512. *Molecular Polarisability. The Anisotropies of the Molecules* PCl₃, OPCl₃, NMe₃, *and* ONMe₃.

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The increase of molecular refractivity from trimethylamine to the oxide and the decrease from phosphorus trichloride to oxychloride have been investigated by determining the principal polarisabilities of these molecules. The polarisability of trimethylamine becomes greater, both along and across the direction of action of the resultant molecular dipole moment, when the oxide is formed. With phosphorus trichloride, addition of an oxygen atom notably reduces the polarisability across $\mu_{\text{resultant}}$. Attempts to calculate principal polarisabilities by using empirical equations involving bond lengths, stretching frequencies, etc., are reasonably satisfactory in three cases, but for phosphorus oxychloride, b_1 emerges *ca.* 20% too large, although a contraction in $b_2 = b_3$ from phosphorus trichloride is qualitatively predicted.

MOLAR Kerr constants at infinite dilution, $_\infty(_mK_2)$, are here recorded at 25° for phosphorus trichloride and oxychloride in benzene and for trimethylamine oxide in dioxan. From the observed dipole moments, molecular refractions, etc., and with an assumption that these molecules have rotational symmetry about the direction of action of $\mu_{\text{resultant}}$, estimates of the principal polarisabilities follow, as in Table 1.

TABLE 1. *Molar Kerr constants, moments, and principal polarisabilities.*

Solute	Solvent	$10^{12}\,_\infty(_mK_2)$	μ, D *	$10^{23}(b_1 + 2b_2)$	$10^{23}b_1$	$10^{23}(b_2 = b_3)$
PCl₃	Benzene	-10.9_2	0.89_0	3.012	0.914	1.049
OPCl₃	,,	-73.8_4	2.42_5	2.936	0.902	1.017
ONMe₃	Dioxan	210.0	5.03	2.505	0.885	0.810

* Calc. by taking the distortion polarisation as $1.05R_D$.

Discussion.—None of these three compounds has previously been examined in this way, nor does the literature indicate the degrees of anisotropy to be expected for the bonds between phosphorus and chlorine or oxygen, or between nitrogen and oxygen. It has, however, been noted [1] with phosphorus trichloride and oxychloride that the smaller molecule has the larger molecular refraction, *i.e.* that the addition of an oxygen atom to the trichloride *reduces* the average polarisability. The results in Table 1 suggest that the diminution occurs more in b_2 than in b_1. Unfortunately, owing to the smallness of $\mu_{\text{resultant}}$ for phosphorus trichloride, its precise value is much affected by the distortion polarisation, $_DP$, used in its extraction from the $_\infty P_2$ observed. A moment of 0.89 D is given when $_DP = 1.05R_D = 27.6$ c.c. Grassi,[2] from a study of the total polarisation of phosphorus trichloride as a vapour, records the temperature-invariant term in the Debye equation $P = A + B/T$ as 32.2 c.c.; taking 32.2 c.c. as $_DP$ yields $\mu_{PCl_3} = 0.75_3$ D, and in consequence $10^{23}b_1 = 0.858$ and $10^{23}(b_2 = b_3) = 1.077$. Nevertheless, although b_1 for OPCl₃ now appears larger than that for PCl₃, we see that diminution of b_2 from PCl₃ to OPCl₃ is still the preponderant change, and evidently that which makes R_{PCl_3} greater than R_{OPCl_3}.

The cases of trimethylamine and its oxide differ from those of the phosphorus halides. Aroney and Le Fèvre [3] found for trimethylamine $10^{23}b_1 = 0.774$ and $10^{23}(b_2 = b_3) = 0.763$; addition of oxygen therefore increases *both* b_1 and b_2, the former ($\Delta b_1 = 0.111$) more than the latter ($\Delta b_2 = 0.047$), consistently with R_{ONMe_3} exceeding R_{NMe_3}.

The causes of these changes in polarisability seem unlikely to be entirely structural in origin because the Y–X bonds in the YX₃ portions of the two oxygenated molecules are,

[1] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, 1953.
[2] Grassi, *Nuovo Cimento*, 1933, **10**, 3.
[3] Aroney and Le Fèvre, *J.*, 1958, 3002.

if anything, slightly more splayed than when in the free YX_3 molecules, a circumstance which—provided $b_L^{P-Cl} > b_T^{P-Cl} = b_V^{P-Cl}$—should tend to make b_2 for $OPCl_3$ larger than b_2 for PCl_3. More probably the process of attaching an oxygen atom in fact changes the polarisabilities of the C–N and Cl–P links in opposite ways. We note that from NMe_3 to $ONMe_3$ the intercentre distance [4] r_{N-O} *increases* by 0·12 Å, while from PCl_3 to $OPCl_3$ r_{P-Cl} diminishes from 2·04 to 1·99 Å. These facts can be reconciled by the arguments of Walsh [5] according to which bond length and bond polarity vary together. The establishment of the strongly [6] polar NO and PO bonds will, by induction, augment the component moments of the C→N bonds and reduce those of the Cl←P bonds; the alterations of r_{XY} from YX_3 to OYX_3 are therefore understandable.

Longitudinal bond polarisabilities and bond lengths. Two [7] empirical connections (equations A and B) between these properties have been suggested:

$$10^{24}b_L^{X-Y} = 0.140 + 0.156d^3 \quad \ldots \ldots \ldots \text{(A)}$$

where d is the intercentre distance r_{XY}, or if Y is a terminal atom, the sum of r_{XY} and the radius of Y, r_Y (*i.e.* 0·995 for chlorine), and

$$\nu_{XY} = 9273Q - 254 \quad \ldots \ldots \ldots \ldots \text{(B)}$$

where $Q = (b_L^{X-Y}/M)^{\frac{1}{2}}/r^2_{XY}$; ν_{XY} being the stretching frequency of the bond X–Y in cm.$^{-1}$, and M is the reduced mass of X–Y.

In the present instances, data taken as in Table 2 lead to the values of b_L^{XY} shown. The

TABLE 2. *Calculation of longitudinal polarisabilities by equations A and B.*

Molecule	XY	r_{XY} (Å)	ν_{XY} (cm.$^{-1}$)	$10^{23}b_L$ (from eqn. A)	$10^{23}b_L$ (from eqn. B)
PCl_3	P–Cl	2·043	488	0·45$_1$	0·61$_4$
$OPCl_3$	P–Cl	1·99	485	0·42$_9$	0·52$_0$
,,	PO	1·45	1290	?	0·45$_3$
NMe_3	C–N	1·47	?	0·050	?
$ONMe_3$	C–N	1·59	?	0·063	?
,,	NO	1·36	960	?	0·10$_6$

values of r_{XY} are as listed in ref. 4. The two P–Cl frequencies are given by Daasch and Smith,[8] that for PO is from Gore [9] and papers cited by him, while ν_{NO} is midway between the limits 950—970 cm.$^{-1}$ reported by Mathis, Wolf, and Gallais.[10] Owing to the absence of definite information regarding r_{YO} for " true " single and " true " double bonds between Y and oxygen (cf. equation iii in ref. 7a), and because ν_{C-N} is uncertain in aliphatic amines generally (cf. Bellamy, ref. 11), Table 2 cannot be completed; nevertheless the opposite trends in b_L^{XY} from YX_3 to OYX_3 are correctly predicted.

Transverse bond polarisabilities. Vogel [12] has recorded dispersion measurements of refractivity from which R_∞ for PCl_3 and $OPCl_3$ may be deduced as 25·33 and 24·69 c.c., respectively; from the former the total polarisability $(b_L^{P-Cl} + 2b_T^{P-Cl})$ of the P–Cl link is 1.004×10^{-23} c.c. (strictly this total must include contributions due to the lone-pair electrons of the phosphorus atom; an analogous remark applies, of course, to Aroney and Le Fèvre's discussion [3] of the N–H and N–C bonds). The apparent transverse polarisability of P–Cl in PCl_3 is therefore 0.194×10^{-23} c.c. Since there is no clear way of disentangling

[4] " Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. Spec. Publication No. 11, 1958.
[5] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 56; 1947, **43**, 60; *Ann. Reports*, 1947, **44**, 32.
[6] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, Toronto, London, 1955 p. 245.
[7] Le Févre, *Proc. Chem. Soc.*, (a) 1958, 283; (b) 1959, 363.
[8] Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.
[9] Gore, *Discuss. Faraday Soc.*, 1950, **9**, 138.
[10] Mathis, Wolf, and Gallais, *Compt. rend.*, 1956, **242**, 1873.
[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 221.
[12] Vogel, *J.*, 1948, 1833.

the refractivities of the P–Cl and the PO links in phosphorus oxychloride, we assume that the ratio $b_{\mathrm{L}}^{\mathrm{P-Cl}}/b_{\mathrm{T}}^{\mathrm{P-Cl}}$ is the same in phosphorus trichloride and oxychloride; accordingly $b_{\mathrm{L}}^{\mathrm{P-Cl}}$ in $OPCl_3$ appears as 0.164×10^{-23}. If $(b_{\mathrm{L}} + 2b_{\mathrm{T}})$ for C–N is the same in trimethylamine as in the oxide, the values of $b_{\mathrm{L}}^{\mathrm{C-N}}$ in Table 2 correspond to values of $b_{\mathrm{T}}^{\mathrm{C-N}}$ of 0.07_2 and $0.06_6 \times 10^{-23}$, respectively. (In this paragraph, for want of guiding information, we presume the two transverse polarisabilities of the P–Cl, PO, and NO bonds to be equal, *e.g.*, $b_{\mathrm{T}}^{\mathrm{P-Cl}} = b_{\mathrm{V}}^{\mathrm{P-Cl}}$.)

Predictions of molecular polarisabilities. With the geometrical details appropriate for these molecules, their principal polarisabilities may be estimated. The Cl·P·Cl angles are [4] $100.1°$ in phosphorus trichloride and $103.6°$ in the oxychloride. By symmetry the resultant dipole moment μ_{res} in each structure will act along the rotational axis, parallel to which also one of the principal molecular polarisabilities, b_1, is measured; b_2 and b_3, the two other polarisabilities, relate to directions which are mutually perpendicular, and also perpendicular to that of b_1. The angles between μ_{res} and a P–Cl bond follow as $62° 16'$ in phosphorus trichloride and $65° 10'$ in the oxychloride. Introduction of the appropriate polarisabilities for PCl and PO therefore yields:

$$10^{23}b_1{}^{\mathrm{PCl_3}} = 0.856 \text{ and } 10^{23}b_1{}^{\mathrm{OPCl_3}} = 1.133.$$

From R_∞, we know $(b_1 + 2b_2)$, so that

$$10^{23}b_2{}^{\mathrm{PCl_3}} = 1.078 \text{ and } 10^{23}b_2{}^{\mathrm{OPCl_3}} = 0.901_5.$$

In trimethylamine oxide the C·N·C angle is reported by Lister and Sutton [13] as $109.5°$, *i.e.*, within the limits $(108° \pm 4°)$ given in ref. 4 for trimethylamine itself; $(b_1 + 2b_2)$ for trimethylamine is 2.299_5 and for trimethylamine oxide is 2.505×10^{-23}. Calculated values follow as in Table 3.

TABLE 3. *Predicted and found principal molecular polarisabilities.*

	$10^{23}b_1$ calc.	$10^{23}(b_2 = b_3)$ calc.	$10^{23}b_1$ found	$10^{23}(b_2 = b_3)$ found
PCl_3	0.856	1.078	0.914 (0.858) *	1.049 (1.077) *
$OPCl_3$	1.133	0.902	0.902	1.017
NMe_3	0.785	0.757	0.774 †	0.763 †
$ONMe_3$	0.879	0.813	0.885	0.810

　　　　* Bracketed values are obtained if μ is taken as 0.75_3 D; see discussion above.
　　　　† From ref. 3.

The only seriously incorrect prediction is that for phosphorus oxychloride. Perhaps the empirical equations are inapplicable to bonds—such as PO—involving *d*-orbitals; alternatively, 1290 cm.$^{-1}$ may not be the appropriate frequency in this case. To obtain $b_1{}^{\mathrm{OPCl_3}} = 0.902 \times 10^{-23}$ requires ν_{PO} to be 964 cm.$^{-1}$.

EXPERIMENTAL

Materials, Methods, etc.—The two phosphorus halides were B.D.H. products, redistilled as required, fractions with b. p. 75—76° (trichloride) and 106—107° (oxychloride) at 760 mm. being taken. Trimethylamine oxide hydrate, prepared according to Meisenheimer,[14] was dehydrated by sublimation at 150°/5 mm., and stored *in vacuo* over phosphorus pentoxide; it had m. p. 220°. Benzene and dioxan were purified by refluxing them over, and then distilling them from, sodium–potassium alloy or sodium, respectively, immediately before making up solutions. Obvious precautions against moist air were taken in all transference operations; unless the dioxan solutions were kept thoroughly dry the insoluble hydrate of trimethylamine oxide was gradually precipitated and prevented electric birefringence measurements.

Apparatus, techniques, symbols used, and methods of calculation, have been as described before.[15,16] Observations are recorded in Table 4 and results summarised in Table 5. The

[13] Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495.
[14] Meisenheimer, *Annalen*, 1913, **397**, 286.
[15] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[16] Le Fèvre, " Dipole Moments," Methuen, London, 3rd Edn., 1953, Chap. 2.

quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indexes, and Kerr effects, respectively, of the solvents and of solutions containing weight fractions w_2 of solute. The following data apply at 25° to the two solvents involved:

	ε_1	d_1	$(n_1)_D$	p_1 (c.c.)	C	H	J	$B_1 \times 10^7$	$_sK_1 \times 10^{12}$
Dioxan...	2·2090	1·0280	1·4202	0·27942	0·16473	2·008	0·4752	0·068	0·01162
Benzene	2·2725	0·87378	1·4973	0·34086	0·18809	2·114	0·4681	0·410	0·0756

TABLE 4. *Dielectric-constant, density, etc., increments from solvent to solutions.*

Phosphorus trichloride in benzene

10^5w_2	1530	3823	6055	6708	7757	9278	9568	10,602	10,665	11,912	14,452	16,788	20,141
$10^4\Delta\varepsilon$	—	—	—	469	545	685	—	—	761	847	1039	1175	1434
$10^5\Delta d$	611	1509	2380	—	—	—	3831	4278	—	—	—	—	—
10^5w_2	4082	5747	8567	11,634	12,045	16,033	21,039	26,770	27,802	29,725	31,808	32,264	
$10^{10}\Delta B$	—22	—27	—43	—56	—62	—82	—102	—137	—143	—161	—168	—171	

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.712$; $\Sigma\Delta d/\Sigma w_2 = 0.399$; $\Sigma\Delta b/\Sigma w_2 = -0.516 \times 10^{-7}$.

Phosphorus oxychloride in benzene

10^5w_2	2272	3393	4497	6951	9223	12,700		
$10^4\Delta\varepsilon$	955	1425	1949	2977	4012	5670		
$10^5\Delta d$	954	1439	1912	2994	4020	5639		
10^5w_2	1369	1433	1541	2637	3936	4359	5447	5483
$10^{10}\Delta B$	—28	—30	—31	—58	—85	—94	—120	—122

whence $\Delta\varepsilon = 4.13w_2 + 0.219_2{}^2$; $\Delta d = 0.415w_2 + 0.0195w_2{}^2$; $10^7\Delta B = -2.041w_2 - 3.12w_2{}^2$.

Trimethylamine oxide in dioxan

10^5w_2	122	181	237	307	392	446	494	532
$10^4\Delta\varepsilon$	521	781	975	1303	1654	1884	2073	2173
$10^5\Delta d$	—10	—11	—16	—22	—25	—29	—31	—37
10^5w_2	101	104	133	141	142	170	185	201	242
$10^{10}\Delta B$	19	19	23	26	24	30	35	31	45
10^5w_2	249	264	269	330	337	345	371	395
$10^{10}\Delta B$	45	47	48	57	59	61	65	67
10^5w_2	237	392	494					
$10^5\Delta n$	10	19	29					

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 41.9$; $\Sigma\Delta d/\Sigma w_2 = -0.0668$; $\Sigma\Delta B/\Sigma w_2 = 17.64$; $\Sigma\Delta n/\Sigma w_2 = 0.0516$.

TABLE 5. *Calculation of results.*

Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	$\infty(_mK_2) \times 10^{12}$
PCl₃	Benzene	0·71₂	0·399	0·003	—1·25₈₅	—10·9₂
OPCl₃	,,	4·13	0·475	—0·015	—4·97₈	—73·8₄
ONMe₃	Dioxan	41·9	—0·065	0·036	259·5	210·0

	∞P_2 (c.c.)	$_DP$ (c.c.)	μ (D)	$(\theta_1 + \theta_2) \times 10^{35}$	$_EP$ (c.c.)
PCl₃	43 8	27·6ᵃ	0·89₀	—2 59₆	25·33ᵇ
,,	,,	32·2ᶜ	0·75₃	,,	,,
OPCl₃	146·6	26·3ᵃ	2·42₈	—17·5₆	24·69ᵇ
ONMe₃	540·8	22·7ᵃ	5·03	49·9₄	21·07ᵈ

a, *i.e.* 1·05 R_D; *b* extrapolated from R's given by Vogel [12]; *c* from Grassi [2]; *d i.e.* 0·97R_D.

Previous Determinations of Dipole Moments.—Wesson [17] lists values, obtained in benzene or carbon tetrachloride, from 0·70 to 0·90 D for phosphorus trichloride, and between 2·36 and 2·42 D for the oxychloride; the trichloride is stated to show $\mu = 1.89$ D in dioxan. Change of solvent does not affect trimethylamine oxide so markedly, Linton [18] reporting 5·02 D in dioxan, against Phillips, Hunter, and Sutton's moment of 4·87 D in benzene.[19]

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[17] Wesson, " Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.
[18] Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.
[19] Phillips, Hunter, and Sutton, *J.*, 1945, 146.