

The Polarisation of the Light scattered by some Organic Vapours.

BY

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Introduction.

In two recent papers,¹ one of the authors has developed an approximate theory of the optical anisotropy of molecules which has been found helpful in explaining the broader features of its dependence on molecular structure. For further progress, it was felt desirable to secure more data regarding the polarisation of light scattered by vapours of substances whose molecular structures are known from other considerations and the experiments described in this paper were undertaken with that view. An extensive series of measurements on the polarisation of the light scattered by organic vapours has been recently published by A. S. Ganesan,² and another series both as regards intensity and polarisation on methane and some of its homologues by Cabannes and Gauzit.³ Most of the substances studied by us differ, however, from those of the above two investigations and the apparatus employed also possesses some features of interest, having been designed for work with vapours which require heating for their production. In this paper, we have given a brief account of our experiments followed by a discussion of the results

¹ 'The Structure of Molecules in relation to their Optical Anisotropy.' Part I, Proc. Roy. Soc. A, Vol. 107, p. 684; Part II in course of publication.

² Phil. Mag. Vol. XLIX, June 1925, p. 1216.

³ Journ de Physique, Ser. VI, Tome VI, pp. 182-198 (June 1925).

obtained and of some points connected with the measurement of depolarisation in gases and vapours; the optical anisotropy of the carbon atom and its significance are also considered.

Apparatus.

The main part of the apparatus consisted of a double-bulbed (diameter of bulbs 5 to 6 cms.) glass tube of the form shown in the figure (Fig. 1).¹ Particular care was taken to see that the smaller bulb was blown clear and uniform with no blob or streak at its bottom. After cleaning and drying, a small quantity of the pure substance was introduced into the tube and, after pumping out the air inside, the horn end of the tube was sealed off. The bulbs and tube were painted black leaving only three small windows, two at the sides of the larger bulb for the entrance and exit of the incident light and the third at the bottom of the smaller one for the observation of the scattered track, the stem of the tube serving as a background. Experiments with a glass cross-tube of the kind used by Cabannes and his co-workers showed that it was difficult to secure anything like the satisfactory background obtained with metal tubes fitted with diaphragms. Since the introduction of metal diaphragms inside the glass cross would lead to the presence of undesirable impurities especially when organic vapours at higher temperatures were being studied, the expedient of a double bulb was adopted, the constriction between the bulbs serving as a sort

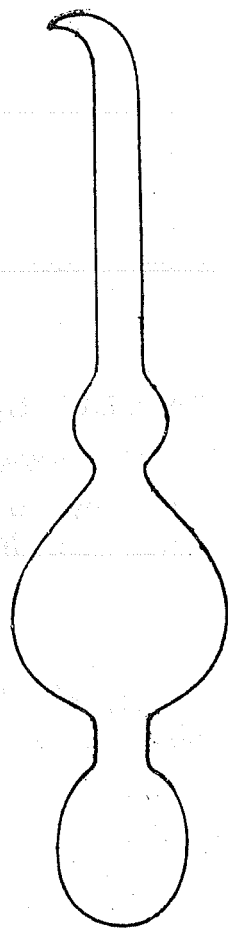


Fig. 1.

¹ The measurements on phenol and the following aromatic compounds were made with bulbs of smaller diameter (about 4 cm.).

of diaphragm, another diaphragm being provided by the slit in the black paint at the bottom of the smaller bulb.

The tube was mounted horizontally inside a thick iron cross tube so that the bigger bulb was at its centre. The cross was thoroughly blackened inside and provided with suitable diaphragms for shutting out stray light and arrangements were made for heating the cross electrically. The background end of the cross tube was closed by a blackened metal cap and the other ends were provided with glass windows.

Sunlight was concentrated by means of a lens at the centre of the bigger bulb and the polarisation in a direction perpendicular to the incident beam was measured in the usual manner with a double image prism and square-ended nicol. The maximum deviation of the incident rays from the axis was not more than 3° or 4° and no correction was made for this deviation. The temperature of the cross was usually kept not far from the boiling point of the substance. The following table gives the values of the depolarisation of the transversely scattered light for the substances studied.

TABLE I.

Substance.	Temperature.	Intensity of weak com- ponent	Intensity of strong com- ponent. ————— × 100
Carbon disulphide ...	40°C	14.3	16.7 (Ganesan) 12.0 (Raman and Rao).
Hexane ...	60°	2.1	3.3 (Ganesan) 1.5 (Cabannes and Gauzit).
Cyclo-hexane ...	60°	1.0	

TABLE I—*contd.*

Substance.	Temperature.	Intensity of weak component ————— × 10 ³	
		Intensity of strong component.	
Benzene	60°C	6.6	6.6 (Ganesan) 6.8 (Raman and Rao).
Phenol	205°	6.1	
Nitro-benzene	"	5.6	
Aniline	"	4.9	
Benzoic Acid	"	5.3	
Salicylic Acid	"	5.3	
Naphthalene	250°	7.9	
Ethyl Bromide	90°	3.2	
Ethylene Bromide	110°	6.7	

The results of measurements by previous investigators are given in column 4.

Discussion.

It will be noticed that the values of the depolarisation for the single-ring aromatic compounds show significant variations among themselves. Aniline has thus a distinctly lower value than benzene showing that the substitution of H by NH₂ reduces the optical anisotropy, which can be explained if the polarisation of the NH₂ group is greater when the incident field is perpendicular to the "plane" of the benzene ring than when it is parallel to it. The same is true of the COOH group in benzoic and salicylic acids. Sir W. H. Bragg's analysis of the structure of benzoic acid crystals shows that the COOH groups of two neighbouring layers of molecules are turned towards each other and lie across the plane of

cleavage. Ganesan has found that the values of the depolarisation for chloro- and bromo-benzene are each .078, thus higher than that of benzene. This is just what we should expect in view of the larger refractivities of chlorine and bromine atoms. Naphthalene again has a larger anisotropy than benzene which is in consonance with its double-ring structure with two benzene rings placed side by side. The compounds ethyl bromide and ethylene bromide with ethane and ethyl alcohol form an interesting series. The values of depolarisation are as follow :—

Ethane016	Cabannes and Gauzit.
Ethyl alcohol017	Ganesan.
Ethyl Bromide032	} Table I.
Ethylene Bromide067	

The substitution of H or OH by the highly refracting bromine atom at the end of the molecule increases the influence of the polarisation of this atom on the other atoms and thus increases the anisotropy. If both the end atoms are replaced by bromine, the effect is accentuated. Krishnan¹ has obtained the same general variations with these substances in the liquid condition and also found that the corresponding chlorides show the same effect but to a smaller degree than the bromides.

Experimental Results of Cabannes and his Co-workers.

One disconcerting feature about the measurements of the depolarisation of light scattered by gases and vapours is the uniformly lower values obtained by Cabannes and his co-workers. The French investigators used a glass cross for their work and took great care in purifying their material. They think that the higher values obtained by other workers may be due to the presence of a trace of some impurity perhaps given out by the black paint used for blackening the insides of the metal crosses. From our experience, we are

¹ Phil. Mag., Vol. L, p. 697 (1925).

inclined to consider it possible that the lower values obtained by Cabannes and his co-workers may have been due to an imperfect background. The inside diameter of their glass crosses was three centimeters and no diaphragms were used for shutting out stray light. It might be thought that an unpolarised background illumination would affect both the components alike and would thus be of little importance, but it is not so. When we adjust the nicol so as to secure equality of brightness of the two tracks produced by the double image prism, its position is such as to cut off most of the illumination in the background of the brighter component and to transmit a considerable part of the illumination in that of the weaker component. The contrast between the track and its background is thus greater in the former case than in the latter, and our tendency either when viewing the tracks visually or when judging the density of photographic images is to overestimate the brightness of the track with the darker background; or in other words, when we think that the two tracks have been adjusted to be of equal brightness, the primary component is really weaker and the estimated value of the depolarisation smaller. For the same background illumination, the percentage error would be greater, the weaker the depolarisation of the scattered light. However, the possibility of the admixture of a small quantity of foreign matter is one to be kept in mind. It would be worth while to obtain careful measurements for a few substances having small values of depolarisation using a glass cross of larger dimensions than that used by Cabannes and his co-workers and provided with proper apertures for shutting out stray light.

Optical Anisotropy of the Carbon Atom.

Ganesan's measurement on the depolarisation of the light scattered by CCl_4 vapour ($\cdot 019$), Krishnan's measurement on CCl_4 liquid ($\cdot 061$) and Cabannes and Gauzit's on CH_4 gas

(015) show definitely that we must assume a certain anisotropy of structure even in these molecules and since the four atoms attached to the central carbon atom are identical, an anisotropy of the carbon atom itself. Cabannes and Gauzit have discussed this point in their paper with reference to CH_4 and they conclude that the carbon atom cannot possess regular tetrahedral symmetry. In this connection, it may be pointed out that according to Bohr's theory, the four outer electrons of the carbon atom, although they would possess considerable symmetry, cannot possess perfectly regular tetrahedral symmetry as their orbits are partly determined by the presence of the two internal electrons describing circular orbits whose planes are at an angle of 120° with each other. The anisotropy of the internal orbits must be reflected in the orbits of the outer electrons and the latter cannot therefore possess *perfect* symmetry. An extension of the argument shows that we must expect a certain amount of anisotropy even in the atoms of the inert gases, and the anisotropy of helium should be particularly marked. The only measurement of the depolarisation of this gas is that made by Lord Rayleigh who fixed an upper limit to its value at 6.5 per cent. An exact measurement of the depolarisation of helium is very much to be desired.
