, and from one in which any bonding does

<sup>3</sup> Hargreaves, *J.*, 1954, 1233.

<sup>4</sup> Coulson, "Valence," Oxford, 1952, p. 314.

not give rise to an element of "structure" in the solution. The equilibrium method of analysis may thus be applied to these postulated forms of 1:2-diphenylethanol. The difference between the heat content of the forms predominating at high temperatures and that of the form prevalent at low temperatures may consist only in the breaking of "bonds" between like molecules, and in conformational energy changes. It is interesting that the heat-content change calculated on this basis is of similar magnitude to the heat of dilution in a non-polar solvent, *e.g.*, benzene or carbon tetrachloride. Since 1:2-diphenylethanol is monofunctional, *i.e.*, it can undergo change or association only through its single hydroxyl group, this relation is to be expected.

The correlation between the most probable value from the Table,  $\Delta H = 5.85$  kcal./mole, and the heat of dilution, 5.7 kcal./mole in carbon tetrachloride and 5.2 kcal./mole in benzene, is very satisfactory, the differences being of the order of the experimental error in the thermochemical experiments.

The values obtained for  $\Delta S$  are in agreement with the suggestion that the low-temperature form is a hydrogen-bridged state. The large value of the entropy change suggests a considerable loosening of the "structure" of the solution in attaining the high-temperature form. The calculations involved are such, however, that at present it would be unwise to place much reliance on the magnitude of the values of  $\Delta S$  so obtained.

*Values and Dispersion of the Rotatory Constants.*—The rotatory constant  $a$  obtained by this analysis is too small to account for the observed rotations in carbon disulphide, chloroform, and pyridine, though in agreement with the values observed in benzene and carbon tetrachloride. It seems likely, however, from the dilution experiments, that some kind of association complex or compound is formed between 1:2-diphenylethanol and chloroform or pyridine, so that the rotatory power observed in these solvents is not strictly that of 1:2-diphenylethanol itself. In carbon disulphide, on the other hand, there is no suggestion from the heat of dilution that complex formation occurs, yet the value of  $a$  is greater than  $a$ . The whole range of observed rotations of the solute under different conditions should lie between the value of  $a$  and that of  $b$ . Compared with the experimental values in different solvents,<sup>1</sup> the values of  $a$  given in the Table are too low by as much as a half. As was pointed out previously,<sup>2</sup> the values of these rotatory constants are more susceptible to error than are  $\Delta H$  or  $\Delta S$ . The values of  $a$  and of  $b$  obtained from the different wavelengths vary widely, so it is useless to consider their dispersion. However, by using the most probable value of  $\Delta H$  and  $\Delta S$  it is possible to calculate  $a$  and  $b$  for each wavelength from the rotation at any two temperatures. By using 333.16° K and 363.16° K the following values are obtained:

$\lambda$ (Å)	$a$	$b$	$\lambda$ (Å)	$a$	$b$
6708	-3.14	69.84	5461	-4.21	108.5
5893	-3.94	90.03	4358	(-1.65)	(197.1)
5780	-4.01	95.71			

Although the magnitudes of these values are probably incorrect their dispersion is of some interest. Results for 4358 Å (see above) being neglected, the  $b$  values show pseudosimple dispersion, the straight-line plot of  $1/b$  against  $\lambda^2$  giving an intercept on the  $\lambda^2$  axis corresponding to  $\lambda_0$  1900 Å. The plot of  $1/a$  against  $\lambda^2$  giving a straight line and a negative value of  $\lambda_0^2$ . The apparent dominance of the "phenyl band"<sup>3</sup> at low temperatures and in alcoholic solution corresponds to the interaction of two dispersions with low values of  $\lambda_0$ . The preponderance of the B form corresponds to the apparent dominance by the longer waveband. The lower rotatory strength of  $a$  than of  $b$  may be due to the possibility of the orientation of the benzene nuclei in the "free" form in such a way that their contributions to the rotatory strengths nearly cancel one another.