129. *Electric Polarisation and Molecular Vibrations: The Ethylene Dihalides and Diacetyl.*

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In continuation of work on anomalous polarisation, some compounds which might show large vibration polarisations, either independent of or varying with temperature, have been examined in solution at 25° and also in the vapour phase over a range of temperature. Fumaronitrile and succinonitrile have been examined in benzene; ethylene dichloride and succinonitrile in dioxan; and dimethylketazine, ethylene dichloride, dibromide, and dicyanide (succinonitrile) in the vapour phase. Preliminary results for diacetyl in the vapour phase were also obtained.

The relative merits of two possible explanations of the temperature variation of the moments of such compounds have been considered on the basis of the results obtained. A theory that there is an equilibrium between *cis*- and *trans*-isomers predicts that the graph of the logarithm of the ratio of their amounts plotted against $1/T$ should give a straight line. Such lines were actually obtained. An analysis of other authors' data for similar compounds in various solvents also gives straight lines. It is emphasised, however, that these observations do not exclude an alternative theory, *viz.*, that there is restricted rotation about the *trans*-position, because appropriate potential functions for the several substances would lead to the same results.

It has been shown that the dipole data, like electron-diffraction data, disagree with the interpretation of the Raman spectra of acetylene tetrachloride and of *cyclo*hexane as signifying that for these molecules there are stable isomers in which non-bonded atoms approach as closely as possible. It is inferred that a similar interpretation made in the case of ethylene dichloride may not be correct.

If the " *trans*-vibration " theory be accepted, the numerical results confirm the conclusions of previous workers that the forces between the two rotatable halves of ethylene dihalide molecules are mainly " steric " forces, and that the repulsion is greater the larger the halogens. The planar fixation in diacetyl indicates " resonance."

The other observations have been briefly discussed.

It has been pointed out by various authors that compounds in which there are large and equal opposed dipole moments frequently have large differences between their total and their electron polarisations. According to Coop and Sutton (J., 1938, 1269) these differences arise from the bending of the dipoles from the non-polar configuration, and for each independent mode of such bending there is a contribution of $4\pi N\mu^2/9V_0$ to the total polarisation at low frequencies (μ is the magnitude of the moments in question, and V_0 is the force constant of bending).

Either a classical or a quantum-mechanical treatment leads to the Sellmeier dispersion formula (Van Vleck, " Electric and Magnetic Susceptibilities," Oxford, 1932, pp. 42—53, 361) from which the above expression can readily be obtained for the particular case of two opposing but displaceable moments, μ, with ν_0, the frequency of the field used for observation, very small relative to ν_t, the natural frequency of vibration of the effective charge, which for atom polarisations is in the infra-red range.

If we suppose that the applied field is effectively static, it is easy to demonstrate that for each angular co-ordinate which is necessary to express completely the possible, independent modes of bending of the opposing dipoles, θ_i, θ_j, ..., there is a contribution $4\pi\mathbf{N}\mu^2/9{}_iV_0$, ${}_iV_0$, ${}_jV_0$, ..., being the appropriate force constants. Let the deformation polarisabilities of a molecule along three rectangular axes be α_x, α_y, α_z, such that the moment induced by a field of strength F acting along the x axis would be $m = \alpha_x F$; then the mean polarisability of a molecule in a statistical assemblage, account being taken of the effect of thermal agitation in keeping the polarisation axes chaotically disoriented relative to the field, is $\alpha = (\alpha_x + \alpha_y + \alpha_z)/3$ (Debye, " Polar Molecules," New York, 1928, p. 34).

Now consider the contribution to the mean polarisability of one dipolar bond in the molecule. If this be assumed to be able to move in one plane only, the molecule can be considered polarisable along one only of three rectangular axes; let us imagine the molecule to be so oriented that this axis, the x axis, lies along the direction of the field. The bending of the dipole in the field is equivalent to the movement of a charge e_i, which has associated with it a force constant k_i. If F is the field strength, $Fe_i = k_i \mathrm{d}x_i$. If μ_i be the moment of the dipole which bends, θ_i its angular co-ordinate relative to some frame of reference within the molecule (see later), and ${}_iV_0$ the associated force constant; then $\mu_i \mathrm{d}\theta_i = \mathrm{d}\mu_i$; and ${}_iV_0 \mathrm{d}\theta_i^2 = k_i \mathrm{d}x_i^2$. From the latter, ${}_iV_0 \mathrm{d}\theta^2 = Fe_i \mathrm{d}x_i = F\mathrm{d}\mu_i$; whence by the elimination of $\mathrm{d}\theta_i^2$ we find $\mu_i^2/{}_iV_0 = \mathrm{d}\mu_i/F = {}_i\alpha_x$.

If now there be another dipole which bends in such a way that it is equivalent to a charge e_j moving along an axis w, in the x, y plane, making an angle ϕ with the x axis; then $F \cos\phi\, e_j = k_j \mathrm{d}w$ and $\mathrm{d}\mu_x = e_j \,.\, \mathrm{d}w \,.\, \cos\phi = \mu \,.\, \mathrm{d}\theta_j \,.\, \cos\phi$. Then ${}_jV_0 \,.\, \mathrm{d}\theta_j^2 = k_j \mathrm{d}w_j^2 = F\cos\phi\, e_j\, \mathrm{d}w = F\mathrm{d}\mu_x$; whence ${}_j\alpha_x = \mu_j^2 \cos^2\phi/{}_jV_0$.

It may similarly be shown that along the y axis ${}_j\alpha_y = \mu_j^2 \sin^2\phi/{}_jV_0$. The *total mean* polarisability of the molecule is therefore $\alpha = ({}_i\alpha_x + {}_j\alpha_x + {}_j\alpha_y)/3 = (\mu_i^2/{}_iV_0 + \mu_j^2/{}_jV_0)/3$; and consequently the total molecular polarisation, $4\pi\mathbf{N}\alpha/3$, is $4\pi\mathbf{N}(\mu_i^2/{}_iV_0 + \mu_j^2/{}_jV_0)/9$.

Clearly, any number of dipoles may be taken into account in this way, and no matter what angle their permitted movements may make with each other they all make a contribution $4\pi\mathbf{N}\mu_i^2/9{}_iV_0$ for *each independent angular co-ordinate needed.* This is not the same as saying the number of dipolar bonds, for in very simple molecules one dipolar bond may have to serve as the frame of reference for another, as, *e.g.*, in mercuric chloride; whereas in more complex ones the frame of reference can often be chosen outside the polar bonds, *e.g.*, the benzene ring can be so used in *p*-dinitrobenzene, but then the polar bonds may be able to oscillate in more than one dimension. The molecules so far considered have had high degrees of symmetry, in that μ and V_0 have been the same for all the bonds in question, so in these instances $P = 4\pi\xi\mathbf{N}\mu^2/9V_0$, where ξ is the number of co-ordinates. Examples of the application of this expression are to be found in the paper by Coop and Sutton (*loc. cit.*).

Davidson and Sutton (J., 1939, 347; see also Sutton, *Ann. Reports*, 1940, **37**, 60) have emphasised that the expression allows both for the polarisation caused by orientation of the molecule in the field while bent by thermal collision, which is often referred to as the *orientation polarisation of a flexible molecule*, and for that arising from the alteration of the equilibrium configurations by the field, which is usually termed the *atom polarisation.* This is because the two polarisations are statistically indistinguishable. Such polarisation through the displacement of atoms from their equilibrium positions may be termed *vibration polarisation.*

The foregoing expression is deduced on the assumption that vibration is harmonic, and that the resultant moment of deformation is proportional to the first power of the displacement from the non-polar configuration. As a rule, neither assumption is valid if the displacement is large; but then, unless the force constant of bending is rather small, the potential energy is at the same time so large that only at high temperatures would there be an appreciable number of molecules in such configurations. The inaccuracy of these simple assumptions is therefore not likely to have any noticeable effect except at high temperatures, and over a considerable range of lower temperatures the polarisation should be independent of temperature. This is true for many of the molecules examined (Coop and Sutton, *loc. cit.*), but the polarisations of some molecules of the type of ethylene dichloride have been found to vary with temperature (see Lennard-Jones and Pike, *Trans. Faraday Soc.*, 1934, **30**, 830, for references to earlier work). In these latter it has, therefore, been supposed that there is a restriction of the rotation of the two halves of the molecule relative to each other which gives a minimum of potential energy in the *trans*- and a maximum in the *cis*-configuration, but which is not great enough to give a force constant comparable in magnitude with that resisting the bending of a covalent bond relative to a neighbouring one (about 2—4.10^{-12} ergs/radian^2/g.-mol.) (see Lothar Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 27; Lennard-Jones and Pike, *loc. cit.*; Altar, *J. Chem. Physics*, 1935, **3**, 460; Beach and Stevenson, *ibid.*, 1938, **6**, 635).

The Raman spectra of this and of similar substances in the liquid phase or in solution are, however, said to show the existence of definite *cis*- and *trans*-isomers (see, *e.g.*, Wu, *ibid.*, 1939, **7**, 965; Langseth, Bernstein, and Bak, *ibid.*, 1940, **8**, 415). If this be so, then any increase of moment with rise of temperature must be ascribed to change in equilibrium between the *cis*- and the *trans*-forms. This conclusion, if correct, would mean that most theoretical treatments of the forces between the two groups in such molecules (see previous references, also Beach and Palmer, *ibid.*, 1938, **6**, 639; and Beach and Turkevich, *J. Amer. Chem. Soc.*, 1939, **61**, 303) are quite inadequate, for they lead to uni-minimal potential functions. Although some progress in the theory of such forces can be made in spite of the ambiguity in the interpretation of the data, it is obviously necessary that this shall be resolved before the theory can develop very far.

In the hope of making this possible, the existing data for the polarisations of substances which might show such temperature effects have been augmented and improved by measurements in solution and in the vapour phase.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene. A.R. Benzene was fractionally crystallised three times and, just before use, was refluxed over phosphoric oxide and distilled in a stream of dry air.

Dioxan. Light's pure dioxan, m. p. 12°, was fractionated once from sodium and refluxed with it before a final distillation in a stream of dry air; b. p. 100·6—101·1° (corr.)/749 mm. (cf. "Organic Solvents," Weissberger and Proskauer, Oxford, pp. 38, 139; 101·2—101·4°/760 mm.).

Fumaronitrile. This was prepared according to the method of Wolf and Straete (*Bull. Sci. Acad. roy. Belg.*, 1935, **21**, 216), and purified by vacuum sublimation, a small electrically heated vapourising furnace suspended in a large evacuated jar being used for the purpose; m. p. (specimen for solution measurements) 95·2—95·4° (corr.): (specimen for vapour measurements) 95·7—95·9° (corr.) (cf. Wolf and Straete, *loc. cit.*, 95·8—96·2°).

Succinonitrile. B.D.H. material was recrystallised from ether; for the specimen used in the vapour measurements the recrystallisation was made more efficient by the use of a centrifuge; m. p. (specimen for solution measurements) 53·9—54·5° (corr.): (specimen for vapour measurements) 56·0—56·3° (corr.) (cf. Timmermans and Hennaut-Roland, *J. Chim. physique*, 1937, **34**, 693; 57·15—57·20°; other authors, 51—54°).

Ethylene dichloride. This was purified by the method described in "Organic Solvents," except that it was first shaken with phosphorus pentachloride; b. p. 83·7—83·9° (corr.)/772 mm. (cf. Timmermans and Martin, *J. Chim. physique*, 1928, **25**, 411; b. p. 83·5°).

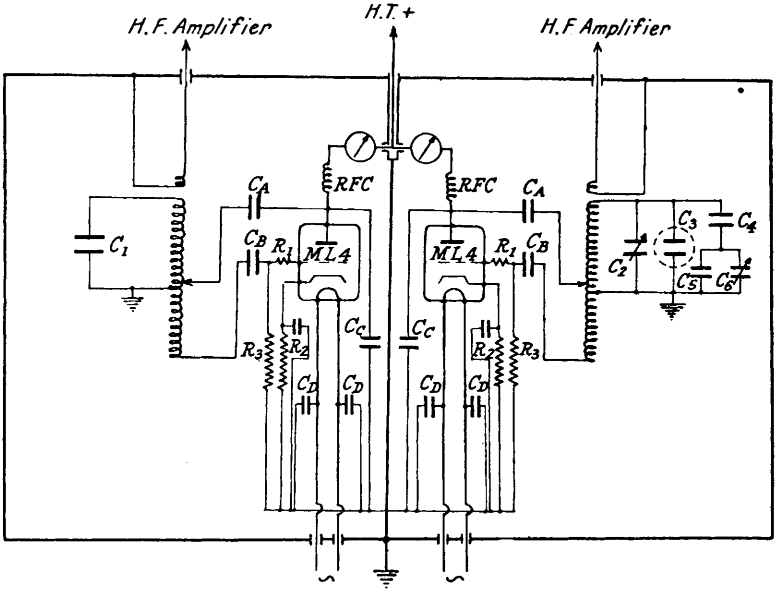
Ethylene dibromide. A commercial specimen was washed with cold concentrated sulphuric acid, sodium carbonate, and water, then dried by calcium chloride, fractionally distilled, frozen out, again dried by calcium chloride, and again fractionally distilled; b. p. 130·8—131·1° (corr.)/751 mm.; m. p. 9·8° (cf. Timmermans and Martin, *ibid.*, 1926, **13**, 733; whence b. p. 131·3°/751 mm.; m. p. 10·0°).

Dimethylketazine. This azine was supplied by Mr. G. E. Coates; b. p. 133·5—133·6°/766 mm. (cf. Barrick, Drake, and Lochte, *J. Amer. Chem. Soc.*, 1936, **58**, 160, b. p. 132—133°).

Diacetyl. This substance was prepared by the method of Olivier (*Bull. Soc. chim.*, 1932, **51**, 99) except that the difficult purification by formation of a phosphoric acid complex was replaced by fractionation with a Podbielniak column. The absolute b. p. of the fraction used is not known accurately, but it boiled over less than 0·1° and gave no reaction for nitrogen, thus showing that the impurity which Olivier detected in this preparation had been removed; b. p. 88·8°/756 mm. (cf. Olivier, *loc. cit.*, 88°/750 mm.).

Apparatus for Measuring the Dielectric Constants of Solutions and Vapours.—The experimental method and the apparatus used for the measurements of polarisations in solution were essentially those described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). The dielectric constants were all based on the assumed standard value of 2·2727 for that of pure dry benzene at 25° (Hartshorn and Oliver, *ibid.*, 1929, *A*, **123**, 664). The symbols used have the following meanings : f_2 mol.-fraction of the solute, d density, n refractive index for the mercury green line, P_2 molecular total polarisation of the solute, ${}_{\mathrm{E}}P_2$ molecular electron polarisation (molecular refractivity) of the solute, ${}_{\mathrm{A}}P_2$ atom polarisation of the solute.

FIG. 1.



C_1, C_2, C_3, C_4, C_5, C_6 : see Coop and Sutton, J., 1270, 1938. C_A 0·01 μF, C_B 0·004 μF, C_C and C_D 0·1 μF. R_1 5000 Ω, R_2 400 Ω, R_3 1 MΩ.

The apparatus described by Coop and Sutton (*loc. cit.*) for the measurement of the dielectric constants of gases and vapours was modified by the circuit of the heterodyne oscillator being completely changed; otherwise the apparatus and experimental method differed only in minor details. Most attempts to devise oscillators of a very high stability have been based on the work of Llewellyn (*Proc. Inst. Radio Eng.*, 1931, **19**, 2063), but his method of calculation is never exact, and is in many cases incorrect, *e.g.*, when a grid leak is used (Colebrook, " Oscillators of Constant Frequency," *N.P.L.*, 1934). Lampkin (*ibid.*, 1939, **27**, 199) has shown that if the valve is tapped across only a small part of the inductance of the tuned circuit the stability is increased. The quantitative explanation of this cannot be given, since accurate circuit analysis where valves are concerned is impossible; but qualitatively it can be seen that the smaller the part of the inductance across which the valve is tapped the smaller will be the effect of changes in the inter-electrode capacities and resistances, arising from changes in the applied voltages, on the characteristics of the oscillating circuit and hence on the frequency of oscillation. The new circuit is shown in Fig. 1. The valve is tapped across only one of the sixty turns of the inductance.

Owing to war conditions, it has been impossible to keep the oscillators under thermostatic control overnight. The observed frequency drift, 1—1·5 cycles/sec./hour, at the end of the day may therefore still be due to incomplete temperature equilibrium.

The dielectric constants are all based on a value of 1·000582 for air free from water and carbon dioxide, at 0° and 760 mm., which is the standard used by Coop. Watson, Rao, and Ramaswamy (*Proc. Roy. Soc.*, 1934, *A*, **143**, 558) showed that if the air is dried by liquid air, after carbon dioxide and water have been removed by means of soda-lime and phosphoric oxide, the dielectric constant decreases to 1·000576 in better agreement with the value calculated by extrapolating the square of the refractive index, 1·000577 (Bender, *Physical Rev.*, 1938, **54**, 179). This observation has been approximately confirmed. The results when liquid air was used were not so reproducible as when it was omitted, but if the air in the former case is taken to have a dielectric constant of 1·000576, then air purified only by soda-lime and phosphoric oxide is calculated to have a dielectric constant of 1·000584 ± 0·000002, in good agreement with the average value used by Coop. The value 1·000582 for air purified without refrigeration was shown to correspond to 1·000989 for carbon dioxide at 0° and 760 mm. (Coop and Sutton, *loc. cit.*; cf. Zahn, *Physical Rev.*, 1926, **27**, 455; 1·000972: Stuart, *Z. Physik*, 1928, **47**, 457; 1·000987: Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1933, **55**, 453; 1·000989: Watson, Rao, and Ramaswamy, *loc. cit.*; 1·000989).

The abbreviations used in reporting the vapour measurements are: T = absolute temperature; N = number of measurements made at the temperature given; p = the pressure range over which measurements were made, to the nearest mm.; P = the total polarisation, being the mean of all measurements at a given temperature; ΔP = the average numerical deviation of the individual values of P from the mean; $P_{\text{calc.}}$ = the polarisation calculated from the mean P–$1/T$ line; P_{E} = electron polarisation. The signs attached in the first column indicate different samples of the material. Other symbols will be explained later.

In all cases where the total polarisation varies with temperature the difference between it and the deformation polarisation (P_{E} plus an allowance for P_{A}, the atom polarisation) has been used to calculate apparent values of the moment. The reason for this will be apparent in the discussion.

Results.

TABLE I.

Measurements in Solution at 25°.

Fumaronitrile in benzene.

f_2.	$\epsilon_{1,2}$.	$d_{1,2}$.	P_2.	$n_1^2{}_{,2}$.	${}_{\text{E}}P_2$.	f_2.	$\epsilon_{1,2}$.	$d_{1,2}$.	P_2.	$n_1^2{}_{,2}$.	${}_{\text{E}}P_2$.
0·004873	2·2751	0·87434	29·8	—	—	0·006108	—	—	—	2·25644	19·89
0·009840	2·2781	0·87514	30·2	—	—	0·010134	—	—	—	2·25575	19·69
0·020043	2·2826	0·87676	29·2	—	—	0·016127	—	—	—	2·25524	19·65
0·039619	2·2936	0·87962	29·7	—	—	—	—	—	—	—	—

The molecule is not expected to have a permanent electric dipole moment, so P_2 should be independent of f_2; and therefore the values are averaged to give $P_2 = 29·7$ c.c. ${}_{\text{E}}P_2 = 19·8$ c.c., so ${}_{\text{A}}P_2 + {}_{\text{O}}P_2 = 9·9$ c.c.; but if we assume that ${}_{\text{O}}P_2 = 0$ we have ${}_{\text{A}}P_2 = 9·9$ c.c.

Succinonitrile in benzene.

0·006368	—	0·87481	—	—	—	0·004258	2·3654	—	334·2	—	—
0·014343	—	0·87604	—	—	—	0·009590	2·4814	—	328·1	—	—
0·024539	—	0·87791	—	—	—	0·016316	2·6354	—	322·1	—	—
—	—	—	—	—	—	0·029797	2·9500	—	309·4	—	—

${}_{\infty}P_2 = 337$. ${}_{\text{E}}P_2$ calculated from Landolt–Börnstein, for Na$_{\text{D}}$ line (cf. Lewis and Smyth, *J. Chem. Physics*, 1939, **7**, 1085) = 20·3 c.c. ${}_{\text{A}}P_2 + {}_{\text{O}}P_2 = 317$. Hence μ (apparent) = 3·90 D. (cf. Williams, *Z. physikal. Chem.*, 1938, *A*, **138**, 75; μ = 3·8 D.; Lewis and Smyth, *loc. cit.*, μ = 3·68 D. in toluene solution at 30°).

Succinonitrile in dioxan.

0·0000	—	1·02790	—	—	—	0·005164	2·3161	—	317·6	—	—
0·007316	—	1·02787	—	—	—	0·009780	2·4163	—	314·5	—	—
0·010008	—	1·02778	—	—	—	0·017281	2·5847	—	312·1	—	—
0·017258	—	1·02777	—	—	—	—	—	—	—	—	—

${}_{\infty}P_2 = 320$ c.c. ${}_{\text{E}}P_2 = 20·3$ (see above). ${}_{\text{A}}P_2 + {}_{\text{O}}P_2 = 300$ c.c. μ (apparent) = 3·80 D.

Ethylene dichloride in dioxan.

0·0000	2·2159	1·02750	—	—	—	0·01338	2·2813	1·02985	93·15	—	—
0·008363	2·2571	1·02924	93·39	—	—	0·01512	2·2902	1·03087	92·12	—	—

${}_{\infty}P_2 = 94·6$ c.c. From the dielectric constant of the solid (Smyth and Hitchcock, *J. Amer. Chem. Soc.*, 1932, **54**, 4631) ${}_{\text{E}}P_2 + {}_{\text{A}}P_2 = 23·9$ c.c. [${}_{\text{E}}P_2$ (calc.) = 21·1 c.c.]. Both the dielectric-constant measurements (White and Morgan, *J. Chem. Physics*, 1937, **5**, 655) and the Raman spectrum of the solid (Mizushima, Morino, and Nozirì, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 63) indicate the absence of free rotation in the solid state. ${}_{\text{O}}P_2$ (apparent) = 70·7 c.c., μ (apparent) = 1·84 D.

TABLE II.

Measurements in the Vapour Phase.

Ethylene dichloride.

T.	*N.*	*p.*	*P.*	ΔP.	$\mu_{app.}$	*T.*	*N.*	*p.*	*P.*	ΔP.	$\mu_{app.}$
308·45°	7	5·9—7·9	51·6	0·05	1·18	441·2°	12	7·9—11·1	52·6	0·2	1·43
334·65	9	6·4—8·6	52·1	0·1	1·24	480·75	7	9·1—11·5	51·8	0·15	1·47
371·55	7	7·7—8·7	52·65	0·1	1·32	524·8	7	10·1—12·3	50·8	0·15	1·51
406·3	5	7·9—9·5	52·6	0·1	1·38						

P_{A+E} is taken to be 23·9 c.c. (see above).

These results are in very good agreement with those reported by Zahn (*Physical Rev.*, 1931, **38**, 524); both sets disagree markedly with Greene and Williams's results (*ibid.*, 1932, **42**, 119).

Ethylene dibromide,

338·85*	8	4·9—6·2	41·8	0·1	0·815	437·0	7	9·3—12·1	43·9	0·17	1·002
338·6	8	4·7—6·5	41·55	0·15	0·807	466·7	8	9·3—13·1	44·0	0·09	1·04
369·2	9	7·1—10·7	42·5	0·17	0·875	496·2	11	9·4—14·5	44·3	0·36	1·08
407·7	8	8·6—11·8	43·25	0·17	0·946						

P_{A+E} is taken to be 29·7 c.c. (Zahn, *Physical Rev.*, 1932, **40**, 291).

* Since the first result differed so widely from Zahn's (*loc. cit.*), a second specimen was measured, but it gave substantially the same result. Although the substance did not decompose until heated above 496° K., it turns brown on warming to 313° K. (40°) in the light (it is possible that a very small amount of air must also be present). It may be, therefore, that Zahn's results were invalidated by decomposition, whereas in the present experiments the heating arrangements excluded light.

The results reported by Greene and Williams (*loc. cit.*) are still higher and less concordant.

Succinonitrile (*ethylene dicyanide*).

443·2	7	1·8—1·4	186	4·5	3·45	513·05	8	3·7—3·0	173	1·2	3·57
478·3	8	3·3—2·6	180	2·2	3·52						

P_{A+E} is taken to be 20 c.c. (cf. above).

Diacetyl.

After being once distilled through a Podbielniak column, a specimen gave very erratic results even at 80°. It was therefore refractionated and it then gave the following results : §

328·45	7	8·0—7·1	43·6	0·2	1·05	437·6	8	13·8—10·4	43·7	0·2	1·22
361·85	8	11·4—8·6	43·6	0·2	1·11	478·1	7	15·0—11·4	43·5	0·3	1·27
398·0	7	12·5—8·9	43·6	0·1	1·16						

P_{A+E} is taken as 22·7 c.c., this being 1·1 times the P_E value calculated for the Na_D line.

§ An attempt was made to confirm these results by preparing a larger quantity of diacetyl and reactionating it three times in the Podbielniak column. The specimen gave results, however, which were too erratic to be worth reporting.

The amount of impurity in the diacetyl prepared by Olivier's method (*loc. cit.*) is only 0·1—0·4% before the final purification; but this small amount might affect polymerisation on the platinum plates of the measuring condenser.

It would possibly be better to purify the diacetyl *via* the phosphoric acid complex described by Olivier. Owing to the war the work has had to be discontinued, but the above results were deemed worthy of record.

Fumaronitrile (trans-*acetylene dicyanide*).

409·8	5	8·6—9·6	29·6	0·2	—

At 457·7° K. there appeared to be slow decomposition, the polarisation, *P*, increasing gradually to 31·3 c.c. in seven measurements. The polarisation at this temperature was taken to be 29·8 c.c. Hence the average value of *P* is 29·7 c.c., exactly the same as in the solution measurement (see above), and so assuming that P_E has the same value too and that P_O is zero, we find $P_E = 9{\cdot}9$ c.c.

Dimethylketazine.

T.	*N.*	*p.*	*P.*	ΔP.	$P_{calc.}$	*T.*	*N.*	*p.*	*P.*	ΔP.	$P_{calc.}$
349·1°	8	5·4—4·6	0·7	80·3	80·1	439·3°	7	8·1—6·4	0·2	71·75	71·8
380·85	7	6·7—5·5	0·2	76·8	76·8	469·2	6	9·1—6·4	0·2	69·7	69·8
409·2	6	7·3—6·1	0·3	74·1	74·2	504·5	8	9·9—6·7	0·3	67·7	67·7

$P_E = 36$ c.c. (Barrick, Drake, and Lochte, *loc. cit.*). If P_A be taken as 0·1 of P_E, $P_{A+E} = 39{\cdot}6$ c.c.; P_{A+E} (from extrapolation of the *P*–1/*T* curve) = 39·7 c.c. $\mu_{app.}$ is found to have a constant value of 1·51 D.; and the values in the column headed $P_{calc.}$ are the total polarisation values calculated on this basis.

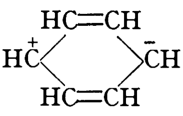
The results at the lowest temperature were very erratic, probably owing to adsorption.

DISCUSSION.

Molecules with No Axis of " Free Rotation."—The solution and the vapour results for the total polarisation of fumaronitrile agree very well (29·7 c.c. in the former as also in the latter). This is another example showing that there is little solvent effect for compounds which have a temperature-independent polarisation. The values for the vibration polarisations of cyanogen (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144), fumaronitrile, and *p*-dicyanobenzene are 8·3, 9·8, and 11·9 c.c., respectively, and so are approximately equal. As was previously shown (Coop and Sutton, *loc. cit.*), they should be exactly equal if the group moments and the force constants of bending are the same in all three. It is impossible to attribute with certainty the observed variations to change in either one of these factors, but it is probable that the increase of distance between the CN groups corresponds to a reduction of their mutual polarisation, a consequent increase of μ, and hence of vibration polarisation. It may be noted that the experimentally determined value of the refractive index shows that there is no exaltation, and that therefore it is unlikely to be shown by the related compound *p*-dicyanobenzene (see Coop and Sutton, *loc. cit.*, and Weissberger and Sängewald, J., 1935, 855).

Molecules with an Axis of " Free Rotation."—The immediate aim in discussing the results for molecules with single bonds joining the polar groups is to decide whether there are *cis*- and *trans*-equilibrium positions or only the latter. This is part of the more general problem of discovering the nature of the forces between the polar groups and the way in which a material medium affects them; and although frequently no definite answer can be given to the immediate question, yet the conclusions drawn are nevertheless often of some value in relation to the larger problem.

The polarisation of ethylene dichloride in dioxan at 25°, *viz.*, 94·6 c.c., is much higher than those found for it in most other solvents; *e.g.*, in n-hexane at 20° it is only 61·6 c.c., in carbon disulphide 63·5 c.c. (Müller, *Physikal. Z.*, 1933, **34**, 689). Also, it is even higher than those in benzene or toluene, which are already abnormally large, *e.g.*, 86·5 c.c. at 30° in benzene (Mizushima, Morino, and Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **25**, 159). If the inter-group forces were Coulombic to any considerable extent, then, irrespective of whether the other forces produce a maximum of potential energy between the *cis*- and *trans*-positions, we should expect that an increase in dielectric constant of the medium would, by decreasing mutual repulsion, increase the proportion of molecules *not* in the *trans*-configuration and so increase the moment. The notable effects of benzene, toluene, and dioxan, which do not have large dielectric constants as measured macroscopically with weak uniform electric fields, may therefore indicate that the dielectric constants in the near neighbourhood of the polar solute molecules are much larger. For dioxan this could arise by orientation in the inhomogeneous field round the solute molecules, for it is only non-polar because the two dipolar ethereal groups in it oppose one another. Benzene might develop a large dielectric constant in the intense field by passing to one of the excited polar resonance states, *e.g.*, (I), which could be drawn for it. A critical examination of the data suggests, however, that the effect is relatively specific,* so it may possibly be due to some degree of loose compound formation. If the compound were a polarisation complex (cf. Briegleb, *Z. physikal. Chem.*, 1935, *B*, **31**, 58) the theories of compound formation and of physical effect would merge.


(I.)

* The remarkable fact that succinonitrile is almost insoluble in most organic solvents, such as carbon tetrachloride, hexane, and carbon disulphide, but is very soluble in benzene and dioxan points to some solute–solvent interaction in these instances. It might therefore be expected that the polarisations in these solvents would be abnormal and, on the analogy of ethylene dichloride, would be large; but the insolubility prevents direct demonstration of this. Lewis and Smyth (*J. Chem. Physics*, 1939, **7**, 1085) have shown that the moment of succinonitrile in toluene increases as the temperature increases and so differs from that of ethylene dichloride in either benzene or toluene, which decreases with increasing temperature although in normal solvents it increases (Mizushima, Morino, and Higasi, *loc. cit.*). Perhaps, therefore, solutions of succinonitrile in benzene and dioxan are not abnormal as compared with those in other non-polar solvents.

It may be noted that benzil has a rather larger moment in benzene and dioxan than in carbon

Because of the complication of solvent effect, the solution measurements prove to be only of minor value in helping a choice to be made between the *cis-trans*-isomer and the *trans*-vibration theory, but some application will be made later (p. 739). Most of the vapour polarisation measurements are of greater value for this purpose.

The constant apparent moment of dimethylketazine, as distinct from the constant vibration polarisation of diacetyl or the varying polarisation and moment of ethylene dichloride, can be explained by the two parts being completely free to rotate, by the proportions of *cis*- and *trans*-isomers being constant, or by their being fixed at an angle not 180° to each other. This would mean either that the potential energy is equal in the *cis*- and *trans*-configurations or that the orientation effect about an N–N link which was predicted by Penney and Sutherland (*Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Physics*, 1934, **2**, 492) is decisive. It is not possible at present to choose between these explanations.

The measurements on ethylene dichloride, dibromide, and dicyanide, as well as diacetyl, warrant more extended discussion. Beach and Stevenson (*loc. cit.*) have shown that, on the vibration polarisation theory,

$$\overline{\mu}^2 = A + B\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\rho = \int_0^{\pi} \cos\phi \; \mathrm{e}^{-V(\phi)\boldsymbol{R}T} \mathrm{d}\phi \Big/ \int_0^{\pi} \mathrm{e}^{-V(\phi)/\boldsymbol{R}T} \mathrm{d}\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

if there is no weight factor, *i.e.*, if the probability of a configuration depends only upon its potential energy and not upon kinetic factors (see p. 735). ϕ is the angle between the planes containing, each, one of the rotating dipoles and the C–C axis ; $V(\phi)$ is the potential energy for the angle ϕ ; and

$$A = \mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos\alpha_1 \cos\alpha_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$B = 2\mu_1\mu_2 \sin\alpha_1 \sin\alpha_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

μ_1 and μ_2 are the rotating dipoles while α_1, α_2 are the angles which these make with the C–C axis, which we shall assume to be known. ρ is thus an average value of $\cos\phi$ and should vary between 0, for free rotation, and -1 for fixation in the *trans*-configuration, whatever the precise form of the potential function. For the results to be consistent with the vibration polarisation theory it is, therefore, at least to be expected that if ρ be calculated from experimental values for μ^2, equation (1) being used with A and B values given by (3) and (4), it should lie between 0 and -1; and if it be plotted against $1/T$, the curve should bend towards the origin (where infinite temperature brings about complete freedom of rotation). By plotting the present results these minimal conditions are seen to be satisfied (Fig. 2).*

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tetrachloride (Caldwell and LeFèvre, J., 1939, 1614; Higasi, *Bull. Chem. Soc. Japan*, 1938, **13**, 158), the increase in moment being only 4—5%, however.

It seems, therefore, that the only well-established examples of gross abnormality in benzene or dioxan solutions of this type of solute are provided when these are *halogen* compounds with what may be described either as restricted rotation or as *trans*-predominance in a mixture of isomers. No restriction means no abnormality: what is probably pertinent is that it also means that the polar groups are relatively far apart. Thus, *e.g.*, *p*-xylylene dichloride has almost equal polarisations in benzene and hexane, both corresponding to complete freedom of rotation (Müller, *loc. cit.*). Restriction does not, however, necessarily mean abnormality, for stilbene dichloride has almost the same polarisations in benzene and in carbon tetrachloride solutions, both corresponding to restriction (Higasi, *loc. cit.*). Although very few non-halogenated solutes of this type have been examined, it appears from the existing evidence that the gross abnormalities are highly specific to solute and solvent, and so may be due to compound formation, as has been frequently suggested (see, *e.g.*, Earp and Glasstone, J., 1935, 1709; Stearn and Smyth, *J. Amer. Chem. Soc.*, 1934, **56**, 1667; Mizushima, Morino, and Higasi, *loc. cit.*).

This might involve ring formation, but there is no definite evidence in support of this, since the moment of ethylene dichloride never reaches, let alone exceeds, the value (*ca.* 2·2 D.) corresponding to free rotation or equal proportions of *cis*- and *trans*-isomers.

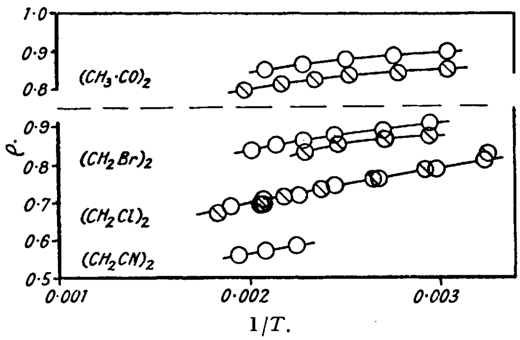
* Zahn's results for ethylene dibromide (*loc. cit.*; also Fig. 2) lie less well on a smooth curve of this kind, probably owing to the difficulties of measuring this substance (p. 732).

Beach and Stevenson tried the following functions expressing the potential energy in the region of the *trans*-position :—

$$\begin{array}{ll} \textit{linear} & V(\phi) = V_\pi(\pi - \phi)/\pi \\ \textit{cosine} & V(\phi) = V_\pi(1 + \cos\phi)/2 \\ \textit{parabolic} & V(\phi) = V_\pi(\pi - \phi)^2/\pi^2 \end{array}$$

(where V is the difference of potential energy in the *trans*- and the *cis*-configurations, *i.e.*, the potential barrier) for the purpose of calculating ρ as a function of T from equation (2). By using the theoretical ρ–$V_\pi/2\boldsymbol{R}T$ curves so obtained and the experimental ρ values, it is then possible to calculate the values of V_π corresponding to the several trial functions at a series of temperatures, and, by comparing the consistency in the sets of values, to choose the best potential function. This has been done for the present observations. In the tables of results (Table III) the rotating moments ($\mu_1 = \mu_2$) are assumed to be equal to those of the ethyl compounds (the significance of the columns headed $\log_{10} N_t/N_c$ is explained below). The percentage variations show that for ethylene dichloride there is nothing to choose between the cosine and the parabolic function, both being rather better than the linear one. ρ values calculated for the cosine functions with $V_\pi = 3{\cdot}69$ (the mean of the first six values only) agree well with those observed at the lower temperatures. The ethylene dibromide data fit the linear function better, with $V_\pi = 6{\cdot}78$ kg.-cals./mol. Succinonitrile could not be measured over a large temperature range, so all potential functions seem equally good for it. For diacetyl the best function is the parabolic one with $V_\pi = 22$—23 kg.-cals./mol. because it leads to the observed temperature independence of the polarisation (see p. 732) : it corresponds, of course, to simple harmonic vibration about the *trans*-position (see p. 728).

FIG. 2.



Plain circles, Bloom and Sutton.
Crossed circles, Zahn.

The alternative treatment, applied particularly by Langseth, Bernstein, and Bak (*J. Chem. Physics*, 1940, **8**, 415), is to suppose that there are two stable forms, *cis* and *trans*, the potential barrier between them being so high as to ensure that there are few molecules in intermediate configurations, but not so high as to allow of the separation of the isomers. In this event

$$N_{trans}/N_{cis} = Se^{V/\boldsymbol{R}_\pi T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where V_π has the same meaning as before, S is a weight factor,* N_{trans} is the number of molecules of the *trans*-form and N_{cis} of the *cis*.

From equation (5)

$$\log_e N_t/N_c - \log_e S = V_\pi/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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* The weight factor S appears when the classical treatment of the distribution of molecules in various configurations is elaborated to take into account the momentum co-ordinates which determine the kinetic energy, as well as the positional co-ordinates which determine the potential energy. If the moments of inertia vary appreciably with the configuration, the fact that the molecule is spinning makes it tend to assume one configuration rather than another, apart from any effect to which the variation of potential energy with configuration may give rise. In the case of the ethylene dichloride molecule it is found theoretically that, crudely speaking, the molecule should tend to spin as nearly as possible about the line joining its main masses, the chlorine atoms, and to reduce its moment of inertia about this axis; and so the *trans*-configuration is kinetically favoured (Altar, *J. Chem. Physics*, 1935, **3**, 460). This effect gives rise to a temperature-independent coefficient by which the exponential temperature term, giving the effect of potential energy upon configuration, is multiplied. If change of configuration produces but little change in moment of inertia, as for example in *p*-xylylene dichloride, the weight factor is nearly unity.

TABLE III.

Ethylene Dichloride.

			V_π.			$\log_{10} N_t/N_c$.	
		$-\rho_{calc.}$ for V_{cos}	cos.	lin.	parab.	$\mu_1 =$	
T.	$-\rho_{exp.}$.	= 3·69.		μ_1 = 2·03.		2·03.	1·87.*
308·45°	0·811	0·812	3·62	3·97	7·20	0·981	0·902
334·65	0·790	0·790	3·65	4·02	6·32	0·929	0·849
371·55	0·763	0·764	3·67	4·13	6·82	0·872	0·791
406·3	0·742	0·739	3·70	4·22	6·68	0·829	0·746
441·1	0·720	0·715	3·62	4·32	6·32	0·788	0·704
480·75	0·703	0·683	3·88	4·53	6·70	0·758	0·674
524·8	0·688	0·651	4·07	4·60	6·91	0·732	0·647
		Mean	3·74	4·26	6·71		
		% Deviation	3·48	4·60	3·43		

Ethylene Dibromide.

		V_π.		
		cos.	lin.	
T.	$-\rho_{exp.}$.	μ_1 = 2·02.†		$\log_{10} N_t/N_c$.
338·85°	0·908	7·79	6·69	1·318
338·6	0·910	7·90	6·74	1·328
369·2	0·892	7·21	6·64	1·253
407·7	0·877	7·08	6·75	1·182
437·0°	0·862	6·84	6·71	1·129
466·7	0·851	6·87	6·91	1·093
496·2	0·838	6·83	6·99	1·055
	Mean	7·22	6·78	
	% Deviation	4·99	1·47	

Values of $V_{parab.}$ were not calculated because a small error in ρ produces a very large change in it.

Succinonitrile (Ethylene Dicyanide).

		V_π.			$\log_{10} N_t/N_c$.	
		cos.	lin.	parab.	$\mu_1 =$	
T.	$-\rho_{exp.}$	μ_1 = 4·03.			3·94.	4·03.‡
443·2°	0·587	2·59	3·11	4·06	0·560	0·582
478·3	0·571	2·70	3·24	4·15	0·538	0·562
513·05°	0·560	2·80	3·37	4·29	0·524	0·545
	Mean	2·70	3·24	4·17		
	% Deviation	2·59	2·78	1·92		

Diacetyl.

		V_π.			
		cos.	lin.	parab.	
T.	$-\rho_{exp.}$.	μ_1 = 2·85.§			$\log_{10} N_t/N_c$.
328·45°	0·897	6·71	6·05	—	1·267
361·85	0·887	6·75	6·28	*ca.* 28	1·222
398·0	0·876	6·89	6·59	23·5	1·178
437·6°	0·863	6·97	6·79	21·7	1·132
478·1	0·851	7·04	7·08	21·7	1·095
	Mean	6·87	6·56	22·3	
	% Deviation	1·60	4·79	3·59	

A small change in ρ produces a large change in $V_{parab.}$.

* μ_{CH_3Cl} = 1·87 D., $\mu_{C_2H_5Cl}$ = 2·03 D. (see Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499; Dipole Index, *Trans. Faraday Soc.*, 1934, **30**).

† $\mu_{C_2H_5Br}$ = 2·02 D. (Smyth and McAlpine, *loc. cit.*).

‡ μ_{CH_3CN} = 3·94 D., $\mu_{C_2H_5CN}$ = 4·03 D. (Groves and Sugden, J., 1937, 158).

§ μ_{COMe_2} = 2·85 D. (Zahn, *Physikal. Z.*, 1932, **33**, 686).

so that if $\log_{10} N_t/N_c$ is plotted against $1/T$ a straight line should be obtained, according to this theory. N_t/N_c is calculated from the expression

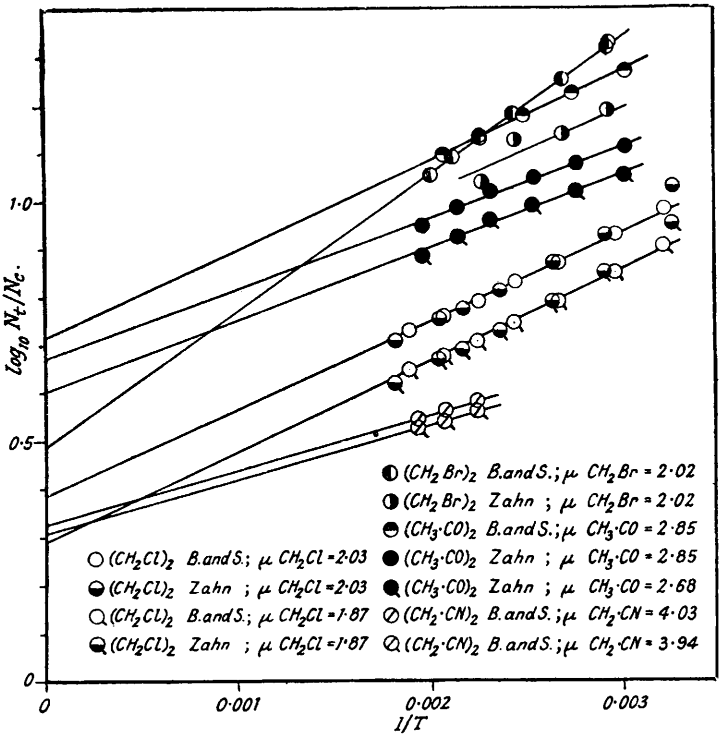
$$\bar{\mu}^2 = (2\mu \sin \alpha)^2/(1 + N_t/N_c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Any temperature-invariant vibration polarisation, or atom polarisation, arising from possible vibrations of the *cis*- and the *trans*-form about their respective potential minima can be estimated roughly in ethylene dichloride by taking the molecular polarisation of the solid substance, which is 13% larger than P_E (calc.). For the other compounds 10% of P_E can be allowed.

The observations herein reported do, in fact, give straight lines when so treated (Table

III and Fig. 3) whether the rotating moment is taken as that of the methyl or the ethyl compound (see the last two columns for ethylene dichloride and succinonitrile in Table III). Zahn's results for ethylene dichloride agree very well too, but (cf. p. 734) those for ethylene dibromide do not give such good straight lines as do ours, while those for diacetyl may give a curve : his results for chlorobromoethane (*Physical Rev.*, 1932, **40**, 291) and for chloroacetone (*Physikal. Z.*, 1932, **33**, 686) are insufficient for any conclusions to be drawn. Taking the rotating moment as that of the appropriate ethyl compound, we find the values of V_π and S to be

FIG. 3.



Substance.	V_π, cals./mol.	S.	Substance.	V_π, cals./mol.	S.
Ethylene dichloride	862	2·33	Succinonitrile	570	2·0
Ethylene dibromide	1309	3·01	Diacetyl	855	5·09

For all these compounds the weight factor S shows that the *trans*-form is favoured, which fact is in qualitative though not quantitative agreement with the theoretical treatments of Altar (*loc. cit.*) and of LuValle and Schomaker (*J. Amer. Chem. Soc.*, 1939, **61**, 3520). It will be noted that the values for the potential barriers are mostly less than 1 kg.-cal./mol. How well these values of V_π and S give straight lines which fit the observed points is shown in the following table.

Ethylene dichloride.			Ethylene dibromide.			Diacetyl.		
T.	$\mu_{obs.}$	$\mu_{calc.}$	T.	$\mu_{obs.}$	$\mu_{calc.}$	T.	$\mu_{obs.}$	$\mu_{calc.}$
308·45°	1·18	1·18	338·85°	0·815	0·812	328·45°	1·05	1·045
334·65	1·24	1·24	338·6	0·807	0·811	361·85	1·11	1·11
371·55	1·32	1·315	369·2	0·875	0·873	398·0	1·16	1·165
406·3	1·38	1·375	407·7	0·946	0·948	437·6	1·22	1·22
441·2	1·43	1·425	437·0	1·002	0·997	478·1	1·27	1·265
480·75	1·47	1·475	466·7	1·04	1·04			
524·8	1·51	1·525	496·2	1·08	1·08			

Measurements in solution at different temperatures also give straight lines, which are straighter the more accurate the measurements; *e.g.*, Smyth's earlier results for ethylene dichloride in different solvents (Smyth, Dornte, and Wilson, *J. Amer. Chem. Soc.*, 1931, **52**, 4242) do not give straight lines, but his later ones do (Stearn and Smyth, *ibid.*, 1934, **56**, 1667) (Figs. 4, 5, 6). These lines are obtained by using the vapour-phase value for the rotating group, so that little correlation between solvent, S, and V_π could be expected; but this point is discussed later.

Although the *cis-trans*-isomer theory predicts these straight lines, their observed existence does not necessarily prove the theory to be correct, for it is possible that a potential function could be found which would lead to the same result on the vibration theory. In principle this could be done in the following way. The expression for $\bar{\mu}^2$ derived from equations (5) and (7) is equated with that from equations (1), (2), (3), and (4), giving

Fig. 4.

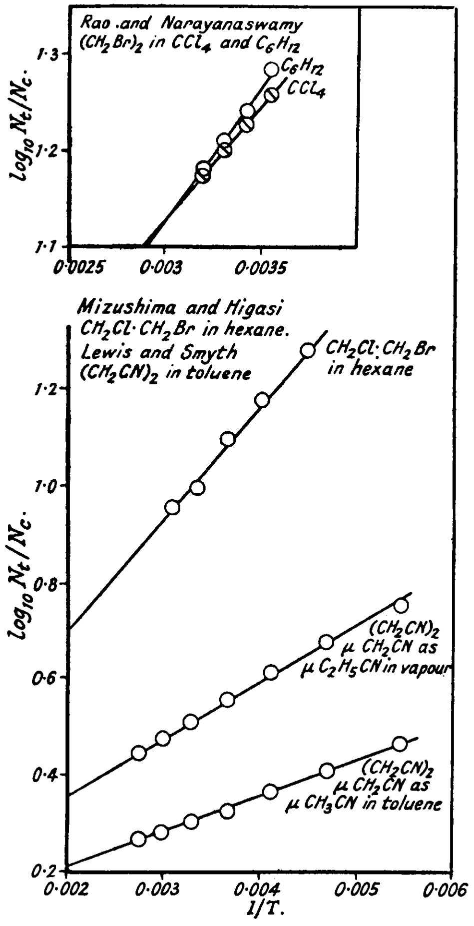


Fig. 5.

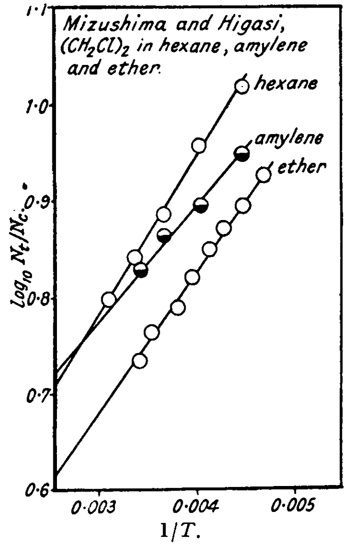
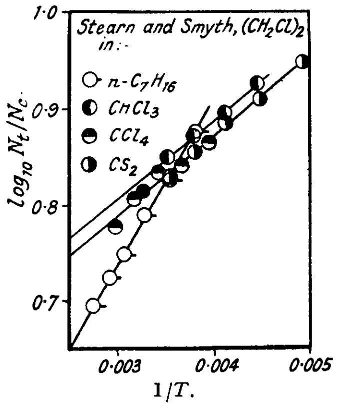


Fig. 6.



$$\frac{(2\mu\sin\alpha)^2}{1+\Sigma e^{\Phi_\pi/RT}} = 2\mu^2\sin^2\alpha\left[1+\frac{\int_0^\pi \cos\phi\, e^{-V(\phi)/RT}d\phi}{\int_0^\pi e^{-V(\phi)/RT}d\phi}\right].$$

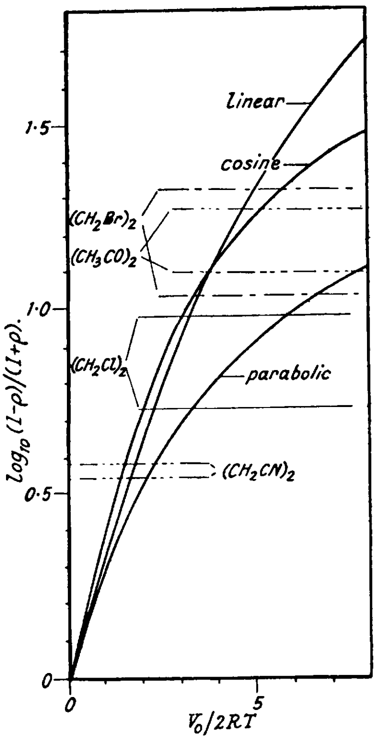
or

$$\frac{1-\Sigma e^{\Phi_\pi/RT}}{1+\Sigma e^{\Phi_\pi/RT}} = \frac{\int_0^\pi \cos\phi\, e^{-V(\phi)/RT}d\phi}{\int_0^\pi e^{-V(\phi)/RT}d\phi} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

In the expression on the left-hand side, Σ and Φ_π replace S and V_π because these quantities in the above expression are empirical parameters derived from the experimental straight lines and are devoid of the physical meaning which S and V_π have according to the *cis–trans* theory. It is required that this integral equation should be solved, given that $V(\phi) = 0$ when $\phi = \pi$ and that $V(\phi)$ is probably a maximum when $\phi = 0$. This equation has an infinite number of solutions, and therefore it is necessary to apply another limitation to $V(\phi)$: the condition chosen is that $V(\phi)$ is independent of temperature, but this equation has not been solved, even approximately.

It is instructive to see what relation is given by the vibration polarisation theory between $\log N_t/N_c$ and $1/T$. By equating expressions for $\bar{\mu}^2$ derived from the two theories, we find $\log N_t/N_c = \log (1 - \rho)/(1 + \rho)$. From the theoretical data of Beach and Stevenson (*loc. cit.*) it is possible to calculate $\log_{10} (1 - \rho)/(1 + \rho)$ for a given potential function and potential barrier V_π and so to plot it against $V_\pi/2\boldsymbol{R}T$. The graphs obtained are straight only over a limited interval of $V_\pi/2\boldsymbol{R}T$; but over the ranges of $\log_{10} (1 - \rho)/(1 + \rho)$ investigated experimentally the curvature is small. This is shown in Fig. 7, wherein the pairs of horizontal lines show the limits of experimental investigation. It should also be remembered that the experimental points fit none of the functions exactly. Moreover, it may be possible, as we have indicated above, to derive a uniminimal potential function which gives a straight line. The present data, therefore, do not enable us to choose between the two theories; and if any decision is now to be made it must be on grounds other than direct experiment of this type.

FIG. 7.



In this connection it may be mentioned that the potential energy difference of only 1300 cals./mol. at most, as deduced from the *cis-trans*-isomer theory (p. 737), is much less than that likely to be predicted on any present theory of the forces involved : but since it was hoped that the theory could be checked by such experiments this approach is unsatisfactory.

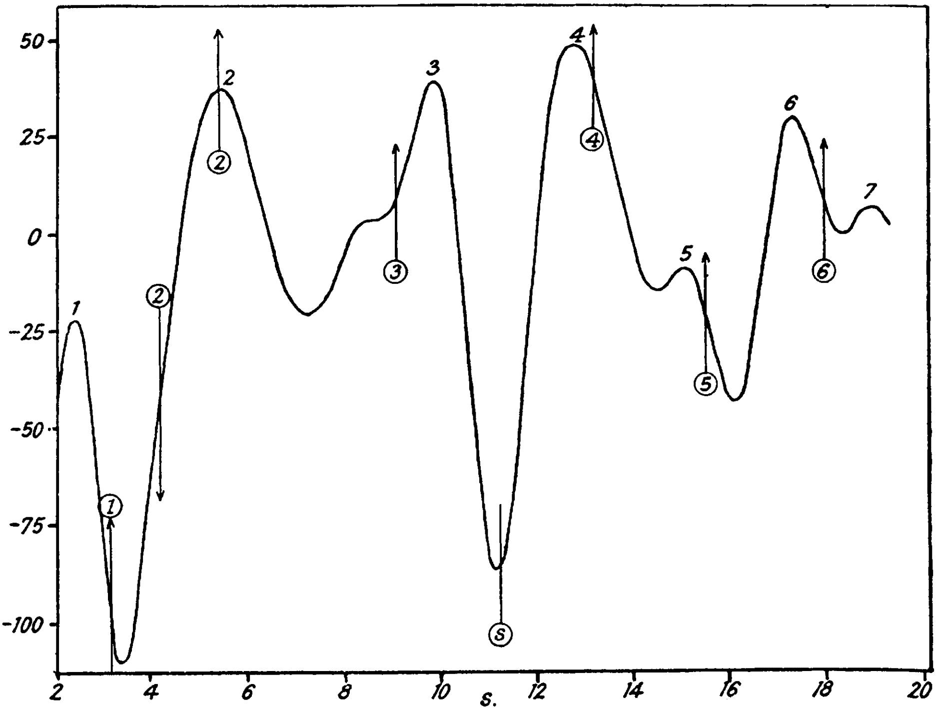
Another point, this time against the vibration theory, is that from Figs. 4, 5, and 6 it can be seen that certain of the lines for the same solute in different solvents cross. Now, according to any simple theory of the forces involved, the higher the dielectric constant of the solvent, the less the forces between the rotating dipoles, and the larger the apparent moment should be (Mizushima, Morino, and Higasi, *loc. cit.*). The crossing of these functions of the moment [$\log_{10} (1 - \rho)/(1 + \rho)$, where ρ is the experimental value] means on the vibration theory that the sign of the difference of the moments reverses, and this indicates that the dielectric constants should do so. In fact, however, they do not.

Spectroscopists have frequently concluded that there are *cis*- and *trans*-forms of ethylene dichloride present in the liquid (see p. 729). Electron-diffraction results do not disagree with this conclusion, for the proportion of the *cis*-form at the temperature at which experiments have been made on ethylene dichloride would be too small to have an appreciable effect on the photographs. The same difficulty arises for diacetyl (LuValle and Schomaker, *loc. cit.*).

On the other hand, both electric polarisation and electron-diffraction results disagree with the analogous conclusions drawn by Langseth and his collaborators from the Raman spectra of *cyclo*hexane and acetylene tetrachloride in the liquid phase (Langseth and Bernstein, *J. Chem. Physics*, 1940, **8**, 410; Langseth and Bak, *ibid.*, p. 403). They conclude that tetrachloroethane consists of isomers, a *cis* C_{2v} form, and two, C_2, at angles of about 120° from the *cis*-one; and they state that in the expression $N_{C_{2v}}/N_{C_2} = e^{E/\boldsymbol{R}T}/S$ which then holds, S is about 2, and E is 1,100 cals./mol., in the liquid phase. Mizushima, Morino, and Kozima (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **1936**, **29**, 111) have determined the dipole moment in various solvents, and it is therefore possible to test the consistency of the different data. The solvent in which the apparent moment is largest is diethyl ether, in which it is 1·97 D. at 25°. There is some difficulty in ascribing a moment to the $-CHCl_2$ group, but the smallest possible value seems to be that of methylene chloride, which is 1·57 D. (Wolf and Fuchs, " Stereochemie," Freudenberg, Vienna, 1932, p. 244; Müller, *loc. cit.*), that of ethylidene dichloride being much larger. If the angle between the two dipolar groups in the C_{2v} form is as large as 127°, the moment of this form is at least 2·5 D.

FIG. 8.

Theoretical Scattering Intensity Curve for Planar Model with $l_{C-C} = 1\cdot54$ A.



Observed features shown by labelled arrows.

Now, from the data of Langseth and Bernstein, $N_{C_{2v}}/N_{C_2} = 3\cdot19$. Hence, if μ_{C_2} is the moment of the C_2 form, we have

$$\bar{\mu}^2 = 3\cdot88 = \frac{\mu^2_{C_{2v}}N_{C_{2v}} + \mu^2_{C_2}N_{C_2}}{N_{C_{2v}} + N_{C_2}} = (2\cdot5^2 \times 3\cdot19 + \mu_{C_2}{}^2)/4\cdot19,$$

whence $\mu_{C_2}{}^2 = -3\cdot6$ D.; so, even on the most favourable assumptions, with $\bar{\mu}^2$ as large and $\mu_{C_{2v}}$ as small as possible, an impossible answer is obtained. Consequently, so far as this comparison of measurements in the liquid phase and in solution is valid, the dipole results show the interpretation of Raman ,spectra to be incorrect. Stevenson and Schomaker (*J. Chem. Physics*, 1940, **8**, 637) have shown that the electron diffraction by the vapour also disagrees with this interpretation.

From the Raman spectrum, again, Langseth and Bak (*loc. cit.*) concluded that *cyclo*hexane is planar, *i.e.*, there is fixation about the C–C bonds, but their arguments have been criticised by Saksena (*Proc. Ind. Acad. Sci.*, 1940, **12**, 321). Stevenson and Schomaker (*loc. cit.*), in comment on this, said that Pauling and Brockway showed that the electron-diffraction pattern from the vapour disproves this structure, but actually these authors only showed that a non-planar structure is satisfactory (*J. Amer. Chem. Soc.*, 1937, **59**, 1223). H. A. Skinner has therefore re-examined their data to see whether these could be compatible with a planar form. He concludes that the derived radial distribution curve shows peaks incompatible with it if the C–C distance is 1·54 A. (the normal value), the C–C–C angle is 120°, and the H–C–H angle is 109·5°. Furthermore, the theoretical scattering curve for this planar model fails to reproduce satisfactorily, either qualitatively or quantitatively, the observed diffraction pattern. Qualitatively, as may be seen from Fig. 8, it fails because it shows a shelf between the second and the third maximum instead of between the third and the fourth.

Its quantitative failure is shown by the data in the table below, where $S = (4\pi \sin \theta/2)/\lambda$ (see Pauling and Brockway, *loc. cit.*) and I is the observed intensity :

Maximum.	Minimum.	I.	$s_{\text{obs.}}$.	$s_{\text{calc.}}$.	$s_{\text{calc.}}/s_{\text{obs.}}$.
1	—	3	3·08	2·40	(0·799)
—	2	—	4·13	3·34	(0·809)
2	—	10	5·48	5·38	0·982
3	—	3	9·03	9·80	(1·085)
Shelf	—	0·5	(11·14)	—	—
4	—	4	13·07	12·62	0·966
5	—	1	15·38	14·98	0·974
6	—	2	17·78	17·20	0·967
7	—	1	20·69	18·82	(0·910)
		Average			0·972
		Average deviation (a) excluding bracketed results			0·006
		(b) including ,, ,,			0·069

The average deviation for maxima 2, 4, 5, and 6 alone is not large, but these are only half the observed singularities, and the overall average deviation is very bad, being much greater than that for the **Z** models (see Pauling and Brockway, *loc. cit.*). In these last two instances the conclusions about configuration from Raman spectra seem therefore to be wrong.

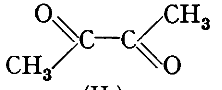
It must be admitted that at present we know very little about the form of the potential function in the ethylene dichloride type of molecule. Even on the major question of whether the *cis-trans*-isomer theory or the *trans*-vibration theory of the properties of this type of molecule is correct, the evidence and arguments are indecisive; although, if they be considered together with those in the analogous cases of acetylene tetrachloride and *cyclo*hexane, it appears that the balance of evidence is against the general hypothesis that there are relatively stable isomers in which the non-bonded atoms approach as closely as possible, and therefore that the latter of the two theories is the more favoured. If the *cis-trans*-isomer theory be accepted, we can derive only the energy difference, V_π, between the isomers. If the vibration theory be accepted, we know only the approximate shape of the lower part of the potential curve (see also Sutton, *Ann. Reports*, 1940, **37**, 64); and the value of the potential barrier, V_π, given by extrapolation has no more literal significance than has, let us say, the cryoscopic constant of a solvent.

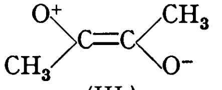
Little can be done, therefore, to use these measurements to check theories of interatomic forces beyond what Beach and his collaborators (Beach and Stevenson, *loc. cit.*; Beach and Palmer, *loc. cit.*; Beach and Turkevich, *J. Amer. Chem. Soc.*, 1939, **61**, 303) or Lewis and Smyth (*J. Chem. Physics*, 1939, **7**, 1085) have already done. They have shown that the forces of repulsion between the two rotating halves of the ethylene dihalides are due much more to exchange repulsions or " steric " forces between the halogen atoms than to electrostatic dipole–dipole interactions, and that these increase in the series ethylene dichloride, chlorobromide, and dibromide, *i.e.*, that the greater the radius of the halogen the more rigid is the *trans*-fixation. This is confirmed by the increase in V_π between the first and the last of these substances which is to be noted in Table III.

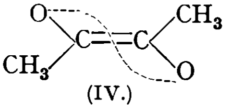
Because equation (8) represents an empirical truth of wide validity, its solution might prove to be a step forward; but even so it is to be feared that the most interesting parts of the potential function would still be unexplored because of the limited temperature ranges which can be used.

There is little prospect that these can be appreciably extended in electric polarisation measurements; but it is possible that electron-diffraction investigations on highly superheated vapours might be profitable, because the time of contact of the vapour with hot surfaces would be much less and because these could be of less highly catalytic material than the platinum used for the cylinders of the gas condenser in the dielectric-constant apparatus. Our plans for attempting this are in abeyance.

It is satisfactory to find that, whether the potential function for diacetyl be bisminimal or uniminimal, the same conclusion about the electronic structure of the molecule is reached. Whether there be an equilibrium between *cis*- and *trans*-forms or an unusually rigid fixation in the *trans*-configuration (V_π for the parabolic function being >20 kg.-cals./g.-mol., see Table III), we conclude that there is a very strong tendency for the molecule to be planar. LuValle and Schomaker (*loc. cit.*) arrived at the same result from their electron-diffraction study of the molecule. This tendency, as they say, can be attributed to resonance between the structure ordinarily assigned, *viz.*, (II), and others in which the central carbon–carbon


(II.)


(III.)


(IV.)

bond is double, *e.g.*, (III) and (IV), because these would confer a certain degree of the stereochemical character of ethylene upon the molecule.

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