209. *The Dipole Moments of Benzoquinone, Beryllium Acetylacetonate, Basic Beryllium Acetate, and* o-*Nitrophenol.*

By H. O. Jenkins.

The object of this paper is to show that the apparent dipole moments of beryllium acetylacetonate and basic beryllium acetate in solution can be calculated from that of benzoquinone. All three compounds are probably non-polar in the free state (the molecular beam method gives a zero electric moment for quinone) but show considerable orientation polarisations in solution. With the aid of a simple theory, the author (this vol., p. 862) has been able to predict that certain symmetrical compounds would show dipole moments in solution, to link the values for similar compounds quantitatively, and also to explain the temperature-invariance of the polarisation. The fundamental assumption of the theory is that each group moment is independent, and that the magnitude of the same group moment in different molecules fluctuates about a most probable value (μ_0) according to the Gaussian distribution formula

$$P(\mu) = Ce^{-\alpha(\mu/\mu_0 - 1)^2/T}$$

the direction remaining constant.

The following formula, deduced in the previous paper for a 1 : 4-benzene derivative, is equally valid for *p*-benzoquinone :

$$\bar{\mu}^2 = \mu_0^2 T/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now beryllium acetylacetonate has a molecule consisting of mutually perpendicular six-membered rings arranged about a central beryllium atom, and each ring contains two carbon–oxygen links which probably resonate between single- and double-bonded character. Since the C—O group moments are relatively far apart, independent solvent fluctuations will occur. Furthermore, the C—O links in different rings are opposed but in line with one another, and thus a similar calculation to that performed for *p*-dinitrobenzene in the previous paper clearly gives the square of the effective moment as

$$\bar{\mu}^2 = 2\mu_0^2 T/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The molecule also contains beryllium–oxygen links of unknown magnitude but these are probably too close together to fluctuate independently.

Now let us consider the molecule of basic beryllium acetate. Its structure has been shown by Pauling and Sherman (*Proc. Nat. Acad. Sci.*, **1934**, **20**, 340) to consist of four BeO_4 tetrahedra with one common corner, the remaining corners being occupied by oxygen atoms of the acetate groups. Moreover, the angle between the oxygen atoms of the carboxyl group is 124° ± 3°. Also the C—O links in the carboxyl group resonate between single and double bonds and are too close together to be regarded as independent. We shall thus regard them as equivalent to a resultant of the same magnitude as a single C—O link, this resultant making an angle of approximately 60° with each C—O link. The problem then reduces to finding the effective moment of a molecule which has three pairs of opposed C—O group moments each of the pairs being mutually perpendicular. As before, the beryllium–oxygen links are considered to be too close together to fluctuate independently.

Thus the square of the effective moment of basic beryllium acetate is

$$\bar{\mu}^2 = \frac{\int_{-\infty}^{+\infty}\iiint\iiint e^{-\alpha(x_1^2+x_2^2+x_3^2+x_4^2+x_5^2+x_6^2)/T}\,(x_1^2+x_2^2+x_3^2+x_4^2+x_5^2+x_6^2-2x_1x_2-2x_3x_4-2x_5x_6)\,dx_1\,.\,dx_2\,.\,dx_3\,.\,dx_4\,.\,dx_5\,.\,dx_6}{\int_{-\infty}^{+\infty}\iiint\iiint e^{-\alpha(x_1^2+x_2^2+x_3^2+x_4^2+x_5^2+x_6^2)/T}\,dx_1\,.\,dx_2\,.\,dx_3\,.\,dx_4\,.\,dx_5\,.\,dx_6}$$

with $x_1 = (\mu_1/\mu_0 - 1)$, $x_2 = (\mu_2/\mu_0 - 1)$, etc., as in the previous paper. The above expression reduces on evaluation to

$$\bar{\mu}^2 = 3\mu_0^2 T/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equations (1), (2), and (3) then predict that the orientation polarisations of benzoquinone, beryllium acetylacetonate, and basic beryllium acetate are in the ratios of 1 : 2 : 3. Values of 8·9—10 c.c. have been given for the orientation polarisation of benzoquinone (Hassel and Naeshagen, *Z. physikal. Chem.*, **1930**, *B*, **6**, 441; Le Fèvre and Le Fèvre, J., **1935**, 1698; Hammick, Hampson, and G. I. Jenkins, *Nature*, **1935**, **136**, 990), and Smith and Angus (*Proc. Roy. Soc.*, **1932**, **137**, 372) give 24 c.c. for the acetylacetonate and 38 c.c. for basic beryllium acetate. If 1—2 c.c. is allowed for experimental error in each determination the agreement is most satisfactory having regard to the nature of the approximations made. All three compounds also have polarisations practically independent of temperature, and the explanation is provided in the previous paper. The slight discrepancy (say, 2 c.c. for the acetylacetonate and 4 c.c. for the basic acetate) can be ascribed to atomic polarisation. It is pleasing that the discrepancy is on the right side, giving the more complicated molecule the larger atom polarisation. Smith and Angus attributed all the excess polarisation over the refractivity to atomic polarisation. This cannot be accepted.

This work was carried out during the tenure of a Commonwealth Fund Fellowship.

THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA. [*Received, April 21st*, 1936.