200. *The Dipole Moments of Certain Polynitro-compounds.*

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DIELECTRIC-CONSTANT and density measurements have been made for dilute solutions of (*a*) benzene in chloroform, (*b*) *p*-dinitrobenzene in chloroform, (*c*) 1 : 3 : 5-trinitrobenzene in chloroform, (*d*) trinitromesitylene in benzene, (*e*) 1 : 3 : 5-trinitro-2 : 4 : 6-triethylbenzene in benzene and in carbon tetrachloride. Some of the results were briefly described in a preliminary note (Jenkins, *Nature*, 1934, **134**, 217). In the meantime a paper on this subject has been published by Le Fèvre and Le Fèvre (J., 1935, 957), but their conclusions cannot be accepted.

Several polynitro-compounds have been investigated, with surprising results. Lütgert (*Z. physikal. Chem.*, 1931, *B*, **14**, 450) measured the polarisations of several hexasubstituted benzene derivatives in benzene, and, finding considerable differences between $_{\infty}P_2$ and $_{E}P_2$, ascribed the residue entirely to atomic polarisation. The compound 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene was said to have an atomic polarisation of 28 c.c., and trinitromesitylene 20 c.c. *p*-Dinitrobenzene and 1 : 3 : 5-trinitrobenzene have also been studied in benzene and naphthalene with similar results, and atomic polarisations or electric moments ascribed depending on the investigator. It is clear that any interpretation given will depend on what structure is assigned to the nitro-group. Since benzene or naphthalene had been consistently used as solvents, there was the possibility that the results were spurious owing to the existence of complexes in solution. The insolubility of *p*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene in other non-polar solvents made the choice of a polar solvent inevitable for them. Polarisations of benzene in chloroform were measured to check the reliability of the solvent.

EXPERIMENTAL.

Materials.—Chloroform. Hopkin and Williams's material was shaken with concentrated sulphuric acid, then with potassium hydroxide solution, washed with water, and fractionally distilled over phosphoric oxide before use. The density of material prepared on different occasions varied slightly.

1 : 3 : 5-*Trinitrobenzene.* 40 G. of *m*-dinitrobenzene, 130 g. of fuming nitric acid, and 250 g. of fuming sulphuric acid were heated together for one week at 140—150°. The mixture was

allowed to cool, poured into water, and the solid filtered off, washed, and recrystallised three times from aqueous acetic acid; m. p. 122°.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene.* The method of Gattermann, Fritz, and Beck (*Ber.*, 1899, **32**, 1122) was used to prepared triethylbenzene, and this was nitrated and recrystallised from glacial acetic acid; m. p. 110°.

The other compounds were prepared or purified in the usual ways.

Measurements.—The dielectric constants and densities were measured at 25° as described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). Single-solution condensers were used, and the cell described by Jenkins and Sutton (J., **1935**, 609) was used for chloroform solutions. The data are collected in the following tables; ε_{25° is the dielectric constant, $d_{4^\circ}^{25^\circ}$ the density, f_2 the mol.-fraction of solute, ${}_\infty P_2$ the total polarisation of solute at infinite dilution, ${}_E P_2$ the calculated electron polarisation for $\lambda = 5890$ A., and ${}_{\lambda=\infty}P_2$ is the electron polarisation at infinite wave-length. The usual atomic and group refractions have been used to calculate ${}_E P_2$.

Benzene in chloroform.

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·726	1·4806	—
0·02341	4·627	1·4646	26·8
0·04451	4·549	1·4502	27·9
0·07104	4·448	1·4323	27·9

${}_\infty P_2 = 27·5 \pm 0·5$, ${}_E P_2$ (calc.) $= 26·2$.

1 : 3 : 5-*Trinitrobenzene in chloroform.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·725	1·4800	—
0·00604	4·694	1·4822	41·2
0·00903	4·679	1·4833	41·4

${}_\infty P_2 = 41·3 \pm 0·5$, ${}_E P_2$ (calc.) $= 44·7$,
${}_E P_2$ (meas.) $= 43·5 \pm 0·4$, ${}_{\lambda=\infty}P_2 = 41·7 \pm 0·4$.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene in benzene.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2727	0·8738	—
0·00641	2·2779	0·8800	84·6
0·00880	2·2809	0·8824	86·0

${}_\infty P_2 = 85·0 \pm 1·0$, ${}_E P_2$ (calc.) $= 72·6$.

p-*Dinitrobenzene in chloroform.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·725	1·4797	—
0·00908	4·677	1·4799	33·8
0·00995	4·674	1·4800	34·4
0·01141	4·666	1·4800	34·2

${}_\infty P_2 = 34·1 \pm 0·5$, ${}_E P_2$ (calc.) $= 38·5$.

Trinitromesitylene in benzene.

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2727	0·8738	—
0·00485	2·2770	0·8782	72·5
0·00599	2·2784	0·8796	73·1
0·00675	2·2789	0·8803	71·0

${}_\infty P_2 = 72·2 \pm 0·5$, ${}_E P_2$ (calc.) $= 59·2$.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene in carbon tetrachloride.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2298	1·5848	—
0·00505	2·2349	1·5811	84·2
0·00642	2·2366	1·5801	84·9
0·00766	2·2375	1·5792	84·0
0·00819	2·2380	1·5788	84·0
0·01100	2·2410	1·5768	83·6

${}_\infty P_2 = 84·1 \pm 0·5$, ${}_E P_2$ (calc.) $= 72·6$.

DISCUSSION.

Benzene in chloroform gives a total polarisation of 27·5 ± 0·5, in satisfactory agreement with 27·0 found by Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 453) by the gas temperature method. For 1 : 3 : 5-trinitrobenzene ${}_\infty P_2$ is found to be 41·3 ± 0·5; Le Fèvre and Le Fèvre (*loc. cit.*) found 46·6. The electronic polarisation at $\lambda = 5890$ A. is calculated to be 44·7. Le Fèvre and Le Fèvre took the difference ${}_\infty P_2 - {}_E P_2 = 1·9$ c.c., and translated this with the aid of an empirical rule into a gas electric moment of 0·4 *D*. The finite moment found is used in their discussion of the structure of the nitro-group. However, an experimental value of ${}_E P_2$ is available, *viz.*, 43·5 ± 0·4 (Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **27**, 11). These authors also give the electron polarisation at infinite wave-length as 41·7 ± 0·4. Now the dielectric constant is measured at virtually an infinite wave-length, and strictly speaking, it is the difference (${}_\infty P_2 - {}_{\lambda=\infty}P_2$) which should be used to calculate electric moments. The present experimental result shows that this difference is zero, and thus 1 : 3 : 5-trinitrobenzene has no electric moment in the polar solvent chloroform. *p*-Dinitrobenzene is found to have ${}_\infty P_2 = 34·1 \pm 0·5$. Le Fèvre and Le Fèvre found 38·9. From group refractions ${}_E P_2$ is calculated as 38·5. These authors again translate their difference of 0·4 c.c. into a gas electric moment of 0·2 *D*. This places too much reliance on their experimental accuracy and on the validity of their conversion rule. Considering that atomic polarisation has been ignored, the correct inference from their results is a zero moment for *p*-dinitrobenzene in the polar solvent chloroform. Unless the result presented in this paper is in error, it would seem that ${}_{\lambda=\infty}P_2$ is 3 or 4 c.c. less than ${}_E P_2$, in which case agreement with the measured $_{\infty}P_2$ would be obtained. Unfortunately, there is no value in the literature for the electron polarisation of *p*-dinitrobenzene at infinite wave-length.

Structure of the Nitro-group.—Le Fèvre and Le Fèvre (*loc. cit.*) suggest a pyramidal structure for the $\geqslant C{-}NO_2$ group, but their arguments are not valid and the structure is untenable. Such a pyramidal structure involves single bonds between the nitrogen and oxygen atoms. Now the single bond distance has been shown to be 1·37 ± 0·02 A., by the diffraction of electrons through α-methylhydroxylamine (Brockway, Beach, and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2693). The double bond distance $N{=}O$ can be calculated to be 1·22 ± 0·02, by using the usual factor. An experimental value of the nitrogen–oxygen internuclear distance in nitromethane gives 1·21 ± 0·02 A. (Brockway, Beach, and Pauling, *loc. cit.*). Pauling and others have also shown that, although a bond may have any intermediate character between the extremes of a pure single and a pure double bond, yet a small amount of double-bond character causes a large decrease in interatomic distance. The nitrogen–oxygen distance in the nitro-group is essentially a double-bond distance, and the structure is a resonating one. This demands a coplanar arrangement.

The argument for the pyramidal structure is commenced by the statement that the force constant characterising the links in an aryl nitro-group is greater than that for a single and less than that for a double bond. There is some discrepancy here. Bond force constants are related to internuclear distances. Badger (*J. Chem. Physics*, 1934, **2**, 28) gives the relation $k_0(r_e - d)^3 = 1{\cdot}86 \times 10^5$ for diatomic molecules, where r_e is the equilibrium internuclear distance and d is a constant depending only on the rows in the periodic table in which the two elements are located. It seems that the single-bond force constant has been calculated from nitrogen dioxide data, but this has a resonating structure and should give a double-bond force constant. Also the double-bond force constant has been calculated from data on nitrous oxide, which was given the old symmetrical structure. Pauling (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293) has shown that the wave function for the nitrous oxide molecule is approximately represented by the sum of the wave functions for unsymmetrical structures with equal coefficients. Finally, it should be mentioned that the suggested finite moment for dinitrogen tetroxide (Zahn, *Physikal. Z.*, 1933, **34**, 461) is quite incompatible with the conclusions of Harris and King (*J. Chem. Physics*, 1934, **2**, 51) from infra-red absorption spectra. These authors require two configurations of nearly the same energy in which the nitro-groups lie in the same plane or are mutually perpendicular. Both configurations have zero electric moment, and the gas temperature experiments of Williams Schwingel, and Winning (*J. Amer. Chem. Soc.*, 1934, **56**, 1427) show that this is so.

The Increase of Electric Moment.—Most molecules have a dipole moment in solution less than in the gaseous state. A number of compounds are now known, however, which show an enhanced moment over that required by the structure. This paper is not concerned with molecules such as hydrogen chloride, but with molecules which are probably non-polar, showing, however, an electric moment in non-polar solvents. Table I gives the relevant data. The electric moments therein (μ, in Debye units) have been obtained from the General Discussion on Dipole Moments (Faraday Society, 1934), with the exception of the results presented now, and those for quinone (Le Fèvre and Le Fèvre, J., 1935, 1697; Hammick, Hampson, and Jenkins, *Nature*, 1935, **136**, 990), for tetramethyl*cyclo*butane-1 : 3-dione (*idem, ibid.*), and for the mercuric halides (Curran and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 2162).

Some investigators have considered that the solution method gives the dipole moment of the free molecule and have thus been led to erroneous conclusions. For example, Curran and Wenzke (*loc. cit.*) stated that the configurations of the mercuric halides are non-linear, since the electric moments in dioxan are considerable. This non-linearity is disproved by the crystal structure evidence and by the gas-temperature dielectric-constant experiments of Braune and Linke (*Z. physikal. Chem.*, 1935, *B*, **31**, 12). It is suggested that Le Fèvre and Le Fèvre have been similarly misled in the case of the symmetrical poly-nitrobenzenes, for Hertel and Romer (*ibid.*, 1933, *B*, **22**, 267), from a study of the crystal structure of picryl iodide and bromide, consider that symmetry considerations require planar molecules.

TABLE I.

Molecule.	Solvent.	μ.
p-Di-iodobenzene	Benzene	0·2
p-Dibromobenzene	,,	0·2
p-Dichlorobenzene	,,	0·2
p-Benzoquinone	,,	0·7
Tetramethyl*cyclo*butane-1 : 3-dione	,,	0·73
p-Cyanonitrobenzene	,,	0·7
p-Dinitrobenzene	,,	0·6
1 : 3 : 5-Trinitrobenzene	,,	0·8
Trinitromesitylene	,,	0·8
1 : 3 : 5-Trinitro-2 : 4 : 6-triethylbenzene	,,	0·8
1 : 3 : 5-Tribromo-2 : 4 : 6-trinitrobenzene	,,	1·1
Diphenylmercury	Decalin	0·54
Di-*p*-tolylmercury	,,	0·74
Di-*p*-fluorophenylmercury	,,	0·87
Di-*p*-bromophenylmercury	,,	0·92
Di-*p*-chlorophenylmercury	,,	1·11
Mercuric chloride	Dioxan	1·29
Mercuric bromide	,,	1·06
Mercuric iodide	,,	0·58

These polar "non-polar" compounds have a further peculiarity in that their total polarisations, although exceeding the electron polarisation, are independent of temperature.

It will now be shown that the existence of the dipole moment and the invariance of the polarisation with temperature can be given a general explanation provided that certain simple assumptions are made. These are :

(*a*) That there is only one molecular species in the gas.

(*b*) That in solution, on account of solute–solvent forces, the moment of a particular link in different molecules has no constant value but fluctuates about a most probable value. A Gaussian distribution law of the following form will be assumed :

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

with the normalisation condition

$$\int_{-\infty}^{+\infty} P(\mu) \, . \, d\mu = 1$$

Here, μ_0 is the most probable value of μ, T is the absolute temperature, and α and C are constants; α is probably a constant only for a group of similar compounds, *e.g.*, for *p*-derivatives of benzene. This distribution formula assumes greater fluctuations the higher the temperature and the greater the value of μ_0.

(*c*) That changes in the moment of any one molecule are slow relative to its time of relaxation in the medium in question.

(*d*) That each group moment is assumed to be independent.

First, consider the case of a monosubstituted benzene derivative, say nitrobenzene. Its effective moment $({}_1\overline{\mu^2})^{1/2}$ can be obtained from the equation

$${}_1\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu}{\mu_0}-1\right)^2} \mu^2 \, . \, d\mu}{\int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu}{\mu_0}-1\right)^2} d\mu}$$

i.e.,

$${}_1\overline{\mu^2} = \mu_0{}^2(1 + T/2\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now consider the case of a symmetrical disubstituted benzene derivative, say *p*-dinitrobenzene. It may be seen qualitatively that, owing to the independence of the fluctuations in the individual group moments, at any instant some molecules are non-polar, but that in most molecules the groups have different moments and there is therefore a resultant moment. By assumption (*c*), this causes an extra polarisation. Denoting the two group moments by μ_1 and μ_2, we get the square of the effective moment given by

$${}_2\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} (\mu_2 - \mu_1)^2 \, . \, d\mu_2}{\int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{a}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} d\mu_2}$$

On evaluation, this reduces to

$$ {}_2\overline{\mu^2} = \mu_0{}^2T/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) $$

Similarly, in the case of a symmetrical trisubstituted benzene derivative, say 1 : 3 : 5-trinitrobenzene, we have

$$ {}_3\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} d\mu_2 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_3}{\mu_0}-1\right)^2} (\mu_1{}^2 + \mu_2{}^2 + \mu_3{}^2 - \mu_1\mu_2 - \mu_1\mu_3 - \mu_2\mu_3) d\mu_3}{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} d\mu_2 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_3}{\mu_0}-1\right)^2} d\mu_3} $$

which gives on evaluation

$$ {}_3\overline{\mu^2} = 3\mu_0{}^2T/2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3) $$

Since α is essentially positive and finite, equations (2) and (3) predict finite electric dipole moments for *p*-dinitrobenzene, 1 : 3 : 5-trinitrobenzene, and similar compounds. Also, the effective moment in, say, a disubstituted benzene derivative is directly proportional to μ_0, the most probable value of the moment of the monosubstituted derivative. This is supported by experiment. *p*-Dinitrobenzene has an electric moment of 0·6 in benzene, and *p*-dichlorobenzene has the value 0·2—0·3. The results given for the mercury compounds in Table I also support this conclusion.

Furthermore, although 1 : 3 : 5-trinitrobenzene, 1 : 3 : 5-trinitro-2 : 4 : 6-triethylbenzene, and trinitromesitylene all show the same moment in benzene and in carbon tetrachloride, because the C–alkyl link moment is small and would be expected to produce little effect, yet 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene has a moment of 1·1, because the C–Br link moment is considerable. It is interesting to notice that, according to Höjendahl (*Physikal. Z.*, 1928, **30**, 391), 1 : 5-dinitronaphthalene has an electric moment of 0·6 in benzene, a value close to that for *p*-dinitrobenzene. The temperature variation will now be considered. Since the orientation polarisation is given by $P_O = K\overline{\mu^2}/T$ and by equation (2), for example, $\overline{\mu^2} = \mu_0{}^2T/\alpha$, we get $P_O = K\mu_0{}^2/\alpha$, an expression invariant with respect to temperature. This again is supported by experiment. Le Fèvre and Le Fèvre (*loc. cit.*) find P_O for *p*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene to be independent of temperature in the range measured, and similar results have been obtained for *p*-benzoquinone (*idem*, J., 1935, 1696).

If an electric moment of 0·6 is assumed for *p*-dinitrobenzene, equations (2) and (3) enable the moment of 1 : 3 : 5-trinitrobenzene to be calculated. The value obtained, 0·74, is in good agreement with that found, 0·8. It may be mentioned that this method of calculating electric moments gets into no difficulty when meta-compounds are considered, and also does not remove the well-known " ortho " anomaly. In addition to other factors entering, our assumption of link independency is probably not true in this case.

It would be difficult rigorously to derive the distribution formula used, and at present it may be regarded as empirical. However, it is reasonable that the formula should give greater fluctuations the higher the temperature and the greater the value of μ_0.

A few consequences of the proposed explanation of electric moments developed by non-polar substances in solution may be mentioned. First, care must be taken in the interpretation of such results as the finite moment of 0·5 found by Weissberger (*Trans. Faraday Soc.*, 1934, **30**, 884) for 1 : 4-dichloronaphthalene. This is regarded as being due to a shift of electrons in the molecule towards the substituents. There may be real evidence for this shift from other sources, but the dipole-moment evidence does not conclusively prove it. Secondly, since all non-polar substances will show the effect in some degree, atomic polarisations determined from the dilute solution method will be on the high side.

SUMMARY.

An explanation is proposed for the electric moments of symmetrical molecules in solution, based on an assumed fluctuation of link moments about a most probable value. The theory explains the temperature invariance of the orientation polarisation, and relates the

electric moment developed in solution by such compounds as 1 : 4-dinitrobenzene to the most probable value of the moment of mononitrobenzene in the same solvent. Some consequences of the theory are discussed and it is considered that atomic polarisations determined by the dilute solution method are on the high side.

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