240. *Measurements of the Electric Polarisations of the Vapours of Some Substances having Anomalous Dipole Moments, and their Bearing on the Theory of Atom Polarisation.*

By I. E. Coop and L. E. Sutton.

The problems remaining over from the two previous papers have been attacked by measuring electric polarisations in the vapour phase, the previous measurements having been made in solution. The results show finally that the anomalous moments are not due to solvent effects. Furthermore, the polarisations are all independent of temperature over considerable ranges, so the compounds are certainly non-polar. Essentially the same results were found with *p*-dinitrobenzene, *p*-nitrocyanobenzene, *p*-dicyanobenzene, and several inorganic tetrahalides, which show similar anomalies.

All of the anomalous compounds have a common characteristic : they would be non-polar in their unperturbed configurations but would become highly polar on being bent or twisted in certain ways. The facts could therefore be qualitatively explained as due either to slow, thermal bendings, or to bendings caused by the applied field, *i.e.*, atom polarisation. But as in the earlier case of beryllium acetylacetonate, so too in all others where the calculations could be made, the vibration frequencies prove to be too high to be compatible with the former theory; the latter must therefore be accepted. This theory leads to a relation between atom polarisation, force constant of bending, and bond moment for a molecule, and it was tested quantitatively by taking experimental values for any two of these and comparing the calculated value of the third with the measured value. In most cases good agreement was found, but an outstanding exception to this is the series of diphenylmercury compounds.

A satisfactory explanation of the polarisations of the diketones was reached from the hypothesis that each C=O bond bends relative to the rest of the molecule and perpendicular to the plane of the double bond.

The work of Finn, Hampson, and Sutton (this vol., p. 1254) on metallic acetylacetonates, and of Hammick, Hampson, and G. I. Jenkins (preceding paper) on symmetrical diketones pointed to atom polarisation as the most likely cause of the anomalous moments of these substances, but did not entirely rule out other possibilities. In order finally to decide whether or not solvent effects are responsible, it was decided to measure polarisations in the vapour phase, and, the better to distinguish between other explanations, to do this over as wide a range of temperature as possible.

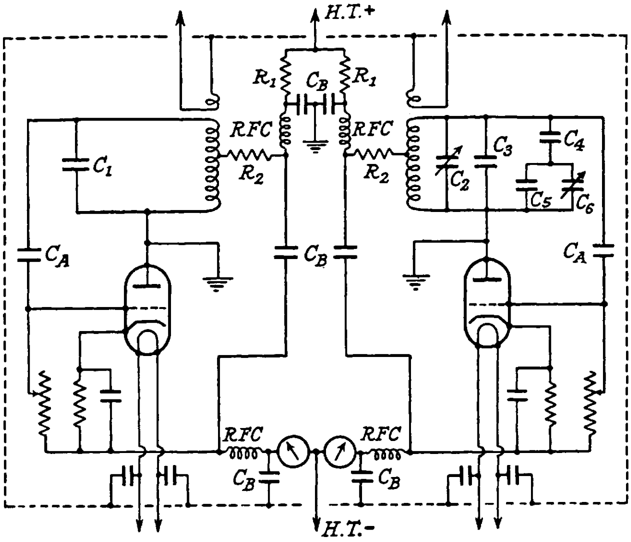
It was suspected that the anomalous moments of a number of other supposedly symmetrical compounds might arise from the same cause, whatever this may be, so the examination was extended to include several *p*-disubstituted benzene compounds, and some tetrahalides.

Experimental.

In order to realise the aim thus outlined, considerable attention had to be given to the design and construction of the apparatus. It had to give good results with vapour pressures of 30—50 mm., for measurements over a large temperature range to be possible. At the same time it had to be of general chemical utility, since most of the substances to be examined were solid at the ordinary temperature and many of them would react with mercury or common metals. The vapour system was therefore separated from the manometer by means of a glass Bourdon gauge, and the plates of the vapour condenser were made of platinum foil. As a result the condenser had a relatively small capacity, of about 100 $\mu\mu$F, but the sensitivity of the apparatus was maintained by keeping the total capacity low. A relatively large inductance was used in order to bring down the frequency to the convenient value of about 10^3 kc.

A heterodyne type of apparatus was decided upon, because of long and favourable experience with a solution apparatus of this kind. Several oscillator circuits described in the literature were tried, including that used by Stranathan (*Rev. Sci. Instr.*, 1934, **5**, 334) and the dynatron circuit used by Groves and Sugden (J., 1934, 1094); the one finally adopted (Fig. 1) is a modification of one suggested to us by Mr. D. A. Bell, of the Marconi Research Department. Except for the system of measuring condensers the two oscillators are identical. The capacity and inductance forming the oscillating circuit are in the anode lead, the anode therefore being earthed. The insulated ends of the condensers are coupled to the grids of the valves (Marconi-Osram M.L. 4) by means of 0·01 μF condensers C_A. The strength of the oscillations is prevented from becoming too great by the resistances R_2 (2500 ohms) and controlled by variable grid-leaks. The remaining set of radio-frequency chokes and by-pass condensers are for decoupling.

FIG. 1.



In order to reduce the cross-coupling of the oscillators and at the same time to obtain sufficient amplification, a stage of H.F. amplification for each oscillator was incorporated. The amplified H.F. currents are fed into a tuned receptor circuit with detector valve in the amplifier proper.

The heterodyne note is tuned by audible beats to that of a valve-driven tuning-fork, as usual.

The entire apparatus is run from A.C. mains. In order to supply stabilised high-tension to the oscillator valves a barretter and " Stabilovolt " tube were incorporated in the way recommended in the Marconi pamphlet. The arrangement proved very satisfactory.

The inductances of the oscillators were made by winding 63 turns of copper wire under tension on to silica formers which are 6″ long and 2¾″ in diameter, and have spiral grooves at 20 T.P.I. cut on them. The tappings are 35 turns from the earthed ends. The condenser C_1 of the reference oscillator is a special Cyldon condenser, and is set permanently at about 150 μμF. In the measuring oscillator, C_2 is a small Cyldon condenser, set near 20 μμF, for rough adjustments; C_3 is the vapour condenser, of about 100 μμF capacity; C_4 is a small fixed condenser (*ca.* 10 μμF) of special ceramic material (" Calit ") with fused-on silver electrodes, which is claimed to have great stability; C_5 is similar to C_4 but of *ca.* 100 μμF capacity; and C_6 is a small, variable, cylindrical condenser (made by the Leybold firm) for fine adjustment and measurement: it has a capacity range of about 25 μμF with 5000 divisions. This arrangement gave a convenient working frequency, together with great sensitivity.

The oscillators, constructed with great rigidity, are inside a duralumin box, 24″ × 18″ × 12″, the two being shielded by a central partition, and the valves and the Leybold condenser being on top of the box. This is inside a large air thermostat, left going continually, wherein the air temperature is maintained constant to within ± 0·1°. This is essential to keep down frequency drifts to reasonable limits; they are only 10 beats, or less, per hour, which corresponds to 0·00002 or less change per hour in dielectric constant of the vapour, or to 0·000003 during the 10 minutes necessary for taking a reading.

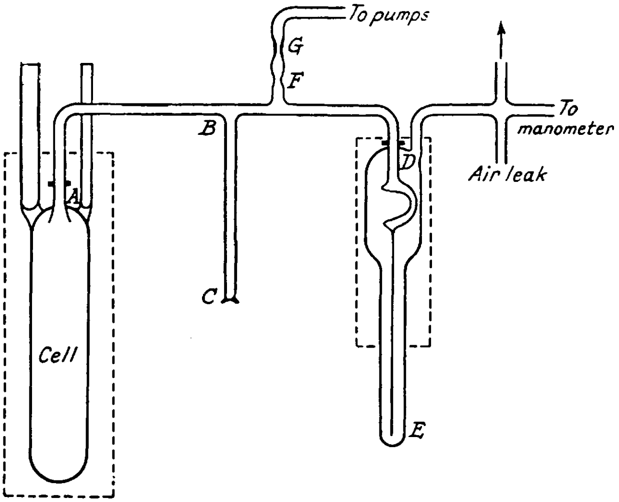
The Vapour Condenser.—This consists of three concentric platinum foil cylinders, of lengths 11, 10, 11 cm. and approximate diameters 2·2, 2·0, 1·8 cm., mounted in a fashion similar to that described by Fairbrother (J., 1932, 43). At both ends of each cylinder, three short, stout platinum wires are welded at 120° to each other; to these are spot-welded short tungsten wires which are sealed into Pyrex beads which cover them completely. The cylinders thus spaced are mounted vertically in a closely fitting Pyrex tube, the three beads at the top being fused to a rod passing up the centre, while the beads at the bottom are shaped so as just to touch the rod. Thus there is no strain on heating or cooling. The leads to the oscillator are of thin platinum wire, taken through covered Pyrex–tungsten seals at the walls, and carefully spaced in separate glass tubes until they emerge from the thermostat. The outer- and inner-most cylinders are earthed.

This type of cell, with plates having a large surface to mass ratio owing to their being of platinum, proved to have the unanticipated virtue of reaching thermal equilibrium with the bath very rapidly. Careful tests showed that temperature equilibrium between the bath, cell, and vapour is reached in a time shorter than that necessary to introduce the vapour.

The cell is firmly clamped in an oil-bath which can be regulated to within ± 0·1° at any temperature up to 250°.

Calibration.—The measuring condenser system is essentially the same as that described by Groves and Sugden (J., 1934, 1094), but the method of calibration differed in that a direct relation was determined between a change of reading on the Leybold condenser and a known change of dielectric constant of the medium in the cell.

FIG. 2.



Dry, carbon dioxide-free air and pure, dry carbon dioxide were used for calibration. From the recorded data we have taken 1·000582 and 1·000987 respectively as the most probable values of ε for these gases at 0° and 760 mm. pressure (see Zahn, *Physical Rev.*, 1926, **27**, 455; Bryan and Saunders, *ibid.*, 1928, **32**, 202; Stuart, *Z. Physik*, 1928, **47**, 457; McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453; Watson, Rao, and Ramaswamy, *Proc. Roy. Soc.*, 1933, *A*, **143**, 558). A curve of $(\varepsilon - 1) \times 10^6$ against scale reading was constructed from some 50 measurements on air at seven different temperatures between 15° and 220°. To check it, carbon dioxide prepared both from sodium bicarbonate and from magnesium carbonate was used, some twenty measurements being made. After van der Waals corrections had been made, the two curves were very nearly identical, and would have been perfectly so if the value of ε for carbon dioxide had been taken as 1·000989. Recalibrations with air were made periodically.

Vapour System.—Fig. 2 shows the vapour control system.

DE is a glass Bourdon gauge forming the partition between vapour and air; it is heated in a well-lagged furnace. An image of the pointer E and of a miniature scale are projected on to a screen, and the gauge calibrated in terms of the scale divisions for making corrections of a few tenths of a millimetre. The gauge is balanced by a wide-bore mercury manometer, from which pressures are read with a cathetometer. The pressure within the vapour system can be read to within ± 0·1 mm.

The substance to be investigated is sealed on in the tube BC or, in the case of liquids, is distilled in a vacuum into the tube. After being evacuated, with the substance cooled in liquid air if necessary, the system is completely sealed off by fusing the constriction G. When it is desired to let air in at the end of an experiment, the tubing above G is bent out of the way, rubber tubing is slipped over FG, and the end clipped. By snapping the thin-walled constriction F a regulated flow of air can then be admitted.

The usual system of liquid-air traps, diffusion pumps, and rotary pump is used for evacuation. The whole system is baked out under vacuum at 200—250° after each substance has been measured.

All tubing in contact with vapour is heated by nichrome wire windings. The pressure of vapour is controlled by the heating of the tube BC, and it was found that by doing this carefully it is possible to maintain the pressure constant to within $\pm$ 0·1 mm. for periods of 5—15 seconds, which is ample time for setting the Leybold condenser to zero beat. Switching the heating current on and off causes a change of space capacity of the leads, owing to the change of potential at A, so the vapour is condensed by shorting the wiring on BC and cooling the tube in liquid air. The average of the in and out readings is taken as one complete measurement, in order to eliminate error due to drift of the reading for vacuum. The process takes about 10 minutes.

In this manner five to ten measurements are made at one temperature, in order to get rid of non-systematic errors and to detect any variation of polarisation with the pressure used; none was found. The polarisation is calculated from the formula

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{20790 \times T \times (\varepsilon - 1)}{p_{\text{mm.}}}, \ (T \text{ in } ^\circ\text{K}),$$

which assumes that the vapours obey the simple gas laws. For the Group IV tetrahalides, van der Waals constants are known, and it has been calculated that the polarisations given for these compounds may be somewhat high, but not by more than 0·15 c.c. For all the other compounds the constants are unknown, but the pressures at which they were measured were much lower, and the temperatures higher, so the errors are certainly very small. No change of polarisation with pressure was observed experimentally.

Preparation and Purification of Materials.—Beryllium acetylacetonate was prepared as described by Finn, Hampson, and Sutton (this vol., p. 1255). M. p. 103—103·6° and 108·1—108·6° (dimorphic) (cf. authors cited).

Aluminium acetylacetonate was made and purified as described by the above-mentioned authors. It was sublimed in a vacuum immediately before use.

Chromium, ferric, and thorium acetylacetonates were supplied by Dr. A. E. Finn, and were repurified by recrystallisations and vacuum sublimation immediately before use.

2 : 2 : 4 : 4-Tetramethyl*cyclo*butane-1 : 3-dione, supplied by Dr. G. I. Jenkins, was repurified by two recrystallisations from ligroin (b. p. 40—60°) and two vacuum sublimations. M. p. 113·7—114·0° (cf. Hammick, Hampson, and G. I. Jenkins, this vol., p. 1264).

p-Benzoquinone. A commercial specimen was steam-distilled, recrystallised once from benzene and three times from benzene–ligroin (b. p. 60—80°), and vacuum-sublimed immediately before use. M. p. 112·8—113·6° (see p. 1264).

2 : 5-Dimethyl-1 : 4-benzoquinone, m. p. 123·6—124·3°, and 2 : 5-dichloro-1 : 4-benzoquinone, m. p. 160·4—161·4°, were both supplied pure by Dr. G. I. Jenkins, but were vacuum-sublimed immediately before use.

Titanium tetrachloride supplied by Mr. M. W. Lister was twice vacuum-distilled over copper bronze.

Germanium tetrachloride. Pure germanic oxide, supplied by Dr. F. M. Brewer, was reduced at 900° with hydrogen, and chlorine then passed over it. The excess of chlorine was removed from the product by copper bronze, and the product fractionated in a vacuum.

Stannic chloride. A laboratory specimen was fractionated, the fraction of b. p. 114°/753 mm. being collected and again fractionated in a vacuum into the apparatus (cf. 114·1°/760 mm., I.C.T.).

Stannic bromide. A pure specimen supplied by Mr. M. W. Lister was fractionated, the middle portion being used.

Stannic iodide. Kahlbaum's product was fractionally sublimed twice.

p-Dinitrobenzene. A sample supplied by Mr. J. B. Bentley was twice sublimed in a vacuum; it showed no change of m. p. 173·5—174·2° (cf. 174°; Wyler, *Helv. Chim. Acta*, 1932, **15**, 23).

p-Cyanonitrobenzene. A laboratory specimen was sublimed twice in a vacuum without change of m. p. 148—149° (cf. 148—149°; Hammick, New, Sidgwick, and Sutton, J., 1930, 1876).

p-Dicyanobenzene. A laboratory specimen was twice sublimed in a vacuum without change of m. p. 221·5—222·5° (cf. 222°; Weissberger and Sängewald, *Ber.*, 1932, **65**, 701).

Tetranitromethane. A sample of m. p. 11·5—12·5° (12·5°; Hammick and Young, J., 1936, 1464) was fractionated in a vacuum, the middle portion being taken.

Results.—In the following tables, the results are given in five columns: (1) Temperature in °C. (signs in this column refer to samples), (2) the approximate pressure range used, (3) the number of complete measurements made, (4) the average numerical deviation of the individual readings from the mean value of the polarisation, (5) the mean value of the polarisation.

P values are based on a standard value of ε = 1·000582 for air at 0° and 760 mm. pressure. The electron polarisations, P_{E}, are taken from the literature.

TABLE I.

Beryllium Acetylacetonate.

T.	p, mm.	n.	ΔP.	P.
184·6°	25—46	10	0·9	86·6
186·2	24—50	10	0·45	86·6
*200·1	52—63	6	0·5	86·0
†211·3	36—62	7	0·6	86·0
220·2	35—73	9	0·35	86·15
†241·5	40—80	7	0·4	85·9
250·2	45—86	3	0·4	85·95
254·7	39—73	11	0·35	86·05

P = 86·0 c.c., P_{E} = 60·5 c.c., $P - P_{\mathrm{E}}$ = 25·5 c.c.

The values of P at 184·6° and 186·2° are undoubtedly too high, as it was observed that P decreases as the pressure decreases. The saturated vapour pressure at 185° is approximately 50 mm. and the polarisations measured near this are about 90 c.c. Of the twenty measurements taken, the average value for pressures greater than 40 mm. is 86·9 c.c., and that for pressures of less than 40 mm. is 86·45 ± 0·5 c.c. Since the proportional error in pressure measurements becomes considerable at low pressures, further decrease of P with decrease of pressure was masked by the scatter of individual measurements. In view of this it is concluded that P would approximate to 86·0 c.c. at lower pressures at these temperatures. In any case, the values at the other temperatures show clearly that P is independent of temperature.

In preliminary work, values of 82 and 84 were obtained, but these low values were traced to decomposition. This had an important bearing on later work, as showing that when acetylacetonates decompose the polarisation is too low.

TABLE II.

Chromium Acetylacetonate.

236·2°	16—21	8	1·4	128·8
256·1	29—41	8	0·8	127·5
*247·1	16—34	8	2·0	133·7

P = 135·5 c.c., P_{E} = 95·3 c.c., $P - P_{\mathrm{E}}$ = 40·2 c.c.

After the first set of measurements at 236·2° there were left 4 mm. of gas which did not condense at room temperature. This was pumped off and a second set then done at 256·1°, but again there were about 4 mm. of residual gas. In both sets of measurements P decreased in successive readings.

Measurements were therefore made with a new sample at 247·1°, great care being taken to avoid overheating. This time, only 1 mm. of gas was left after eight measurements had been made; the average of these was 133·7 c.c., but the average of the first three was 135·2, and that of the last three was 131·8 c.c. The most probable value is taken as 135·5 ± 0·5 c.c.

Such measurements obviously can give no information about the dependence or otherwise of polarisation upon temperature.

TABLE III.

Aluminium Acetylacetonate.

247·1°	23	1	—	129·3
247·1	31	1	—	130·3
*229·1	12	1	—	132·8

P = 130·8 c.c., P_{E} = 91·1 c.c., $P - P_{\mathrm{E}}$ = 39·7 c.c.

This proved even more unstable than the chromium compound. In the first attempt at 247·1° P decreased from 129 to 126 in three readings; the residual gas was then pumped off, and in a further determination P again decreased from 130 to 125 in three readings. A fresh sample was then tried at 229·1°, and P decreased from 132·8 to 126 c.c. in six readings.

Only the first measurements of each of these are given in the table. It is probable that the true value of P is slightly greater than the average of these, but the latter is the figure quoted, 130·8 c.c.

TABLE IV.

Ferric Acetylacetonate.

229·1°	9—54	3	1·7	145·4

P = 146·6 c.c., P_E = 91·5 c.c., $P - P_E$ = 55·1 c.c.

The values found for P were 146·3, 147·0, and 142·8 c.c., the low third value being due to decomposition. The most probable value is therefore taken as the average of the first two, *i.e.*, 146·6 c.c. During an attempt to take a fourth reading the substance decomposed suddenly, so further measurements were abandoned.

TABLE V.

Thorium Acetylacetonate.

238°	11—20	2	1·7	199·7

P = 200 c.c., P_E = 127·5 c.c., $P - P_E$ = 72·5 c.c.

This substance proved very unstable, darkening even on vacuum sublimation. In the first run P decreased from 198·0 to 143 c.c. in three readings, and with a new sample, from 201·5 to 173 in three readings. The value taken for this compound is the average of the first measurements on the two samples.

Summary. Decomposition prevented accurate measurements being made on any but the beryllium compound. It appeared to take place not on the platinum surfaces but on the walls of the glass tubing, brownish deposits being formed thereon.

TABLE VI.

*Tetramethyl*cyclo*butanedione.*

*90·0°	32—43	6	0·45	46·9
99·5	75—90	8	0·2	46·9
138·5	62—127	6	0·1	46·95
*149·9	47—107	6	0·3	46·9
174·9	75—117	5	0·3	47·3
*203·5	56—112	4	0·4	47·2

P = 46·9 c.c., P = 37·7 c.c., $P - P_E$ = 9·2 c.c.

This substance was found to be unstable above 150°, decomposition taking place within the cell. Many attempts were made to obtain reproducible values above 150°, but they were unsuccessful, for not only did P increase as successive measurements were taken, but after these high-temperature measurements had been made, high and irreproducible values of P were invariably obtained at the lower temperatures, with the same sample.

The values given for 174·9° and 203·5° are averages of the first few readings on two samples, and they are certainly too high. Nevertheless, the polarisation is very constant over a range of 60°, so it may safely be concluded that the substance is non-polar.

TABLE VII.

p-*Benzoquinone.*

119·5°	36—54	7	0·5	36·5
*139·6	40—107	8	0·4	37·05
†169·6	48—123	9	0·2	36·5
195·6	50—168	5	0·06	36·3
†198·0	70—137	7	0·2	36·9
228·5	74—168	6	0·1	36·4
†246·5	85—164	7	0·1	36·2

P = 36·55 c.c., P_E = 28·32 (λ = 5461) c.c., $P - P_E$ = 8·2 c.c.

2 : 5-*Dimethyl*-1 : 4-*benzoquinone.*

141·9	28—77	8	0·4	47·4
195·3	44—95	6	0·15	47·4
246·3	41—98	6	0·13	47·35

P = 47·4 c.c., P_E = 38·37 (λ = 5461) c.c., $P - P_E$ = 9·0 c.c.

2 : 5-*Dichloro*-1 : 4-*benzoquinone.*

181·0	45—67	7	0·2	46·3
245·4	46—87	7	0·2	46·3

P = 46·3 c.c., P_E = 38·4 (λ = 5461) c.c., $P - P_E$ = 8·0 c.c.

The results for *p*-benzoquinone were quite good for the sample measured at 119°, 195°, and 228°, but the other measurements were not nearly so consistent as could have been desired. This may be attributed to decomposition, since the quinone darkened slightly during a run.

The stabilising effect of the methyl and chloro-groups in the other compounds is marked; there were no signs of decomposition even at 250°. The results for the latter compounds are very consistent, and prove beyond doubt that the quinones are non-polar.

TABLE VIII.

p-Dinitrobenzene.

*199·6°	29—41	6	0·2	46·53
208·9	42—70	5	0·1	46·48
227·4	41—71	5	0·2	46·34
244·5	41—87	5	0·2	46·46
*245·7	44—79	5	0·1	46·58
†255·2	39—84	6	0·2	46·46
‡255·2	41—99	6	0·3	46·46

$P = 46{\cdot}47$ c.c., $P_E = 38{\cdot}25$ § c.c., $P - P_E = 8{\cdot}2$ c.c.

§ See Tiganik (*Z. physikal. Chem.*, 1931, *B*, **13**, 425), 38·0; Le Fèvre and Le Fèvre (J., 1935, 957), 38·5.

p-Dinitrobenzene is comparatively stable. Small traces of a gas, less than 1 mm. pressure, which condensed in liquid air, were produced after continued use of the same sample. This appeared not to affect the polarisation values very much, but to ensure good results measurements were made on four samples, as indicated.

TABLE IX.

p-Cyanonitrobenzene.

208·9°	46—63	5	0·15	47·54
227·5	47—69	5	0·2	47·40
250·7	38—58	6	0·2	47·42

$P = 47{\cdot}45$ c.c., $P_E = 38{\cdot}6$ * c.c., $P_O = 0{\cdot}3$ c.c., $P - P_E - P_O = 8{\cdot}6$ c.c.

* See Hammick, New, Sidgwick, and Sutton (J., 1931, 1876), 38·6; calc., 38·5.

The moments of nitrobenzene and of benzonitrile are 4·39 and 4·23 D. respectively (Groves and Sugden, J., 1934, 1094). Hence, taking the moment of *p*-cyanonitrobenzene to be equal to the difference, 0·16 D., the orientation polarisation at 200—250° is 0·3 c.c. as given above.

TABLE X.

p-Dicyanobenzene.

199·8°	24—38	5	0·25	48·36
217·3	34—73	6	0·1	48·40
250·7	41—82	9	0·2	48·36

$P = 48{\cdot}4$ c.c., $P_E = 36{\cdot}5$ c.c., $P - P_E = 11{\cdot}9$ c.c.

Weissberger and Sängewald (J., 1935, 855) obtained a value of 40·5 c.c. for the electron polarisation of this compound in very dilute solution, but since this is higher than any calculated value, a mean of two such values has been taken above; that calculated from the molecular refractivities of benzonitrile and of benzene for the sodium D line is 36·94 c.c.; that from values for benzene, hydrogen, and cyanogen (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144) is 35·84 c.c.

TABLE XI.

Tetranitromethane.

81·8°	38—96	6	0·25	38·6

$P = 38{\cdot}6$ c.c., $P_E = 36{\cdot}0$ c.c., $P - P_E = 2{\cdot}6$ c.c.

The P_E value is the mean of two experimental ones, 35·3 (Weissberger and Sängewald, *Ber.*, 1932, **65**, 701) and 36·6 (Mr. M. W. Lister, priv. comm.). The substance was not very stable, and the polarisation decreased slightly as successive readings were taken. *P* may therefore be somewhat greater than the above value, but not by more than 0·3 c.c. Owing to decomposition, no reliable measurements could be obtained above 100°.

TABLE XII.

Titanium Tetrachloride.

100·3°	48—115	7	0·3	41·40
208·8	43—120	6	0·3	41·25

P = 41·3 c.c., P_E = 37·8 c.c., $P - P_E$ = 3·5 c.c.

Ulich, Hertel, and Nespital (*Z. physikal. Chem.*, 1932, *B*, **17**, 21) report a value for P_E for the pure liquid of 37·8 c.c., which they consider to be more accurate than that of 43·2 c.c. reported by Bergmann and Engel (*Physikal. Z.*, 1931, **32**, 507); the former has been taken.

TABLE XIII.

Germanium Tetrachloride.

96·2°	49—102	6	0·2	37·92
147·6	52—120	5	0·1	37·96
228·0	57—102	5	0·15	38·06

P = 38·0 c.c., P_E = 31·5 c.c., $P - P_E$ = 6·5 c.c.

The van der Waals correction to P, for a pressure of 100 mm. and temperature of 100°, is — 0·10 c.c.; this therefore is the maximum error from this cause.

TABLE XIV.

Stannic Chloride.

90·1°	39—112	5	0·2	45·6
142·6	42—123	6	0·2	45·4
200·3	48—144	5	0·1	45·5

P = 45·5 c.c., P_E = 35·2 c.c., $P - P_E$ = 10·3 c.c.

Ulich, Hertel, and Nespital's value of P_E for the pure liquid is taken. The van der Waals correction for 100 mm. at 100° is — 0·15 c.c.

TABLE XV.

Stannic Bromide.

145·2°	24—58	6	1·0	55·7
183·7	42—95	6	0·3	55·6
245·8	52—118	5	0·2	55·5

P = 55·6 c.c., P_E = 46·8 c.c., $P - P_E$ = 8·8 c.c.

P_E was calculated from the above value for the chloride.

TABLE XVI.

Stannic Iodide.

252·7°	32—85	6	0·3	81·4

P = 81·4 c.c., P_E = 66·0 c.c., $P - P_E$ = 14·5 c.c.

P_E was calculated from the above value for the chloride.

DISCUSSION.

Acetylacetonates.—The results of the measurements on the acetylacetonates are collected in Table XVII, which gives the total polarisations in the vapour and in solution, the electron polarisation, the difference between the total and the electron polarisations, and the percentage fraction which this difference is of the electron polarisation.

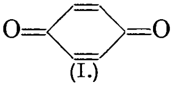
TABLE XVII.

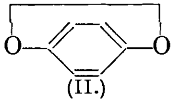
Compound.	$P_{\text{vap.}}$.	$P_{\text{soln.}}$.	P_E.	$P_{\text{vap.}} - P_E$.	$100(P_{\text{vap.}} - P_E)/P_E$.
Be$^{\mathrm{II}}$	86·0	87·5	60·5	25·5	42
Cr$^{\mathrm{III}}$	135·5	137·5	95·3	40·2	42
Al$^{\mathrm{III}}$	130·8	134·0	91·1	39·7	44
Fe$^{\mathrm{III}}$	146·6	148·6	91·5	55·1	60
Th$^{\mathrm{IV}}$	200	195·6	127·5	72·5	57

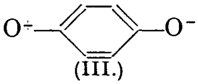
For all of them the vapour total polarisations are much nearer to the solution total polarisations than to the electron polarisations. It is therefore clear that, except possibly to a very minor degree, the anomalous polarisations are not due to solvent effects of any kind.

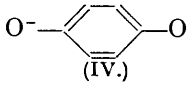
As stated by Finn, Hampson, and Sutton (this vol., p. 1259), the other possible explanations are that (1) the chelate rings have lower symmetry than modern theory requires, (2) the compounds are incompletely chelated, (3) they have large atom polarisations, (4) the molecules bend slowly out of the symmetrical normal configurations, under thermal impacts, and orient as dipoles in the field. The first two causes would certainly require the polarisation to vary with temperature, but, as Table I shows, the polarisation of the beryllium compound, which may be taken as typical, is constant within experimental error from 184·6° to 254·7°, or from 0·002185 to 0·001895, on the reciprocal temperature scale used in the Debye law plot. Further, since it is reasonable to consider the results in Table XVII together with the determinations in various solutions at 25° (see Table XVIII), we see that there is a fall of at most 1·5 c.c. in polarisation from 25° to 255°, or from 0·003356 to 0·001895 on the reciprocal scale. It can therefore be safely concluded that beryllium acetylacetonate is fully chelated and that the acetylacetonate chelate rings have two planes of symmetry passing through the CH and the M atoms, as required by the theory of " resonance."

Symmetrical Diketones.—The anomalous polarisations of the quinones and of tetramethyl*cyclo*butanedione are likewise shown not to arise from solvent effect nor to provide any evidence that the molecules have *permanent* dipole moments. Temperature invariance of the polarisation is particularly well shown by the two substituted *p*-benzoquinones, which are more stable than the parent substance. Taking solution measurements into account, we see that the change of polarisation for the dimethyl derivative between 25° and 246° is only 0·4 c.c., and for the dichloro-derivative between 25° and 245° is only 0·9 c.c. Inasmuch as no polar structures have been proposed for these compounds, this conclusion does not contradict previous views; it agrees with suggestions made that the simple quinonoid structure (I) is in resonance with others having Kekulé type rings such as (II) (Pauling and Sherman, *J. Chem. Phys.*, 1933, **1**, 606) and (III), likewise (IV)


(I.)


(II.)


(III.)


(IV.)

[Robinson, two lectures on " An Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Inst. Chem., 1932]; (I) and (II) are non-polar, and (III) and (IV), being of equal importance, would neutralise each other's polarity. Hammick, Hampson, and G. I. Jenkins (previous paper) showed that the polarisations of diones in solution contradict one deduction from the simple quinonoid structure, and indicate resonance of the kind described above; since the present measurements confirm theirs, they support this conclusion.

TABLE XVIII.

Compound.	$P_{\text{vap.}}$.	$P_{\text{soln.}}$.	P_E.	$P_{\text{vap.}} - P_E$.	$100(P_{\text{vap.}} - P_E)/P_{\text{vap.}}$.
Tetramethyl*cyclo*butanedione	46·9	48·5	37·7	9·2	24
p-Benzoquinone	36·55	37—38	28·3	8·2	29
2 : 5-Dimethyl-1 : 4-benzoquinone	47·4	47·8	38·4	9·0	23·5
2 : 5-Dichloro-1 : 4-benzoquinone	46·3	47·2	38·4	8·0	21
p-Dinitrobenzene	46·47	45·6	38·25	8·2	21
p-Nitrocyanobenzene	47·45	46	38·5	—	
	Allowing 0·3 for P_0			8·6	22
p-Dicyanobenzene	48·38	43	36·5	11·9	33

Symmetrical Dinitro- and Dicyano-compounds.—The measurements on *p*-dinitrobenzene show conclusively that there is no appreciable solvent effect upon its polarisation. This is particularly interesting because, in view of the well-known tendency of polynitrobenzenes to form solid complexes with aromatic hydrocarbons, and the fact that the only common, non-polar solvent in which *p*-dinitrobenzene is reasonably soluble is benzene, it had seemed reasonable to expect a specific effect in this case (Bennett, *Ann. Reports*, 1929, **25**, 130).

The measurements also prove finally that *p*-dinitrobenzene is non-polar.* The present results being combined with those in benzene solution at 25° (*e.g.*, Le Fèvre and Le Fèvre, J., 1935, 957), the change of polarisation between 25° and 250° is found not to be more than 1 c.c.

If, as reported by James, King, and Horrocks (*Proc. Roy. Soc.*, 1935, *A*, **153**, 225) from an *X*-ray investigation of the crystal structure, the nitro-groups are notably unsymmetrical about the C—N axes, it is obvious that the molecule would be non-polar only in certain configurations (cf. quinol dimethyl ether): since there are no known or probable energetic reasons to the contrary, it is reasonable to suppose that the restraints necessary to keep it so would not be fully operative in the vapour at 250°, and therefore that such a molecule would exhibit polar character. The fact that it does not throws considerable doubt upon such an asymmetric structure for the nitro-group. Moreover, the fact that Brockway, Beach, and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2693) found no asymmetry in this group in nitromethane is further reason for doubting its asymmetry in nitrobenzenes. On the resonance theory it would be expected to have the oxygens symmetrical about the C—N bond axis.

p-Nitrocyanobenzene and *p*-dicyanobenzene show anomalous polarisations of the same order as that of *p*-dinitrobenzene, which also are temperature invariant over about 50° in each case. Weissberger and Sängewald (J., 1935, 855) found a lower value of $P - P_E$, 3·1 c.c., than that now reported for the dicyano-compound, and so found no anomaly; but, owing to the extreme dilution of the solution which they had to use, a greater error is probable in their measurements than in the vapour measurements, which gave no particular difficulty. If, as before, the results for *p*-nitrocyanobenzene in solution at 25° (Hammick, New, Sidgwick, and Sutton, J., 1930, 1876) are combined with the present ones, the polarisation is seen to increase by 1·5 c.c. between 25° and 250°; the compound, therefore, is certainly not very polar. The difference of the moments of nitrobenzene and benzonitrile reported by Groves and Sugden (J., 1934, 1094) is only 0·16 D., which corresponds to a change of 0·2 c.c. over this temperature range.

The new results for tetranitromethane confirm the conclusion previously reached from solution measurements. (Williams, *Physikal. Z.*, 1928, **29**, 271, 683; Bretscher, *Helv. Phys. Acta*, 1928, **1**, 355; Weissberger and Sängewald, *Ber.*, 1932, **65**, 701; M. W. Lister, priv. comm.) that it is non-polar. This substance shows no anomalous polarisation.

Tetrahalides.—The tetrahalides examined all proved to be non-polar, as anticipated, but several of them showed considerable polarisation anomalies. The data are in Table XIX, relevant data of other workers being included.

TABLE XIX.

Tetrahalides, MX_4.

M.	X.	$P_{vap.}$.	P_E.	$P_{vap.} - P_E$.		$100(P_{vap.} - P_E)/P_E$.
C	F	10·15 *	7·29 *	($\lambda = \infty$)	2·86	39
	Cl	28·0 †	25·78 ‡	($\lambda = \infty$)	2·2	8·5
		27·0 ‡	25·78 ‡	($\lambda = \infty$)	1·2	5
Si	F	13·84 *	8·38 *	($\lambda = \infty$)	5·46	65
Ti	Cl	41·3	37·8	($\lambda = 5893$)	3·5	9
Ge	Cl	37·98	31·5	($\lambda = 5893$)	6·5	21
Sn	Cl	45·5	35·2	($\lambda = 5893$)	10·3	29
	Br	55·6	46·8	($\lambda = 5893$)	8·8	19
	I	81·4	66·9	($\lambda = 5893$)	14·5	22

* Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.

† Sānger, *Physikal. Z.*, 1926, **27**, 556.

‡ Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138.

Various suggestions, some general and some specific, have been made from time to time as to the cause of the anomalous polarisations in these several classes of compound (see

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* As shown by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171), H. O. Jenkins' measurements in chloroform solution are not satisfactory proof of this (see also Finn, Hampson, and Sutton, this vol., p. 1262).

this vol., p. 1255, for a summary). We consider that the essential similarity of the phenomena for all classes indicates that the fundamental cause is the same in all of them. It remains to consider whether this is slow, thermal bending or atom polarisation, these two now being the only possibilities.

Thermal Bending Hypothesis.—As was explained in the paper by Finn, Hampson, and Sutton, the "thermal bending" or "flexibility moment" theory postulates that the molecules oscillate about non-polar, mean configurations, owing to the energy imparted by thermal collisions, and that they do this so slowly that they orient like permanent dipoles in the applied field, while still bent one way. It was shown (*loc. cit.*) that, provided (1) they vibrate in simple harmonic motion (*i.e.*, if the potential energy is expressible as $V_0\phi^2/2$, $\pi - \phi$ being the angle between the dipoles) and (2) Maxwell–Boltzmann statistics apply, then the mean polarisation would be independent of temperature. If, however, they vibrate anharmonically (higher powers of ϕ than the square being required in the expression for potential energy), then the polarisation would vary with temperature. This may be seen by evaluating a more general expression for the polarisation than that used previously (Finn, Hampson, and Sutton, this vol., p. 1261), having for a potential function $V = (V_0\phi^2 + V_1\phi^4)/2$; only even powers will occur in such a problem, for which the potential function must be symmetrical, *i.e.*, must have the same value whether ϕ is positive or negative:

$$P = \frac{4\pi N}{9kT}\mu_1^2 \frac{\int_{-\infty}^{+\infty} \phi^2 e^{-\frac{(V_0\phi^2 + V_1\phi^4)}{2kT}} d\phi}{\int_{-\infty}^{+\infty} e^{-\frac{V_0\phi^2 + V_1\phi^4}{2kT}} d\phi} = \frac{4\pi N\mu_1^2}{9V_0}\left(1 - \frac{6kTV_1}{V_0^2}\right)$$

whence

$$\frac{1}{P}\frac{dP}{dT} = \frac{6kTV_1}{V_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Thus, the sign of V_1 determines that of $(dP/dT)/P$, since V_0^2 must be positive; the polarisation decreases or increases with rise of temperature according as V_1 is positive or negative, *i.e.*, as to whether the vibrations become stiffer or easier as the amplitude increases. It is impossible to estimate accurately how big the effect would be, but it may be remarked that a polarisation of 8 c.c. at 250°, as found for *p*-benzoquinone, corresponds to a moment of 0·81 D.; and if this be attributed to the bending of two C=O bonds, each of moment 2·5 D., then the average angle between them must be 161·5° (or $\phi = 18{\cdot}5°$), at which point anharmonicity effects might be expected to show. Alternatively one may say that, since the vibrators must have periods of the order of 10^{-12} to 10^{-11} sec. or more, in order to be slow compared with the time of dipole orientation (about 10^{-12} sec.), their quanta must be so small ($h\nu = 94{\cdot}3$ cals./g.-mol. for $1/\nu = 10^{-12}$ sec.) that they would be quite highly excited at temperatures of 300—500° K., and consequently that the effect of anharmonicity would be expected to show. The fact that in no case was any variation of polarisation with temperature observed, although a variety of molecular types was examined, therefore counts against the "thermal bending" or "flexibility moment" theory.

A much stronger case against it comes from considering the possible periods of vibration of the molecules examined. As was shown in the two preceding papers, since a direct calculation of the force constant V_0 for the hypothetical vibration is possible through the relation

$$P = (4\pi N\mu_1^2)/9V_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for a single, one-dimensional oscillator, the period can be calculated *if* the mode of vibration is known, and if the positions and masses of the atoms in the molecule are known. For the theory to be self-consistent these calculated periods must, as explained on p. 1261, be of the order of 10^{-12} or 10^{-11} sec., or even longer. This requirement is, indeed, now emphasised by the observation that there is no consistent difference between the polarisations in solution and in the vapour, for, since the time of relaxation or of orientation is less in the latter state than in the former, this fact would mean that the period of bending is much greater than the time of relaxation in either solution or vapour; therefore, probably, that it is at least 5×10^{-11} sec. If it were of the same order as that in solution, *i.e.*, about 10^{-12} sec., then the polarisation in the vapour would be larger than that in solution. The calculated periods are, however, not greater but less than 5×10^{-12} sec. for beryllium acetylacetonate (p. 1262), for *p*-benzoquinone and tetramethyl*cyclo*butanedione (p. 1268), and for *p*-dinitrobenzene and *p*-dicyanobenzene, which, if the groups be assumed to oscillate perpendicular and parallel to the plane of the benzene ring, would have periods of about 3—4×10^{-13} sec. The approximations in the calculations are all such as to make the result too large rather than too small; these are (1) the assumption that all the polarisation is due to one mode of vibration, which may give too small a value of V_0, (2) neglect of anharmonicity, if V_1 is positive, (3) neglect of atom polarisation, (4) neglect to use a proper reduced mass in the beryllium acetylacetonate calculation. This essential requirement is, therefore, not satisfied and consequently we reject the thermal bending theory as an explanation of the results.

The Theory of Atom Polarisation.

By a process of elimination we conclude that the phenomena must be due to atom polarisation. It is, however, desirable to have some more positive reason for accepting this explanation, so we must consider on what conditions this type of polarisation could have the magnitude now ascribed to it, and whether these are likely to be satisfied. First it seems desirable to summarise the present theory of atom polarisation. When any molecule is subjected to an electric field, it is elastically deformed. The positive charges move toward the negative end of the field, and *vice versa*; the molecule is " polarised," or a dipole is created. If the restoring forces which resist the deforming process obey Hooke's law, this moment is proportional to the field strength : the proportionality factor, multiplied by $4\pi N/3$, is called the molecular polarisation. The deformations which occur can be divided into those which involve only movements of electron " clouds " relative to nuclei, and those which involve movements of nuclei relative to one another; the latter give rise to the so-called atom polarisation. Every relative movement of nuclei which is associated with a change of electric dipole moment of the molecule must occur when a field is applied : such movements are changes in length of polar bonds, changes of angle between polar bonds within a group, and the bending or twisting of polar groups relative to one another. If we consider the deformation produced by a field which is not static but is alternating with a frequency ν_0 we have to take account of the tendency of the internuclear movements to take place with certain natural frequencies, ν_i, etc., which depend upon the respective restoring forces, f_i, etc., and effective masses moved. If the former are Hooke's law forces, the relation $\nu_i = \sqrt{f_i/m_i}/2\pi$ holds. The average degree of deformation depends upon the average amplitude forced by the field upon these vibrators, and classical methods give the relation

$$P = \frac{4\pi N\alpha}{3} = \frac{N}{9}\frac{e_i^2}{\pi m_i(\nu_i^2 - \nu_0^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for an *independent, one-dimensional* oscillator, where ν_i is the natural frequency of vibration of an effective mass m_i carrying an effective charge e_i. The total atom polarisation is the sum of such terms for all effective oscillations, *i.e.*, for all those which are accompanied by changes in dipole moment, which means all those that have fundamentals " active " in absorption or emission spectra. Van Vleck (" The Theory of Electric and Magnetic Susceptibilities," Oxford, 1932, p. 46) has pointed out that this result remains valid with quantum mechanics. A molecule may be excited into vibration by thermal collisions, and if a field is then applied its effect is to change the mean positions about which the active vibrations occur. Provided that the restoring forces, which are determined by the displacements from the original mean positions, obey Hooke's law, it may be shown that the polarisation is independent of temperature (Debye, " Polare Molekeln," Leipzig, 1929, p. 17). Inasmuch as atom polarisation involves no orientation of the molecule, it is independent of the time of orientation in the case of a polar molecule.

In equation (3) $f_i/4\pi^2\nu_i^2$ may be substituted for m_i, giving

$$P_A = 4\pi N e_i^2 \nu_i^2/9f_i(\nu_i^2 - \nu_0^2), \text{ which, when } \nu_0 \longrightarrow 0, \text{ reduces to}$$

$$P_A = 4\pi N e_i^2/9f_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for an independent, one-dimensional oscillator.

For changes of bond length e_i is $d\mu/dl_{AB}$, l_{AB} being the bond length, but, as van Vleck showed (*op. cit.*), even if e_i be equivalent to a full electron charge on each atom A and B, f_i is so large that P_A is less than 0·5 c.c. per highly polar bond. Hence, were no other type of internuclear movement possible, P_A could not have the magnitude now attributed to it in molecules with only small numbers of highly polar bonds. This conclusion is borne out by the work of Cartwright and Errera (*Proc. Roy. Soc.*, 1936, *A*, **154**, 138), especially as the P_A values which they found for polar substances are likely to be upper limits, owing to the difficulty of making proper allowance for the effects of dipole dispersion.

For changes in the angles between two similar dipoles, at a normal angle π,

$$P_A = 4\pi N \mu_i^2/9V_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where μ is the magnitude of the moments, and V_i the force constant of bending defined by the relation $V = V_i\phi^2/2$.

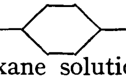
Now, van Vleck suggested that P_A may be larger for polyatomic molecules than for diatomic ones because of the possibility of the former having relatively low-frequency vibrations. As Cartwright and Errera pointed out (*loc. cit.*), these may be either the fundamentals of bending motions in the molecule or, in some cases, the combination (difference) frequencies of fundamentals in the near infra-red; but it seems unlikely that the latter will frequently be important, and in forming a simple picture of the phenomenon under discussion they will be ignored. Equation (4) shows .that, in a static field, the important condition is that the molecule shall be easily deformable to a polar state in at least one way, which is only so when there are possibilities of bending or twisting of fairly polar groups relative to one another. Equation (5), or its equivalent in more complex systems than a single, one-dimensional oscillator, can be obtained very simply by equating the electrical forces and the restoring forces in the deformed system along three perpendicular axes.

Qualitative Comparison of Deduction and Fact.—All the substances which are now suspected of having atom polarisations larger than 5 c.c., including the co-ordination compounds of palladium (Mann and Purdie, J., 1935, 1549), platinum (Jensen, *Z. anorg. Chem.*, 1935, **226**, 284), and gold (Burawoy and Gibson, J., 1934, 860; 1935, 219), do in fact offer such possibilities, and hence the most obvious qualitative condition of the theory is satisfied. The theory leads us further to expect that related compounds should have similar $P - P_E$ values, and in several cases this proves to be true. Thus, cyanogen, like *p*-dicyanobenzene, has one of 8·3 c.c. (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144); carbon suboxide is reported to have a moment of 0·7 D. (Le Fèvre and Le Fèvre, J., 1935, 1696), which is much more probably an atom polarisation of 10·5 c.c. and thus is close to the values for the other diones (Table XVIII), which are 8—9 c.c.; nitrogen tetroxide has, however, been shown by Williams, Schwingel, and Winning (*J. Amer. Chem. Soc.*, 1936, **58**, 197) to have a total polarisation of 16·87 c.c. between 25° and 125° and a molecular refractivity for the sodium D line of 16·73 c.c., so this substance, like tetranitromethane but unlike the symmetrical polynitrobenzenes, has a small P_A. A plausible explanation of these exceptions is that the nitro-groups, by virtue not merely of their highly polar character but more of their branched, **Y** structure, can inhibit each other's freedom of movement when at such close quarters as they are in nitrogen tetroxide and tetranitromethane, so V_i is large and P_A small. Thus, from measurements of the entropy of nitrogen tetroxide, Giauque and Kemp (*J. Chem. Phys.*, 1938, **6**, 40) conclude that the molecule probably has the symmetrical structure $O_2N{-}NO_2$ and that there certainly is no freedom of rotation of the two nitro-groups relative to each other.

The atom polarisations of the tetrahalides also may be correlated if we assume that they are due chiefly to bending. There are two fairly well-defined tendencies: the first is for

P_A to increase, for a given halogen, the later the period of the central atom; the other is for P_A to fall, for a given central atom, the later the period of the halogen. Both are paralleled by the change in polar character of the bonds which would be expected on general principles (the electro-positive character of the central atom increasing with its period, and the electro-negativity of the halogen decreasing), and for which evidence comes from electric dipole moment data (J. G. Malone, *J. Chem. Phys.*, 1933, **1**, 197; M. G. Malone and Ferguson, *ibid.*, 1934, **2**, 99; Smyth, *J. Amer. Chem. Soc.*, 1938, **60**, 183). The correlation has already been pointed out by Smyth (*ibid.*, 1929, **51**, 2051), but the assumption which we have made supplies a reason for it, since μ^2 is likely to change more than V_0 in the series. It may be noted that, although the C—F bond in methyl fluoride has a moment no greater than that of C—Cl in methyl chloride ($\mu_{CH_3F} = 1{\cdot}81$; $\mu_{CH_3Cl} = 1{\cdot}86$), P_A for carbon tetrafluoride is reported to be 2·86 c.c. and that for carbon tetrachloride is given as 2·2 or 1·2 c.c. While too much weight should not be put on such small differences, this may, if real, be connected with two other facts: (1) that the mutual induction, which reduces the effective bond moments, is less in fluoroform than in chloroform (thus the ratio μ_{CHX_3}/μ_{CH_3X} is 0·90 for fluorides, and 0·54 for chlorides), so that the effective bond moment would be greater in carbon tetrafluoride than in carbon tetrachloride; (2) that the repulsion between the halogens is somewhat less in the fluoromethanes than in the chloromethanes, as shown by electron diffraction work, for there is less distortion from the tetrahedral angle in methylene fluoride than in methylene chloride (see Brockway, *J. Physical Chem.*, 1937, **41**, 747; Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473), so V_i would be somewhat less in the former than in the latter. These factors must be considered in the other sets of halides also, and may be seen to augment the changes anticipated from ideas about polar character.

Quantitative Comparisons.—In seeking more quantitative tests of the hypothesis that atom polarisation is due chiefly to bending of the molecule by the field, we may either calculate an atom polarisation from other data and compare this with $P - P_E$, or we may take the observed difference and calculate a force constant, a bond moment, or a frequency from it and compare this with the observed value. Both courses are logically equivalent, but one is sometimes more convenient than the other.

Mercury Compounds.—Braune and Linke (*Z. physikal. Chem.*, 1935, *B*, **31**, 12) calculated mercury–halogen bond moments from $P - P_E$ values, frequencies from Raman spectra, and interatomic distances from electron diffraction data for mercuric chloride, bromide, and iodide. They equated $P - P_E$ to the sum of the atom polarisations arising from the asymmetric linear vibration and from two-dimensional bending, and made limiting allowances for the former. The limits so obtained for μ_{HgCl} were 2·33—2·66 D., and values of the same order were found for the Hg–Br and Hg–I bonds. At the time there were no data with which these values could be compared, but G. I. Jenkins has since found the moment of phenylmercuric chloride to be 3·14 D. and has concluded that μ_{HgCl} is approximately 3 D. (private communication from Dr. G. I. Jenkins; data soon to be published): in view of the probable reduction of bond moments by mutual induction in mercuric chloride this is good agreement, and it supports Braune and Linke's assumption that $P - P_E$ for these compounds is atom polarisation. On the other hand, it can readily be seen that the anomalous $P - P_E$ values of diphenylmercury and its *pp'*-derivatives, observed in decalin solution by Hampson (*Trans. Faraday Soc.*, 1934, **30**, 877), cannot be explained away as atom polarisation *if* the force constant of bending therein is assumed equal to the average for the mercuric halides, for μ_i is smaller and $P - P_E$ larger, than for the latter. Hampson concluded that the phenyl–mercury bond moment is small, and has the negative end towards mercury; the moment of the unit Cl——Hg is therefore numerically less than that of chlorobenzene (1·60 D. in hexane solution) and so, using a value $V_0 (= V_i) = 2{\cdot}5 \times 10^{-12}$ erg/radian²/molecule for the force constant, P_A from bending is only about 2 c.c.* whereas $P - P_E$ is 19·7 c.c. The period of oscillation is about $1{\cdot}5 \times 10^{-12}$ sec., which is hardly long enough for the molecule to gain additional polarisation by orienting as a dipole while bent. The *ad hoc* suggestion that the force constant is

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* The oscillator is assumed to be two-dimensional, like the mercuric halides, so that $P_A = 8\pi N\mu^2/9V_0$.

particularly small in these compounds receives no support from the fact that V_0* for dimethylmercury is 4·7 × 10^{-12} erg/radian²/molecule, according to Thompson and Linnett's assignment (*Proc. Roy. Soc.*, 1937, *A*, **160**, 539) of ν_2 = 156 cm.$^{-1}$.

Dicyano-compounds.—Cyanogen contains two independent oscillators, each C≡N bond relative to the central C–C bond, and each of these is two-dimensional; therefore $P_A = 16\pi N\mu^2/9V_0$. According to Groves and Sugden (J., 1937, 1992) μ is about 3 D. (this also is roughly the moment of hydrogen cyanide, 2·88 D.); Sho-Chow Woo (*Z. physikal. Chem.*, 1937, *B*, **37**, 399) gives a value of 2·93 × 10^{-12} erg/radian²/molecule for V_0; P_A is therefore 11·4 c.c. The observed value of $P - P_E$ is rather less, 8·3 c.c. Now, mutual induction between the C≡N dipoles in cyanogen may be considerable because of their nearness, and if the effective moment of each were thereby reduced to 2·5 D., P_A would be reduced to 8 c.c. In *p*-dicyanobenzene, which otherwise is essentially the same system, even to the possibilities of resonance structures, the mutual induction between the widely separated dipoles would be small. The fact that $P - P_E$ is greater for this substance (11·9 c.c.) than for cyanogen can thus be given a reasonable explanation.

The moments of nitrobenzene and of benzonitrile are very nearly equal (Groves and Sugden, J., 1934, 1094), so the moments of the polar groups probably are so too (see Groves and Sugden, J., 1937, 1992); therefore, if also in *p*-dicyanobenzene, *p*-nitrocyanobenzene, and *p*-dinitrobenzene each group is a two-dimensional oscillator with about the same force constant, as is likely,† the similarity of the P_A values for these three substances can be understood.

Tetrahalides.—No precise test of the hypothesis can be made with the data for the tetrahalides, for the bond moments are not accurately known and the force constants have not been evaluated. However, by using the best available values of the former it is possible to derive force constants and show that these are of a reasonable order of magnitude. It may be shown that for a tetrahedral molecule $P_A = 16\pi N\mu^2/9V_0$, where V_0 applies to the bending of any one valency relative to another. From the ratio of the moments of fluoroform and methyl fluoride (see p. 1282) μ_{CF} in carbon tetrafluoride would appear to be about 1·5 D., whence, since P_A = 2·86 c.c., V_0 = 2·66 × 10^{-12} erg/radian²/molecule. The moment of triethyl stannichloride, $(C_2H_5)_3SnCl$, is 3·44 D.; mutual induction is smaller the farther apart the chlorine atoms are, so the bond moment in stannic chloride is probably about 3 D., whence, since P_A = 10·3 c.c., V_0 = 2·95 × 10^{-12} erg/radian²/molecule. Similarly, from the moment of trimethyl stannibromide, $(CH_3)_3SnBr$, 3·32 D., μ_{SnBr} in stannic bromide can be assessed as 2·8 D., whence, from P_A = 8·8 c.c., V_0 = 3·0 × 10^{-12} erg/radian²/molecule. The consistency of these values, and their agreement with other force constants which were obtained spectroscopically, are points in support of the theory. Stannic iodide admittedly gives an anomalous result; this may be due to the effect of a combination frequency.‡

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* V_0, as defined above, equals the k_α used by Thompson and Linnett.

† The results found by Birtles and Hampson (J., 1937, 10) indicate that this may not be exactly true of the nitro-group, but provide no measure of the departure.

‡ *Note, added August 20th,* 1938.—Hölemann and Goldschmidt, in a paper which we overlooked (*Z. physikal. Chem.*, 1934, *B*, **24**, 199), report values for the molecular refractivities of the stannic halides in the vapour phase, for a variety of wave-lengths including that of the sodium D line (5893 A.) and infinity. In the following table their values for both of these wave-lengths are used, in order that comparisons may be made with the values in Table XIX for other tetrahalides. The new $P_{vap.}$—P_E values, and the percentages which these are of the P_E values are also given.

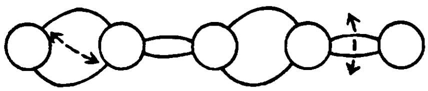
		P_E.		$P_{vap.}$—P_E.		%.	
	$P_{vap.}$	λ = 5893.	$\lambda = \infty$.				
$SnCl_4$	45·5	35·9	34·6	9·6	10·9	26·7	31·5
$SnBr_4$	55·6	50·2	47·7	5·4	7·9	10·8	16·6
SnI_4	81·4	78·4	70·1	3·0	11·3	3·8	16·1

On using the results for λ = 5893, the values of P_A fall from chloride to iodide, as anticipated in the discussion, and so the anomaly noted on this page is removed. It persists, however, if the results for $\lambda = \infty$ be used, and this rather suggests that the extrapolation to obtain P_E at infinite wave-length may not be altogether satisfactory.

Acetylacetonates.—It is similarly impossible to treat the acetylacetonates exactly. The moment of an acetylacetonate chelate ring including a metal atom is not known, but from the moments of the ether and ketone co-ordination compounds with beryllium, aluminium, titanium, and tin halides (see Ulich and Nespital, *Z. angew. Chem.*, 1931, **44**, 750; Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 153; Ulich, Hertal, and Nespital, *ibid.*, 1932, *B*, **17**, 21), which range from 6—9 and average about 7·5 D., it appears likely that the moment required would be near this mean value. Accepting this value, using the data in Table XVII, and the appropriate atom polarisation formulæ,* it may be shown that for the beryllium, chromium, aluminium, iron, thorium, and zirconium compounds V_0 is 3·7, 3·6, 3·6, 2·6, 2·6, and 3·1 $\times 10^{-12}$ erg/radian^2/molecule respectively. These apply to the bending of a chelate ring held to an atom by two bonds. Their magnitude is reasonable, and the variations are what might be expected. The relatively high polarisations of the ferric and thorium compounds indicate a large μ, or a small V_0, both of which would follow from the bonds to the central atom being unusually polar in character.

Diketones.—The last group of compounds to be discussed is that of the diones. Now that it is known that *p*-benzoquinone is non-polar and that there is no appreciable solvent effect on $P - P_E$ it is clear that Cartwright and Errera's results (Hammick, Hampson, and G. I. Jenkins, this vol., p. 1265) show the existence of an atom polarisation of at least 8 c.c. A striking point is that *p*-benzoquinone, its 2 : 5-dimethyl- and 2 : 5-dichloro-derivatives, tetramethyl*cyclo*butanedione, and carbon suboxide all have approximately equal $P - P_E$ values, of 8—10 c.c. In connection with the thermal bending, or flexibility moment theory, Hammick, Hampson, and G. I. Jenkins (*loc. cit.*) discussed the consequences of such bendings in the ring compounds as would involve the C=O groups moving perpendicularly to the plane of the normal ring. They pointed out that, quite apart from the question of whether or not the oscillation would be slow enough, the observed facts could not be accounted for by bendings in this mode because (1) the substitution of bromine atoms or methyl groups for hydrogen on the benzoquinone ring does not alter the polarisation and (2) the force constants of bending could not be expected to be even approximately equal in the six-membered, unsaturated, and the four-membered, saturated rings, yet the polarisations are the same. To these reasons may be added another: that the ring compounds, bending in this way, must be considered as *single*, one-dimensional oscillators, with $P_A = 4\pi N\mu^2/9V_0$, whereas carbon suboxide has *two*, independent, one-dimensional oscillators, and thus has $P_A = 8\pi N\mu^2/9V_0$. The reason for this is that, unless the classical stereochemistry of the latter is entirely obliterated by the resonance (Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860), the C = O groups have to oscillate in planes at right angles, owing to the anisotropic character of the double bonds; this is true whether the molecule bends about the middle carbon atom or the end ones, as may be seen from Fig. 3.

FIG. 3.



Finally, as Hammick, Hampson, and Jenkins showed, the frequency of oscillation of *p*-benzoquinone, calculated for the above mode, disagrees with the absorption frequency observed by Cartwright and Errera.

The objections to this mode apply with equal force whether it is considered in connection with thermal bending or atom polarisation. Now, it may readily be seen that if each C=O group bends relative to the ring, or the C=C bond, in a plane perpendicular to the plane of the double bond between carbon and oxygen, *i.e.*, in the plane of the ring, all the compounds have two independent, one-dimensional oscillators. Thus, the polarisation equations, and the values of μ and of V_0 are the same, or nearly so, in all the compounds, and the constancy of the atom polarisation is explained. This alternative mode is therefore much the more probable one. Finally, if the period of vibration of *p*-benzoquinone in this mode be calculated, it is found to be 3·0 $\times 10^{-13}$ sec., which is in good agreement with the observed value, 2·8 $\times 10^{-13}$ sec. The atom polarisations of these diones seem, therefore, to be explained.

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* If the number of chelate rings be X, then $P_A = 4\pi XN\mu^2/9V_0$, provided that each ring bends only perpendicular to its own plane.

These simple considerations break down when applied to carbon dioxide, for $P - P_E$ is less than 1 c.c. (van Vleck, *loc. cit.*). This doubtless is because of the great importance of structures other than the double double-bonded one in the resonance hybrid, and of strong coupling between the oscillations.

Effects of Anharmonicity.—The questions of anharmonicity and its possible effect on the temperature dependence of atom polarisation merit a brief discussion. It was mentioned that if the restoring force, in the vibrations set up by the combined thermal and electrical influences, be proportional to the extension from the normal of the unperturbed system, then P_A is temperature-independent. Otherwise P_A is temperature-dependent. A potential function with quartic terms being assumed, as on p. 1279, the same relation between P and T is found as for the other problem, Eqn. 1, although the initial integral * and the physical argument behind it are different. Now, the ratio of force constants, V_1/V_0, might reasonably be expected to be roughly independent of V_0 for bending movements in molecular systems; thus, the larger V_0 is the smaller V_1/V_0^2 is likely to be. If V_0 is of the order 2—4 × 10^{-12} erg/radian^2/molecule, anharmonic symptoms are unlikely to be noticeable at temperatures of 250° or less, for the average amplitude of bend of one dipole relative to the other would be about 10—12°, and electric fields of ordinary strengths would change the angle further by only a very small fraction of 1°. These considerations are, admittedly, based on a classical treatment, but it is unlikely that a rigorous quantum-mechanical treatment would lead to a different conclusion.

Summing-up.—It seems appropriate to give in conclusion some generalisations about atom polarisation which are derived from the foregoing discussion.

(1) A molecule containing two or more groups of moment 2·5 D., or over, which may be bent relative to one another with average ease (force constant about 2—4 × 10^{-12} erg/radian^2/molecule) will have an atom polarisation of at least 5 c.c.

(2) Since atom polarisation depends upon the presence of polar groups in the molecule, whereas electron polarisation does not, the former cannot be expected to be even approximately a constant fraction of the latter.

(3) In general, atom polarisation is not additive, but it may be roughly so in particular series of compounds. Each polar group, in a molecule containing several such, may make an "intra-group" contribution towards the total, and there is also an "inter-group" contribution from the relative bending of groups. If, for any reason, the latter is much smaller than the former, then the polarisation is proportional to the number of polar groups; but this appears to be an unusual circumstance. In particular series such as the acetylacetonates, or the di-, tetra-, and hexa-halides, it can be shown that if μ and V_0 are constant the inter-group contribution is proportional to the number of polar rings, bonds, or groups; but, since μ and V_0 must in fact vary in such series, exact proportionality cannot be expected. Compounds containing only one polar group would not fall into line, because in such there would be no inter-group contribution, only an intra-group one.

(4) If several compounds contain essentially the same oscillating systems, they have nearly the same atom polarisations.

(5) If the atom polarisation of a substance can be attributed to one vibration, or to several of the same kind, a relation between polarisation, moment, and force constant can be derived, and used to calculate any one of these three quantities if the values of the other two are known.

If, further, the actual mode of vibration is known, the frequency may be calculated.

These conclusions do not necessarily conflict with those of Groves and Sugden (J., 1937, 1779) that the atom polarisation of aliphatic ethers and amines can be taken as 5% of the electron polarisation, for these compounds contain no highly polar groups or bonds. It

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$$P_A = \frac{4\pi N e_i x}{9} = \frac{4\pi N e_i}{9} \frac{\int_{-\infty}^{+\infty} x e^{-\frac{V_0 x^2 - V_1 x^4}{2kT} + \frac{e_i x F}{kT}} \, dx}{\int_{-\infty}^{+\infty} e^{-\frac{V_0 x^2 - V_1 x^4}{2kT} + \frac{e_i x F}{kT}} \, dx}$$

appears, however, that these particular cases can hardly provide an adequate basis for a general empirical rule concerning atom polarisation. By using the principles outlined in this paper it should frequently be possible to estimate atom polarisation with sufficient accuracy for dipole moment determinations.

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