

The Principal Optical Polarisabilities of the Naphthalene Molecule

By

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1. Introduction.

In a previous communication¹ the principal diamagnetic susceptibilities of the naphthalene molecule were calculated from those for the naphthalene crystal and the known orientations of the molecules in the crystal lattice. It was thus found that the two principal susceptibilities of the molecule in the plane of its benzene rings are nearly equal, and are about a fourth of the susceptibility along the normal to the plane of the benzene rings. A knowledge of the principal optical polarisabilities of the molecule will also be of great interest. But their evaluation from the known refractivities of the crystal is not so simple as the evaluation of the magnetic constants of the molecule. In the latter case, owing to the extreme feebleness of the diamagnetic moments induced in the molecules, their mutual influence when they are grouped together as in the crystal, is negligible, whereas in the optical case the influence is quite large. This makes the correlation of the optical polarisabilities of the molecule with those of the crystal complicated.

It is, however, possible to calculate the optical polarisabilities of the molecule indirectly from other considerations.

¹ 'Nature', Vol. 130, p. 698 (1932).

It is the purpose of the present paper to give an account of these calculations.

2. *The Principal Optical Polarisabilities.*

The structure of the naphthalene molecule has been studied by x-ray methods by Bragg,² Robertson³ and Banerjee.⁴ Considerations of the symmetry of the molecule suggest the following directions for its three principal axes :

(1) along the line joining the centres of the two benzene rings ;

(2) along a direction in the plane of the benzene rings, perpendicular to the first axis ;

(3) along the normal to the plane of the rings.

We shall denote the optical di-pole moments induced in the molecule per unit field of the electric vector of the light-wave, acting respectively along these three directions, by b_1 , b_2 and b_3 . We shall denote the principal magnetic susceptibilities of the molecule along these directions by a_1 , a_2 and a_3 respectively. As has already been mentioned, the a 's for the naphthalene molecule are known.

There are three important optical quantities which involve the optical polarisabilities of the molecule :

(1) the well-known Lorentz constant of refraction, which involves $b_1 + b_2 + b_3$;

(2) the depolarisation factor of the light scattered by the molecules in the fluid state, which involves

$$(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 ;$$

(3) thirdly, the well-known Cotton-Mouton constant, which involves

$$(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1).$$

² 'Proc. Phys. Soc.', Vol. 34, p. 33 (1921).

³ 'Roy. Soc. Proc.' A, Vol. 125, p. 546 (1929).

⁴ 'Ind. Jour. Phys.', Vol. 4, p. 557 (1930).

From a knowledge of the above three physical quantities, it is possible to calculate the three b 's.

3. The Lorentz Constant.

The Lorentz relation is

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N \cdot \frac{b_1+b_2+b_3}{3}, \quad \dots\dots\dots(1)$$

where n is the refractive index of the fluid, ρ is its density, M is the gram molecular weight, and N is the Avogadro number per gram molecule. It is well-known that this relation holds, to a first approximation, over such large ranges of densities as correspond to the liquid and the gaseous states.

For naphthalene, taking the gram molecular refractivity $\left(\frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho}\right)$ for the D-lines as 44.37, we obtain

$$b_1 + b_2 + b_3 = 52.42 \times 10^{-24}. \quad \dots\dots\dots(2)$$

4. The Depolarisation of Light-scattering.

The depolarisation factor τ for the light transversely scattered by a gas, when the incident light is unpolarised, is given by the well-known relation

$$\frac{(b_1-b_2)^2 + (b_2-b_3)^2 + (b_3-b_1)^2}{(b_1+b_2+b_3)^2} = \frac{10\tau}{6-7\tau}, \quad \dots\dots(3)$$

The value of τ is not appreciably affected by small changes in the wave-length of the incident light. For naphthalene vapour τ has been measured by Ramanathan,⁵ Cabannes⁶ and Ramakrishna Rao.⁷ Rao's value, which agrees almost exactly with that of Ramanathan, is $\tau = 0.079$. Cabannes's value is

⁵ 'Proc. Ind. Assn. Sc.,' Vol. 9, p. 206 (1926).

⁶ 'Compt. Rendus,' Vol. 182, p. 885 (1926).

⁷ 'Ind. Jour. Phys.,' Vol. 2, p. 64 (1927).

higher, *viz.*, 0.10. Adopting the former value, and using the value of $b_1 + b_2 + b_3$ given in (2) above, we obtain

$$(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 = 398.4 \times 10^{-4} \text{Å}^2. \quad \dots\dots(4)$$

5. The Cotton-Mouton Constant.

The Cotton-Mouton constant of a liquid is given by the relation

$$C_m = \frac{n_{\parallel} - n_{\perp}}{\lambda H^2} = \frac{3M(n^2 - 1)^2}{80\pi n \lambda k T N \rho} \frac{(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)}{(b_1 + b_2 + b_3)^2}, \quad (5)$$

where λ is the wave-length of the incident light, H is the magnetic field, n_{\parallel} and n_{\perp} are the two principal refractive indices of the liquid in the field, k is the Boltzmann constant per molecule and T is the absolute temperature. Salceanu⁸ has recently made extensive measurements on the Cotton-Mouton constant of molten naphthalene at different temperatures. His values refer to $\lambda = 0.578\mu$ and the values given in Table I have been calculated for $\lambda = 0.589\mu$ (D-lines) from his data with the help of Havelock's relation. The gram molecular refractivity of naphthalene for these wave-lengths were taken to be 44.46 and 44.37 respectively. The last column in the table gives the values of

$$a = \frac{(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)}{(b_1 + b_2 + b_3)^2}, \quad \dots (6)$$

calculated from these data with the help of relation (5).

TABLE I.

T(°K.)	$C_m \times 10^{13}$	a
361.5	18.80	1.46
373	17.26	1.40
377.2	17.03	1.41
387	16.75	1.43
410.5	15.62	1.45
442	14.86	1.55

⁸ 'Compt. Rendus,' Vol. 191, p. 486 (1930).

If we reject the first value which refers to a temperature close to the melting point of the substance (*viz.*, 353° K.), the values of α are found to increase with rise of temperature. This is indeed what we should expect, since it is well known that the effective optical anisotropy of a molecule in the liquid state is appreciably smaller than that for the molecule in the state of vapour, and that in the former state, as the temperature is gradually increased, the value of the effective anisotropy also increases and tends to approach the vapour value at sufficiently high temperatures.⁹ We may, therefore, adopt for the value of α of the naphthalene molecule,

$$\alpha = 1.60. \quad \dots \quad \dots \quad \dots \quad (7)$$

Hence we obtain, using the value of $b_1 + b_2 + b_3$ given in (2),

$$(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1) = 4.40 \times 10^{-51}. \quad (8)$$

The Cotton-Mouton constant of solutions of naphthalene in carbon tetrachloride (which is magneto-optically inactive), has also been measured recently by Chinchalkar in this laboratory, and he obtains a value $C_s = 1.56 \times 10^{-12}$ per gram of naphthalene in 1 c.c. of dilute solution. Using the following relation for C_s for such solutions in an inactive solvent, *viz.*,

$$C_s = \frac{\pi N(n^2 + 2)^2}{185\pi\lambda kTM} \left[(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1) \right]. \quad (9)$$

where n is the refractive index of the solution, and M is the molecular weight of the solute, we obtain

$$(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1) = 2.91 \times 10^{-51}. \quad (10)$$

This value is naturally much less than the value obtained above for higher temperatures.

⁹ K. S. Krishnan and S. R. Rao, "Ind. Jour. Phys.," Vol. 4, p. 39 (1929).

6. *The Optical Constants of the Naphthalene Molecule.*

Since the a 's for the naphthalene molecule are known, the three equations (2), (4) and (8) enable us to calculate the b 's. The values of the a 's are ¹⁰

$$\left. \begin{aligned} a_1 &= -6.50 \\ a_2 &= -7.09 \\ a_3 &= -30.88 \end{aligned} \right\} \times 10^{-29} \text{ c.g.s. e.m.u.} \quad \dots (11)$$

Also from considerations of the structure of the molecule, b_1 should be greater than b_2 . Hence we obtain from (2), (4) and (8)

$$\left. \begin{aligned} b_1 &= 26.8 \\ b_2 &= 14.1 \\ b_3 &= 11.5 \end{aligned} \right\} \times 10^{-24} \text{ c.g.s. e.s.u.} \quad \dots \dots (12)$$

Thus the polarisability of the molecule along its long axis, viz., b_1 , is more than double the polarisability b_3 along the normal to the plane of the molecule.

¹⁰ See 'Phil. Trans.' A, Vol. 231, p. 253 (1933). The values of the a 's given here were calculated from the principal susceptibilities of naphthalene crystal, on the basis of the orientations given by Banerjee for the two molecules in the unit cell of the crystal, viz. that the a_1 axes of the molecules lie in the (010) plane, and their a_3 axes are inclined at plus and minus 25° to the (010) plane. Since the present paper was written, Robertson has published the results of a further x-ray study of the crystal ('Roy. Soc. Proc.' A, Vol. 142, p. 678 (1933)), and suggests slightly different orientations for the molecules. The corresponding values of the a 's will differ only *slightly* from those given here.