The Heats of Dissolution and the Optical Rotatory Dispersion of 1 : 2-Diphenylethanol.

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The heats of dissolution of 1 : 2-diphenylethanol in selected solvents have been determined. Correlation of these measurements with the optical rotatory dispersion of the substance has been attempted. The measurements tend to support the view that the rotatory dispersion of the alcohol may largely be explained in terms of the " structure " of the solution. The use of a thermistor in a bridge circuit as a thermometer in a semimicro-calorimeter is described.

Gerrard and Kenyon (*J.*, 1928, 2564) examined the rotatory dispersion of 1 : 2-diphenylethanol in various solvents in the visible spectrum at room temperature, and also the variation of the dispersion of the homogeneous substance with temperature. Although they were unable to examine the homogeneous substance below 60° (m. p. 67°), if their results are extrapolated to room temperature it will be seen that the values obtained are very similar to those observed in ethyl-alcoholic solution. This suggests that the two systems may be similar in the origin of their dispersion and that the " structure " of the solution is one of the major factors determining the dispersion. Since hydrogen-bridge formation is clearly the most likely cause of such liquid " structure " it was decided to measure the heats of dissolution or dilution of 1 : 2-diphenylethanol in the same solvents. In view of the small quantities of the substance then available it was necessary to use a semimicro-calorimeter which yields results of a moderate accuracy.

EXPERIMENTAL

Thermometer.—A " Stantel " thermistor, type F2311/300, was used in conjunction with a bridge circuit as shown in Fig. 1. The apparatus consisted of a rotary-type Post Office box combined with a rotary potentiometer (resistance 60 ohms) of Admiralty " Inpot " A.C. pattern. A 50,000-ohms resistance was used in series with the 2-volt accumulator to minimise the heating effect of the thermistor, which is otherwise noticeable with the small volumes used in these experiments. The galvanometer (Tinsley 4500H) had a sensitivity of 200 mm. per microamp. at 2 metres. At room temperature the sensitivity of the thermistor with the above equipment was about 0·0025°. It was calibrated throughout the range against a Beckmann thermometer.

Heating Circuit.—See Sturtevant, " Technique of Organic Chemistry," Interscience Publ., New York, Vol. I, " Calorimetry," 1945, p. 331.

Heater.—" Minalpha " wire (35 S.W.G.) was wound on a glass tube forming a duct for the stirrer. The stirrer guide was sealed at the top with a gas-tight seal to prevent " pumping." The resistance of the heater was about 10 ohms; it dissipated about 2 watts. A much larger wattage is desirable but was not feasible with the potentiometers available.

Pipette.—A special " self-emptying " pipette with a Soxhlet-type syphon was used [Fig. 2*a*]. The pipette was operated by a plunger in such a way that no air was drawn in from outside the calorimeter. The most satisfactory form of plunger from the chemical point of view was a loop formed in a stainless-steel wire which was then twisted to form a handle. A pad of cotton wool was worked into the loop.

Mode of Operation of the Calorimeter.—The calorimeter was charged with the solid material. The pipette was filled with solvent and weighed, with covers over the holes X and Y [Fig. 2*a*] and then placed in the calorimeter. The stirrer was started, and the whole apparatus allowed to reach a steady temperature. The plunger was then depressed, and the temperature decrease read. The cotton-wool plug was moistened with solvent, after which it acted as an efficient seal, and the plunger was not allowed to make contact with the body of the solvent. The pipette and any remaining solvent were re-weighed at the end of the experiment.

Accuracy.—The accuracy obtained in the determination of the temperature decrease on dissolution was 1% or better, since with the dilute solution used in these experiments the dissolution was virtually instantaneous when compared with the rate of heat loss through the walls of the calorimeter. In other experiments, where an attempt was made to determine heats of dilution directly, much more concentrated solutions were required initially; with these the accuracy was much less owing to the time taken for the solute to dissolve. The actual temperature changes occurring on dilution can, however, be measured very accurately owing, again, to their instantaneous nature. In experiments made to determine the heat equivalents of the calorimeter and contents, however, the accuracy was rather less than in the other determination, being 3—5%, owing to the low power available which results in a relatively large correction for heat losses.

FIG. 1.

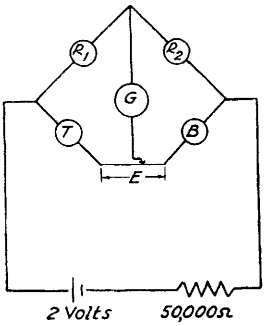

FIG. 1. B = Balancing resistance;
E = rotary potentiometer;
G = galvanometer;
R_1 and R_2 = ratio arm resistances;
T = thermistor.

FIG. 2*a*.

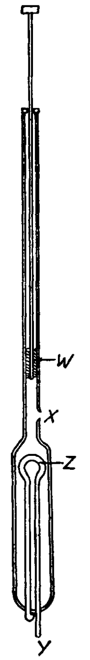

FIG. 2*a* (scale 1 : 3). *Pipette.*
W = Cotton-wool plunger; X and Y = apertures; Z = Soxhlet syphon.

FIG. 2*b*.

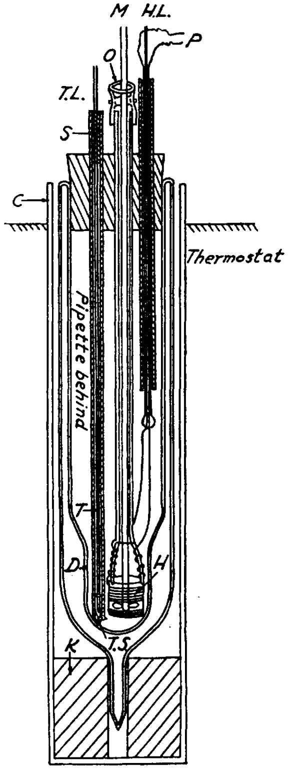

FIG. 2*b*. *Calorimeter, partly sectional.*
C = copper jacket; D = Dewar flask; H = heater; $H.L.$ = heater leads; K = cork support; M = drive from motor (0·05 h.p. fitted with 40-watt resistance and a brake); O = oil seal; P = potential leads; S = wax seal; T = thermistor; $T.L.$ = thermistor lead; $T.S.$ = thermistor shield.

The 1 : 2-diphenylethanol used was kindly supplied by Dr. Gerrard; recrystallised from ethyl ether and light petroleum, it had m. p. 66—66·5°.

Solvents.—These were fractionally distilled, dried as follows, and redistilled immediately before use. Drying agents : for carbon disulphide, phosphoric oxide; for carbon tetrachloride, chloroform, and acetone, calcium chloride; for ethyl alcohol, diethyl phthalate and sodium. Benzene of recrystallisable grade was purified by freezing.

DISCUSSION OF RESULTS

Comparison of the values of the optical rotatory power and the heats of dilution (as measured by $\Delta H—L$, where ΔH = the heat of dissolution to give a dilute solution and L = latent heat of fusion of the solute) of solutions of 1 : 2-diphenylethanol suggests that solvents may be classified into three groups so far as their interaction with this substance is concerned. For ethyl-alcoholic and acetone solutions $\Delta H—L$ is small, as was to be expected. The heat of dilution is approximately the same in the benzene, carbon disulphide, and carbon tetrachloride solutions at ~5·4 kcal./mole. The pyridine solution, on the other hand, shows a positive heat of dilution, and chloroform is anomalously placed. The rotatory dispersion of the chloroform solution makes it likely that there is a slight evolution of heat on dilution owing to combination with the solute, since the magnitude of the heat of dilution in chloroform is less than that observed in benzene, carbon disulphide, and carbon tetrachloride, where it may be assumed that no new " bonds " are formed during the dilution process. This behaviour is in conformity with other work that shows chloroform to have a tendency to dipolar association or the formation of other weak linkages in excess of that shown by solvents such as carbon tetrachloride (*e.g.*, Zellhoefer, Copley, and Marvel, *J. Amer. Chem. Soc.*, 1938, **60**, 1337; Macleod and Wilson, *Trans. Faraday Soc.*, 1935, **31**, 596; Le Fèvre, *ibid.*, 1937, **33**, 207).

TABLE 1

Thermostat temperature 25°. In each measurement 10 c.c. of solvent were added to 1 g. of solute, giving a concentration of 2—5 moles %.

Solvent	Dielectric constant	$[\alpha]_{4358}$ *	$[\alpha]_{5461}$ *	ΔH, kcal./mole	ΔH, Joules/mole	$\Delta H - L$, kcal./mole	$\Delta H - L$, Joules/mole
C_5H_5N	12·3	− 14·5°	−11·00°	−2·73	−11·4	+1·5	+ 6·3
$CHCl_3$	4·8	− 12·02	− 9·71	−7·5	−31·4	−3·3	−13·8
CS_2	2·6	− 9·00	− 8·15	−9·5	−39·8	−5·3	−22·2
C_6H_6	2·3	− 0·20	− 3·00	−9·4	−39·3	−5·2	−21·8
CCl_4	2·2	+ 6·90	+ 1·00	−9·9	−41·4	−5·7	−23·9
$COMe_2$	20·7	+ 44·63	+22·10	−5·8	−24·3	−1·6	− 6·7
EtOH	24·3	+120·8	+64·9	−5·6	−23·4	−1·4	− 5·9
Homog. extr'd. ...	—	+120	+67	—	—	—	—

$L^{39°}$ = − 4·6 kcal./mole (19·3 joules/mole).
$L^{27·7°}$ = − 4·3 kcal./mole (18·0 joules/mole).
$L^{25°}$ (by extrapolation) = − 4·2 kcal./mole (17·6 joules/mole).
* The rotatory powers are from Gerrard and Kenyon (*loc. cit.*).

A qualitative correlation can be seen between the heats of dilution (as measured by $\Delta H - L$) and the magnitude of the rotatory powers, and particularly the rotatory strengths of the shorter wave-band corresponding to the sum of C–OH, C–C, and C–H absorption. The small negative value of the heat of dilution of the ethyl-alcoholic and acetone solution suggests that the heat of formation of the solute–solute and solvent–solvent " bonds " may be less than that of the solute–solvent " bonds." If the value of ΔH for the heat of dissolution of 1 : 2-diphenylethanol in ethyl alcohol is subtracted from that of the heat of dissolution in benzene a value of 4 kcal. per mole is obtained, whilst $\Delta H - L$ for the benzene solution yields 5·4 kcal. per mole for the energy required to overcome the intermolecular forces in the alcohol, compared to the 3 kcal./mole for the hydrogen-bridge bond in methanol (Redlich and Kister, *J. Chem. Phys.*, 1947, **15**, 849).

The plot of $[\alpha]$ against λ for the homogeneous material at 60° deviates from that of a *simple* dispersion curve by less than the experimental error, so it is not surprising that an attempt to derive a two-term equation from four experimental points was unsuccessful. On the other hand, the method of deriving a two-term Drude equation by the use of approximately known absorption frequencies of the molecule and two experimental points yields the results given in Table 2.

The justification of this method lies in the obvious " complexity " of the dispersion (Lowry, " Optical Rotatory Power," Longmans Green, 1935, p. 124) and in the implication of the one-electron theory (Condon, *Rev. Mod. Phys.*, 1937, **9**, 432) that most electronic transitions will contribute to the activity of the molecule.

In the carbon disulphide, benzene, and chloroform solutions the visible region of the spectrum includes the " sensitive " region of the dispersion. Hence, widely varying dispersion ratios are obtained together with the appearance of discontinuity. An analysis of the rotatory powers into rotatory strengths shows that continuity does, in fact, exist throughout the range of solvents.

It may be argued that in the case of the ethyl-alcoholic and acetone solutions the system contains an element of " structure " lacking in the other cases and that the rather high values of the rotatory power observed in these solvents are due to the " tying " of the active molecule in one configuration. This is in conformity with the finding, by Kauzman, Walter, and Eyring (*Chem. Reviews*, 1940, **26**, 380) among others, that ring formation increases the rotatory power approximately ten-fold. This simple picture becomes somewhat blurred when the dispersion is examined, since it is shown below that, whilst the rotatory strength of the phenyl band is increased by the " partial lattice " formation, that of the hydroxyl band is decreased. According to the polarisability theory of rotatory power (Kirkwood, *J. Chem. Phys.*, 1937, **5**, 479, and particularly Bernstein and Pedersen, *ibid.*, 1949, **17**, 888) the rotivity, Ω, due to an asymmetric carbon group, as in *sec.*-butyl alcohol, may be considered as being due to two rotivities of opposite sign and a third of lower power corresponding to the different configurations about a single bond ($\Omega_1 + \Omega_2 + \Omega_3 = 0$). The observed rotatory power $\{[\alpha] = [\Omega](n^2 + 2)/3\}$ then depends on the proportion of each configuration present. If it could be shown that these different configurations have different optically active absorption frequencies then restriction of rotation, and of configuration, would be sufficient in itself to explain the observed dispersion of 1 : 2-diphenylethanol. On the other hand if, as seems likely, the absorption frequencies are approximately the same, then the dispersion must be explained in other terms.

TABLE 2

$[\alpha]_\lambda = p/(\lambda^2 - \lambda_1^2) + q/(\lambda^2 - \lambda_2^2)$, $\lambda_1 = 0{\cdot}25\mu$ and $\lambda_2 = 0{\cdot}15\mu$ being taken as very approximate wave-lengths for the benzenoid and hydroxyl bands and the $[\alpha]$ values being used for $\lambda = 0{\cdot}5461\mu$ and $\lambda = 0{\cdot}4358\mu$.

Solvent	Temp.	*p*	*q*	Solvent	Temp.	*p*	*q*	ΔH (kcal./mole)
Homog.	125°	6·94	6·33	C_5H_5N	20°	4·59	8·40	−2·75
,,	115	7·32	6·16	$CHCl_3$	20	4·60	8·05	−7·5
,,	100	8·58	6·48	CS_2	20	4·58	7·53	−9·5
,,	90	9·97	5·92	C_6H_6	20	5·50	7·26	−9·4
,,	80	9·32	5·28	CCl_4	20	6·86	7·86	−9·9
,,	70	10·29	4·98	$COMe_2$	20	9·58	5·10	−5·8
,,	60	11·05	4·16	EtOH	20	17·77	3·11	−5·6

In the case of the pyridine solution where a solute–solvent complex is apparently formed, some difference in the absorption from that of the simple molecule is to be expected, and possibly associated with it some change in the dispersion also. The method of calculation of the rotatory strengths used above makes it possible that the variation in the rotatory strengths shown in Table 2 is really to be attributed to a change in the frequency of the absorption band. However, if the increase in the rotatory strength of the shorter wave-band in going from benzene to pyridine solution is to be attributed entirely to this cause, the wave-band would have to be shifted some 600 Å towards the red. In chloroform solution the corresponding shift would be 400 Å. Neither of these shifts seem reasonable. Furthermore, a shift in the absorption wave-length would not account for the variation between alcoholic and benzene solutions. It may be noted that there is some correlation between the rotatory strengths and heats of solution of 1 : 2-diphenylethanol and the dielectric constant of the solvent. This relationship may be expected to be rather that between two effects with the same cause, than that between cause and effect. It is therefore necessary to attribute the variation of the rotatory strengths largely to the other factor which may affect them, *viz.*, the symmetry of the molecule or group (Condon, *loc. cit.*).

In the discussion of the effects of configurational changes in an optically active molecule on the symmetry of the field in which its electrons " move " it is convenient to consider the effect of these changes in an analogous model which does not contain an asymmetric centre, since it is a reasonable assumption that symmetry changes occurring in this case may be superimposed upon the asymmetry of the active molecule. If the active 1 : 2-diphenylethanol molecule is included in a hydrogen-bridge network structure the symmetry of the O–H group may be considered to be increased, whereas the formation of a complex between the hydrogen of the hydroxyl group and the nitrogen of the pyridine molecule may be considered to increase the dissymmetric field in which the optical electrons of the hydroxyl group move. The imprecise use of the terms element of symmetry or increase in the dissymmetry is clearly to be deprecated—they are used here for want of better terms. As an example of their implication in this case, if the hydrogen-bridge structure were to be such that the O–H–O bonds were of equal length, then a new element of symmetry would definitely be introduced into a hydroxyl group : it would receive a diad axis. Though the lengths of the bonds in O–H–O are not generally considered to be equal (Davies, *Ann. Reports*, 1946, **43**, 14) the dissymmetry of the field introduced by this non-symmetry of bond length may be slight compared with the general gain in the symmetry of the field accompanying the association.

It appears from a model that the large value of the rotatory strength of the 2500 Å band of the homogeneous substance at the lower temperatures and of the alcoholic solution at 20° must be connected with a tendency of the phenyl groups to orientate themselves as nearly parallel to one another as possible. In the *trans*-phenyl position much closer packing appears to be possible than in the *cis*-phenyl position. In 1 : 2-diphenylethane the *cis*-phenyl position has two planes of symmetry whereas in the *trans* there is one plane and a centre. The non-asymmetric remainder of the 1 : 2-diphenylethanol molecule might therefore be considered to have rather similar symmetry from the point of view of optical activity in either *cis*- or trans-position. The greatest dissymmetry will be shown by two intermediate configurations about the central C–C bond with approximately equal and opposite contributions to the rotatory strengths ; these are, however, unlikely in a hydrogen-bonded structure for spatial reasons. The most probable configuration in the close-packed state appears to be a *trans*-phenyl position in which the rotation of the phenyl groups is restricted owing to close packing, and the central bond of the $\cdot CH(OH)\cdot CH_2\cdot$ group is twisted out of the plane of the phenyl groups, thus removing both a plane and a centre of symmetry. This element of dissymmetry will be superimposed upon the dissymmetry of the remainder of the molecule, giving a higher rotatory strength to the phenyl band, and its contribution will diminish as freedon of rotation is increased with rise of temperature. It is noteworthy in connection with the general symmetry of the substance that its melting point is some 20° below what might be expected by analogy with the simple ethane derivatives.

Though it may be considered that dissymmetry is not a quantity variable by degree but a quality capable of difference only in kind, it can also be argued that the variation of rotatory strengths with change of structure is, in part at least, a measurement of dissymmetry. That this is so follows from the fact, demonstrated above, that the variation of rotatory strengths with changed conditions cannot be accounted for purely in terms of the strengths of the electronic binding which would be reflected in the absorption frequencies of the molecule, nor is it usual for solvent effects to have a marked influence on the intensities of the absorption of the system. The changes in the rotatory strengths must therefore involve a change in the structure and symmetry of the system. Though there may be other ways of explaining the rotatory dispersion of 1 : 2-diphenylethanol, a satisfactory qualitative picture is obtained in this way.

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