

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Magneto-Optic Rotation. III. Carbon Disulfide in Substituted Benzenes¹BY CHAS. E. WARING, HERBERT H. HYMAN² AND SAMUEL STEINGISER²

This is the third paper of this series reporting on the applications of magneto-optic investigations to typical problems in chemistry. In our last paper^{1b} the simple structure of liquid carbon disulfide was questioned in light of certain experimental anomalies in the Verdet constant of carbon disulfide in benzene. To establish more definitely the points raised by that paper, the Verdet constants of carbon disulfide in several substituted benzenes and cyclohexane were determined.

Experimental

Materials and Apparatus.—The carbon disulfide was the same as previously reported. Its physical constants were b. p. 46.3°, d_{25} 1.2551 g./cc., n_D^{25} 1.6234; lit. values are 46.3, 1.2554, and 1.6239, respectively.

The other chemicals were the purest obtainable. They were distilled from phosphorus pentoxide through an efficient fractionating column. In each case only those fractions were collected which boiled at the literature value within the limit of error of the conventional mercury in glass thermometer. The density and refractive index of each substance at 25° both as measured and from the literature are

	d , exptl.	d , lit.	n_D , exptl.	n_D , lit.
Toluene	0.8611	0.8610	1.4929	1.4928
Chlorobenzene	1.1006	1.1010	1.5220	1.5218
Bromobenzene	1.4877	1.4886	1.5566	1.5565
Nitrobenzene	1.1963	1.1982	1.5501	1.5499
Cyclohexane	0.7763	0.7750	1.4235	1.424

All of the values except the density of nitrobenzene and possibly cyclohexane are well within the limit of error of the experimental technique employed and probably the literature values as well. There is no concentration of impurity in any material great enough to affect the measurements or the conclusions drawn.

The solutions were prepared using calibrated pipets. The densities employed in the calculations of weight and therefore mol percentages from the measured volumes were experimental ones. Measurements of densities of the same solutions before filling and after emptying our tube gave identical results, confirming our belief that evaporation errors were wholly negligible.

Densities were measured on a Christian Becker chainomatic specific gravity balance, calibrated against distilled water. For some of the earlier measurements an Ostwald-Sprengel type pycnometer (5-cc. capacity) was used, but the chainomatic gave results of apparently the same precision.

(1) Nos. I and II of this series are (a) Magneto-Optic Rotations of Paramagnetic Ions, *THIS JOURNAL*, **60**, 2294 (1938). (b) Magneto-Optic Rotation: Carbon Disulfide and Benzene Solutions, *ibid.*, **62**, 2028 (1940).

(2) Submitted in partial fulfillment for the Master of Science degree.

sion with much less effort. The relative densities are reliable to at least 0.05%.

The refractive indices were measured in an Abbe refractometer. They are probably good to at least 0.03%.

The apparatus employed for determining the Verdet constants has been described.^{1b} A G. E. sodium vapor lab arc was used as our source of sodium light. The water jacket surrounding the tube was maintained at about 25° by circulating thermostated water through it by means of a small pump. The entrance and exit temperature of the circulating water was measured and the average temperature used in correcting the measured Verdet constants to 25°.

Measurements.—The apparatus was calibrated against carbon disulfide. The Verdet constant of this substance at 25° was taken as 0.04190 unit. All other Verdet constants are expressed in terms of this primary standard. This is equivalent to the standard adopted in our last paper where $V_{15}(\text{CS}_2)$ was defined as 0.04240 unit. The constant of the apparatus for this set of measurements was 0.017625 Verdet unit/degree/ampere, with an a.d. 0.000040, A.D. 0.000007, % D. 0.04%.

For every solution measured the Verdet constant is the average of thirty-six independent readings of the rotation and the current, eighteen with the field in each direction. The largest percentage deviation for any solution was 0.06%. The "probable error" is in all cases below 0.05% and this value may be taken as indicative of the reliability of the measurements. Thus the Verdet constants reported are probably good on the relative scale we employ to about 0.000025 unit.

The molecular Verdet constants $\overline{MV}/D = V$ are therefore reliable to about 0.002 unit or 0.1%, since their precision involves the precision of the independently measured densities, concentrations, and Verdet constants.

Data.—Table I summarizes the experimental data. The Verdet constants, densities and refractive indices for the various solutions investigated give smooth curves when plotted against mole %. The molecular refractivities give the expected straight lines when plotted in similar fashion. The molecular Verdet constants are plotted in Fig. 1. For the purposes of the following discussion the significant features of these

curves are the breaks near the pure carbon disulfide end and the extrapolated straight line portion.

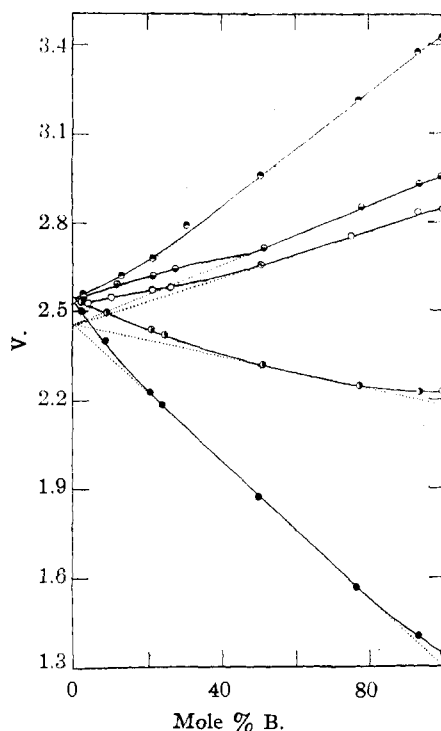


Fig. 1.—○, Toluene; ●, chlorobenzene; ◼, bromobenzene; ◻, nitrobenzene; ●, cyclohexane.

Discussion

As has been pointed out many times the molecular Verdet constants are proportional to the rotation of a single molecular group and if the partial molecular constant of any substance changes in solution it indicates either a change in the structure of some molecular group or the existence of a new molecular species in the solution. On these curves the partial molecular Verdet constant of carbon disulfide, no matter what its value in the presence of small amounts of foreign material, is reduced in dilute solutions to a value of 2.46 ± 0.02 for all of the substances investigated. The value previously found for carbon disulfide-benzene system was 2.44. Although the benzene system was observed at 15° , this function as we have pointed out is virtually independent of temperature for small changes (provided these temperature changes do not produce a change of intramolecular structure). This extrapolated value, which may reasonably be regarded as the molecular Verdet constant of carbon disulfide in the absence of any mutually interactive

TABLE I						
Mol. % B	V_{25}	d_{25}	V_{25}	$n_{D,25}^{25}$	$N_{D,25}^{25}$	
B = Toluene						
0.00	0.04190	1.2551	2.540	1.6234	21.39	
4.33	.04027	1.2220	2.531	1.6118	21.86	
10.84	.03863	1.1796	2.549	1.5968	22.48	
21.23	.03624	1.1206	2.571	1.5767	23.50	
26.07	.03524	1.0962	2.581	1.5681	23.96	
50.56	.03144	0.9958	2.658	1.5340	26.28	
77.05	.02853	.9148	2.757	1.5089	28.86	
93.41	.02725	.8747	2.834	1.4967	30.43	
100.00	.02660	.8610	2.844	1.4929	31.06	
B = Chlorobenzene						
2.87	.04101	1.2404	2.551	1.6173	21.77	
11.77	.03927	1.2181	2.592	1.5930	22.37	
21.74	.03720	1.1956	2.618	1.5854	23.59	
27.42	.03642	1.1875	2.641	1.5780	24.06	
51.39	.03290	1.1493	2.714	1.5520	26.36	
77.78	.03061	1.1206	2.852	1.5332	28.93	
93.70	.02940	1.1065	2.927	1.5243	30.39	
100.00	.02891	1.1010	2.954	1.5220	31.16	
B = Bromobenzene						
2.79	.04131	1.2639	2.562	1.6179	21.72	
12.96	.03935	1.2992	2.623	1.6050	22.96	
21.26	.03843	1.3375	2.681	1.5990	24.01	
30.52	.03739	1.3495	2.793	1.5910	25.26	
50.57	.03545	1.4029	2.957	1.5757	27.59	
77.20	.03367	1.4518	3.213	1.5335	31.02	
93.50	.03271	1.4750	3.374	1.5581	33.16	
100.00	.03247	1.4886	3.424	1.5566	33.93	
B = Nitrobenzene						
2.33	.04099	1.2485	2.532	1.6193	21.68	
8.98	.03857	1.2408	2.497	1.6079	22.39	
20.88	.03464	1.2268	2.440	1.5930	23.88	
24.76	.03381	1.2260	2.420	1.5904	24.15	
51.22	.02798	1.2090	2.318	1.5684	27.12	
77.27	.02397	1.2000	2.246	1.5568	30.15	
93.65	.02216	1.1965	2.225	1.5518	32.07	
100.00	.02166	1.1963	2.228	1.5501	32.80	
B = Cyclohexane						
2.18	.04038	1.2331	2.498	1.6142	21.57	
8.64	.03683	1.1797	2.398	1.5904	21.98	
20.73	.03129	1.0928	2.226	1.5527	22.75	
23.89	.03001	1.0731	2.183	1.5448	23.02	
49.93	.02193	0.9385	1.871	1.4872	24.57	
76.49	.01601	.8407	1.567	1.4466	26.13	
93.40	.01325	.7928	1.398	1.4295	27.22	
100.00	.01240	.7763	1.343	1.4235	27.64	

forces, differs markedly from the experimental value for pure carbon disulfide, 2.540.

There is no reason to suspect compound formation in the solutions investigated. Therefore it is necessary to postulate some change in the internal molecular structure of carbon disulfide on going from the pure material to fairly high concentrations of foreign liquids.

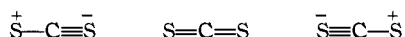
Since carbon disulfide has zero dipole, an as-

sociation of the usual type is impossible. Furthermore, there is considerable evidence that such ordinary association while it produces an effect on the Faraday rotation proper, produces a compensating density effect so that the molecular Verdet constant curve would not be affected.

However, there are certain properties of carbon disulfide, such as its long liquid range, which are not readily explainable on the grounds of a simple structure.

Considering the next possibility, a change in the internal bond structure of the carbon disulfide, we must first examine the reliability of the usual conception of the pure CS₂ structure. Although all texts regard the structure as simply a linear doubly bonded S=C=S arrangement, there is no experimental evidence for this. Hibben³ points out that the Raman spectrum of carbon disulfide does not give the values that would be predicted for this doubly bonded carbon to sulfur, and several attempts to strain it to so fit have been shown inconsistent with the data. However, it does not reveal any complex associated structure. There has been no acceptable explanation of the experimental Raman spectrum of liquid carbon disulfide offered up to the present.

Measurements on the magnetic susceptibility of carbon disulfide vapor reveal the presence of three resonance forms



If these forms exist in the liquid state as well, it is possible to construct a hypothesis which will satisfy all the known requirements somewhat along the following lines.

Although the over-all dipole of liquid carbon disulfide would be zero if the first and third forms existed in equal amounts, as is obviously necessary, any single resonating molecular group would undoubtedly have a resultant internal dipole which would bind it loosely to an adjacent resonating group. The introduction of a foreign species would tend to destroy the stability of the binding between the unsymmetrical resonating forms and therefore their internal stability. If the amount of foreign material became so great that the symmetrical doubly bonded carbon disulfide were the only stable structure, the partial molecular Verdet constant would become stabilized at a value which would be the same irrespective of the foreign material added.

(3) "The Raman Effect and its Chemical Applications," A. C. S. Monograph No. 80, Reinhold Pub. Corp., New York, N. Y.

In other words, the molecular Verdet constant value of 2.46 may be considered as describing the behavior of carbon disulfide molecules in the absence of solute molecules, but without having the possibility of approaching each other: that is, a condition where solute molecules have been withdrawn but the space they occupied remains vacant. Under such conditions the charge cloud associated with each molecular group or the eigenfunctions describing it will be separate and the structure of the carbon disulfide would be comparatively rigid.

Actually, however, the removal of solute molecules allows the carbon disulfide molecules to approach each other more and more closely. Finally, a large proportion of the carbon disulfide molecules approach each other and enter the resonating state we have postulated. Here they tend to lose their individual eigenfunctions. As the eigenfunctions become more indiscriminant, the less rigid this intramolecular structure becomes and the more susceptible to external influences, in this case, a magnetic field.

This prediction of behavior is, of course, exactly what can be seen from the experimental data. However, we would expect the nature of the foreign substance added to influence the amount necessary to disturb the pure carbon disulfide structure. Table II summarizes this effect. We note that the greater the internal pressure (as given in the table by the equivalent expression of Hildebrand $a^{1/2}/V$), the less material is required to effect the initial reduction in the molecular Verdet constant of carbon disulfide.

TABLE II

Substance	Dipole 18°	Vol./ mol. 25°, cc.	V _{25°}	Int. press. $a^{1/2}/V$	Dev. range, ^a %
Carbon disulfide	0	59.8	2.540	9.98	
Benzene	0	89.4	2.672	9.00	5-40
Toluene	0.4	106.9	2.844	8.62	0-40
Chlorobenzene	1.56	102.2	2.954	9.52	12-40
Bromobenzene	1.49	105.4	3.424	8.95	5-25
Nitrobenzene	4.0	102.9	2.225	?	?
Cyclohexane	0	108.8	1.346	7.80	0-25

^a This range is the portion of the curve which does not lie on a straight line ending in either 2.54 or 2.46 at the carbon disulfide axis.

On the other hand, the initial slight resonance effect that raises the value of the partial molecular Verdet constants from its extrapolated value is dependent, on our hypothesis, solely on the pres-

ence of enough pairs of carbon disulfide groups being in contact to produce a measurable effect. A study of the curves reveals, therefore, that no special property of the solvent can be found to control this rise. However, it is obvious that the nearer the molecular Verdet constant is to that of carbon disulfide, the slighter the change in the partial molecular Verdet constant of that substance that is necessary to show itself on the curve. So that while an equal elevation over the extrapolated value takes place at the same initial mole per cent., it is not apparent in the case of cyclohexane and bromobenzene until a higher concentration of carbon disulfide is reached.

The fact that the permanent dipole of the foreign materials apparently has no effect on any aspect of these curves serves to indicate that it is the presence of a neighboring substance with a reversible or at least variable dipole that stabilizes the unsymmetrical carbon disulfide forms.

This would be expected on the hypothesis we have presented and confirms the validity of the entire concept as an explanation of this specific Verdet constant effect.

To complete this hypothesis, it is necessary to show how the resonating structure would have a different molecular Verdet constant than the simple doubly bonded structure that we have postulated is the final form, although to simply assume it, is not unreasonable if the Verdet constant is in any way a function of structure. The quantitative quantum mechanical treatment of the Faraday effect has not yet been applied to anything but the odd electron structures that produce the characteristic rotation of paramagnetic ions.

However, as we have pointed out earlier in this paper, if the appropriate eigenfunctions were to

be assigned to the simple $S=C=S$ structure so that its molecular Verdet constant could be calculated as 2.46, it is not unreasonable to suppose existence of the resonating forms and their resulting interaction would so affect the electron distribution of the liquid carbon disulfide that the external magnetic field would have an augmented effect. We may shortly be able to determine that electron distribution in the pure liquid by observing what alteration in these eigenfunctions is necessary to produce the experimental molecular Verdet constant of 2.540.

Whatever the change in structure actually is, it merely is one that affects the response of the internal electron configuration to a magnetic (or electrical) field. Thus the molecular refraction using the Lorenz-Lorentz formula gives a normal straight line for these solutions when plotted against mole per cent.

Thus we see, in a qualitative way at least, how the magneto-optic rotation can be used as a powerful tool in chemical research. Further work in the use of this tool is now in progress in this Laboratory.

Summary

The Verdet constants, densities and refractive indices of solutions of carbon disulfide in toluene, chlorobenzene, bromobenzene, nitrobenzene and cyclohexane were measured at 25°.

The molecular Verdet constants and molecular refractivities were calculated for each of these solutions.

A resonance structure for liquid carbon disulfide is postulated and shown to be consistent with all experimental data and to explain several previously known anomalies.

BROOKLYN, NEW YORK

RECEIVED MARCH 3, 1941