

439. Molecular Polarisation and Molecular Interaction. Part III.*
The Interaction of Ethers, Sulphides, and Phosphines with Poly-
halogenated Hydrocarbons.

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Following work on the interaction of amines with carbon tetrachloride and other non-polar halogenated hydrocarbons, molecular polarisation and dipole-moment evidence is presented indicating that ethers, organic sulphides, and phosphines can also act as donors to polyhalogenated hydrocarbons resulting in a weak donor-acceptor interaction.

THE measured dipole moment of a solute in a non-polar solvent is related to the moment in the vapour phase and to solute-solvent interactions which can be: (i) more or less general or (ii) quite particular. Type (ii), which includes hydrogen bonding between solute and solvent molecules (*e.g.*, aniline in 1,4-dioxan¹) and donor-acceptor interaction (*e.g.*, iodine in benzene²), often involves significant redistribution of electrical charge. In the absence of molecular interaction—type (ii)—in a series of non-polar solvents, the apparent moment of a solute usually changes slightly and in a fairly consistent direction with changing dielectric constant of solvent.³ This is type (i) interaction.

It follows that, in the absence of type (ii) interactions, if a polar solute is measured in

TABLE I.
 Dipole moments in benzene and carbon tetrachloride solutions where no
 interaction is likely.^a

Compound	μ_B (D) ^b	μ_{CT} (D) ^c	$\mu_{CT} - \mu_B$ (D)	Compound	μ_B (D) ^b	μ_{CT} (D) ^c	$\mu_{CT} - \mu_B$ (D)
n-Propyl iodide	1.84	1.86	0.02	<i>p</i> -Chlorobenzyl chloride	1.71	1.72	0.01
n-Butyl bromide	1.98	1.98	0.00	<i>o</i> -Nitrotoluene	3.79	3.81	0.02
t-Butyl chloride	1.94	1.95	0.01	1-Bromo-2-phenyl- ethylene	1.54	1.53	-0.01
Bromobenzene ...	1.53	1.51	-0.02	Nitromesitylene ...	3.65	3.63	-0.02
Cyanobenzene ...	4.02 *	4.03 †	0.01	<i>p</i> -Diethoxybenzene	1.76	1.72	-0.04
		4.05 ‡	0.03	Nitrobenzene	3.94	3.93	-0.01

^a Found in Wessen, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948. The values have not been recalculated by a single method since the small difference would not be affected. ^b B = benzene. ^c CT = carbon tetrachloride.

* At 20°. † At 0°. ‡ At 40°.

two non-polar solvents of similar dielectric constant, then the resulting moment should be closely similar. This is borne out in Table I for a variety of polar solutes in benzene and carbon tetrachloride which have very similar dielectric constants (2.273 and 2.227, respectively, at 25°). Only sets of values which could be found together in one publication have been used, and although this considerably reduced the number of values which could be quoted, it minimised the probable errors in the small differences.

* Part II, *J.*, 1962, 157.

¹ Few and Smith, *J.*, 1949, 753.

² Fairbrother, *J.*, 1948, 1051.

³ Müller, *Trans. Faraday Soc.*, 1934, **30**, 729.

The substances listed in Table I are mostly halogeno- or nitro-organic compounds, and the values of $\mu_{CT} - \mu_B (= \Delta\mu)$ are quite small. We suggest that for simple solutes, with dipoles similar to those in Table I, a difference between the apparent dipole moments in benzene and carbon tetrachloride solutions greater than 0.04D is evidence for an interaction between the solute and one, or both, of the solvents.

We have shown previously⁴ that the little-studied interaction between polyhalogenated hydrocarbons and amines can be investigated by dipole-moment or polarisation measurements. The apparent dipole moments of most amines are higher in carbon tetrachloride than in benzene,⁵ and the difference ($\Delta\mu$) gives a measure of the extent of interaction. To indicate the magnitude of the effect a selection of $\Delta\mu$ values for such compounds, in which there are no appreciable steric effects, is given:

	$\Delta\mu$ (D)		$\Delta\mu$ (D)		$\Delta\mu$ (D)
Butylamine	0.11	Triethylamine	0.07	3-Methylpyridine	0.13
Piperidine	0.16	4-Methylpyridine ...	0.15	Pyridine	0.12

The pK_a value of an amine is considerably influenced by the electron density at the nitrogen atom. Since amines of high pK_a value tend to have the highest $\Delta\mu$ values,⁴ it is probable that the interaction with polyhalogenated hydrocarbons involves some transference of electron density from the amine, *i.e.*, the amine is donor in a weakly bonded complex.

Ethers, sulphides, and phosphines can also act as donors in the formation of certain co-ordination complexes. The next step was to see whether the dipole moments or total polarisation of some of these compounds in carbon tetrachloride and benzene solutions indicate any interaction with carbon tetrachloride.

EXPERIMENTAL

Polarisation Measurements and Purification of Solvents.—The heterodyne-beat capacitance meter used to measure dielectric constants, calculation of total polarisation or dipole moments,

TABLE 2.
Polarisation data at 25°C.

$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2	$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2
<i>Diphenyl ether in benzene</i>				<i>Diphenyl ether in carbon tetrachloride</i>			
639	2.2728	1.14432	2.24250	556	2.2282	0.63051	2.12445
1946	2.2740	1.14401	2.24269	1364	2.2297	0.63075	2.12489
4756	2.2769	1.14340	2.24323	3518	2.2335	0.63139	2.12614
6186	2.2784	1.14310	2.24364	3986	2.2344	0.63151	2.12632
10,060	2.2823	1.14225	2.24433	6711	2.2399	0.63230	2.12818
18,505	2.2913	1.14039	2.24619	13,241	2.2527	0.63418	2.13180
18,558	2.2913	1.14035	2.24619	14,879	2.2555	0.63466	2.13273
$\epsilon_{12} = 2.2720 + 1.039w_2$;		$v_{12} = 1.14445 - 0.2209w_2$;		$\epsilon_{12} = 2.2269 + 1.934w_2$;		$v_{12} = 0.63037 + 0.2872w_2$;	
$n_{12}^2 = 2.24230 + 0.209w_2$;		${}_2P_\infty = 80.07$ c.c.;		$n_{12}^2 = 2.12405 + 0.591w_2$;		${}_2P_\infty = 80.18$ c.c.;	
$R_D = 52.83$ c.c.;		$\mu = 1.15D$ (1.13 ^a).		$R_D = 53.74$ c.c.;		$\mu = 1.14D$.	
<i>Dibutyl ether in benzene</i>				<i>Dibutyl ether in carbon tetrachloride</i>			
1826	2.2744	1.14478	2.24257	668	2.2282	0.63081	2.12381
2530	2.2745	1.14489	2.24233	1252	2.2293	0.63121	2.12361
3859	2.2761	1.14512	2.24188	1971	2.23	0.63169	2.12337
5580	2.2776	1.14547	2.24119	2745	2.2320	0.63225	2.12314
6271	2.2782	1.14558	2.24092	3683	2.2339	0.63285	2.12267
8729	2.2803	1.14600	2.24002	4207	2.2350	0.63321	2.12250
8987	2.2804	1.14605	2.23996	5384	2.2371	0.63672	2.12203
$\epsilon_{12} = 2.2725 + 0.900w_2$;		$v_{12} = 1.1445 + 0.1766w_2$;		$\epsilon_{12} = 2.2269 + 1.914w_2$;		$v_{12} = 0.63038 + 0.6721w_2$;	
$n_{12}^2 = 2.24332 - 0.380w_2$;		${}_2P_\infty = 73.28$ c.c.;		$n_{12}^2 = 2.12414 - 0.394w_2$;		${}_2P_\infty = 75.61$ c.c.;	
$R_D = 40.96$ c.c.;		$\mu = 1.26D$ (1.22D ^a).		$R_D = 40.52$ c.c.;		$\mu = 1.31D$.	

⁴ Sharpe and Walker, *J.*, 1961, 2974.

⁵ Sharpe and Walker, *J.*, 1962, 157.

TABLE 2. (Continued.)

$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2	$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2
<i>Diethyl ether in benzene</i>				<i>Diethyl ether in carbon tetrachloride</i>			
812	2.2737	1.14467	2.24197	369	2.2290	0.63064	2.12355
1710	2.2753	1.14490	2.24152	730	2.2305	0.63095	2.12332
2307	2.2768	1.14504	2.24122	1316	2.2329	0.63137	2.12305
3408	2.2785	1.14529	2.24074	1770	2.2345	0.63167	2.12273
4934	2.2812	1.14563	2.24011	2315	2.2371	0.63211	2.12244
5654	2.2828	1.14582	2.23972	2821	2.2388	0.63249	2.12209
7005	2.2849	1.14614	2.23909	3595	2.2422	0.63307	2.12154
$\epsilon_{12} = 2.2721 + 1.84669w_2$;		$v_{12} = 1.14446 + 0.2427w_2$;		$\epsilon_{12} = 2.2275 + 4.065w_2$;		$v_{12} = 0.63037 + 0.7518w_2$;	
$n_{12}^2 = 2.2432 - 0.460w_2$;		${}_2P_\infty = 56.37$ c.c.;		$n_{12}^2 = 2.12380 - 0.610w_2$;		${}_2P_\infty = 61.63$ c.c.;	
$R_D = 23.63$ c.c.;		$\mu = 1.27D$ (0.74, 1.14, 1.27, 1.27, 1.22D ^a).		$R_D = 22.89$ c.c.;		$\mu = 1.38D$.	
<i>Diethyl ether + carbon tetrabromide (mole fraction 0.095) + benzene *</i>				<i>Diethyl ether + carbon tetrabromide (mole fraction 0.223) + benzene.</i>			
$10^6 w_2$	ϵ_{12}	n_{12}^2		$10^6 w_2$	ϵ_{12}	n_{12}^2	
1108	2.3488	0.88393		1044	2.4400	0.68558	
2252	2.2517	0.88449		1797	2.4427	0.68615	
3188	2.3541	0.88496		2264	2.4445	0.68641	
4563	2.3583	0.88567		3073	2.4471	0.68705	
5229	2.3600	0.88598		3926	2.4500	0.68759	
6506	2.3633	0.88665		4803	2.4528	0.68822	
$\epsilon_{12} = 2.3457 + 2.714w_2$;		$v_{12} = 0.88337 + 0.5016w_2$;		$\epsilon_{12} = 2.4362 + 3.543w_2$;		$v_{12} = 0.68487 + 0.6968w_2$;	
${}_2P_\infty = 60.01$ c.c.				${}_2P_\infty = 60.57$ c.c.			
$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2	$10^6 w_2$	ϵ_{12}	v_{12}	n_{12}^2
<i>Diallyl sulphide in benzene</i>				<i>Diallyl sulphide in carbon tetrachloride</i>			
1221	2.2742	1.14444	2.24257	708	2.2292	0.63073	2.12504
2699	2.2767	1.14445	2.24251	1507	2.2315	0.63110	2.12504
3950	2.2787	1.14444	2.24247	2287	2.2340	0.63148	2.12507
5766	2.2814	1.14444	2.24239	3053	2.2366	0.63187	2.12516
6996	2.2834	1.14442	2.24230	3864	2.2390	0.63228	2.12533
7905	2.2850	1.14442	2.24227	4729	2.2421	0.63272	2.12541
9580	2.2875	1.14442	2.24218	5486	2.2447	0.63309	2.12549
$\epsilon_{12} = 2.2722 + 1.614w_2$;		$v_{12} = 1.14445 - 0.0032w_2$;		$\epsilon_{12} = 2.2267 + 3.245w_2$;		$v_{12} = 0.63037 + 0.4937w_2$;	
$n_{12}^2 = 2.24264 - 0.047w_2$;		${}_2P_\infty = 73.47$ c.c.;		$n_{12}^2 = 2.12480 + 0.136w_2$;		${}_2P_\infty = 76.49$ c.c.;	
$R_D = 37.16$ c.c.;		$\mu = 1.33D$.		$R_D = 36.73$ c.c.;		$\mu = 1.39D$.	
<i>Methyl sulphide in benzene</i>				<i>Methyl sulphide in carbon tetrachloride</i>			
1766	2.2788	1.14455	2.24251	799	2.2330	0.63078	2.12299
3639	2.2855	1.14461	2.24215	1717	2.2399	0.63127	2.12299
5561	2.2918	1.14472	2.24180	3566	2.2531	0.63219	2.12299
7689	2.2992	1.14479	2.24137	4635	2.2604	0.63280	2.12297
8497	2.3026	1.14483	2.24121	5338	2.2658	0.63314	2.12297
8723	2.3031	1.14483	2.24113	6451	2.2741	0.63372	2.12297
10,672	2.3104	1.14495	2.24086	7959	2.2851	0.63451	2.12302
$\epsilon_{12} = 2.2725 + 3.521w_2$;		$v_{12} = 1.14445 + 0.0458w_2$;		$\epsilon_{12} = 2.2272 + 7.254w_2$;		$v_{12} = 0.63036 + 0.5216w_2$;	
$n_{12}^2 = 2.24282 - 0.187w_2$;		${}_2P_\infty = 63.17$ c.c.;		$n_{12}^2 = 2.12299 + 0.000w_2$;		${}_2P_\infty = 68.48$ c.c.;	
$R_D = 19.45$ c.c.;		$\mu = 1.46D$ (1.40D ^a).		$R_D = 19.49$ c.c.;		$\mu = 1.55D$.	
<i>Triphenylphosphine in benzene</i>				<i>Triphenylphosphine in carbon tetrachloride</i>			
843	2.2730	1.14427	2.24364	415	2.2277	0.63046	2.12495
1253	2.2739	1.14412	2.24400	1171	2.2299	0.63066	2.12556
2453	2.2752	1.14379	2.24433	2081	2.2330	0.63088	2.12643
3964	2.2772	1.14340	2.24499	2784	2.2342	0.63105	2.12710
6502	2.2808	1.14266	2.24583	4346	2.2385	0.63142	2.12848
11,623	2.2873	1.14135	2.24790	4529	2.2390	0.63148	2.12868
13,600	2.2902	1.14084	2.24871	6251	2.2438	0.63189	2.13014
$\epsilon_{12} = 2.2721 + 1.315w_2$;		$v_{12} = 1.14445 - 0.2664w_2$;		$\epsilon_{12} = 2.2267 + 2.744w_2$;		$v_{12} = 0.63038 + 0.2401w_2$;	
$n_{12}^2 = 2.24345 + 0.379w_2$;		${}_2P_\infty = 133.44$ c.c.;		$n_{12}^2 = 2.12460 + 0.885w_2$;		${}_2P_\infty = 142.44$ c.c.;	
$R_D = 86.43$ c.c.;		$\mu = 1.52D$ (1.45, 1.39D ^a).		$R_D = 88.05$ c.c.;		$\mu = 1.63D$.	

^a Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

* For these three-component mixtures w_2 is the weight fraction of diethyl ether and each polarisation measurement was carried out by making up six solutions of diethyl ether (weight fraction range 0.001—0.01) in a solvent mixture composed of a known concentration of halogenated hydrocarbon in benzene.

and the purification of benzene, carbon tetrachloride,⁴ and carbon tetrabromide have been described.⁵ Diphenyl ether was distilled (b. p. 252—253°/755 mm.; lit. 252°) and partially frozen twice to give large crystals (m. p. 28·5°; lit. 28°).

Dibutyl and diethyl ethers were shaken with dilute sulphuric acid, sodium hydroxide solution, and water, dried (K_2CO_3), and fractionated from sodium; b. p.s were 139·5°/750 mm. (lit. 142·0°/760 mm.) and 34·5° (lit. 34·5°/76 mm.), respectively.

Dimethyl and diallyl sulphides were dried (K_2CO_3) and fractionated; b. p.s were 37·5° (lit. 37·5°) and 141° (lit. 140°), respectively.

Triphenylphosphine was recrystallised from ethanol and dried under vacuum; it had m. p. 79—80° (lit. 79·5°).

Results.—These are given in Table 2.

DISCUSSION

Oxygen Compounds.—Table 3 shows the dipole moments and $\Delta\mu$ values for diphenyl, dibutyl, and diethyl ethers in benzene and carbon tetrachloride solutions. With the exception of diphenyl ether the relative $\Delta\mu$ values can best be explained by a weak interaction between the ethers and carbon tetrachloride.

TABLE 3.

Dipole moments and $\Delta\mu$ values for ethers.

Ether	μ_B (D)	μ_{CT} (D)	$\Delta\mu$ (D)
Diphenyl.....	1·15	1·14	—0·01
Dibutyl	1·26	1·31	0·05
Diethyl	1·27	1·38	0·11

In an interaction of this sort, the ether will act as the electron donor. But diphenyl ether is unlikely to be capable of interacting in this way. The bulky phenyl groups considerably reduce the possibility of close approach between the oxygen atom and carbon tetrachloride molecules, and, in addition, the electron density of the oxygen lone-pair electrons will be reduced by mesomerism with the π -electron systems of the rings. The expectation of negligible interaction is justified by the very low $\Delta\mu$ value.

There is no reduction in electron density at the oxygen atom by the mesomeric effect in alkyl ethers. The butyl groups of dibutyl ether, however, will still considerably hinder the approach of interacting molecules. In diethyl ether the hindrance is much reduced. The $\Delta\mu$ values, which suggest increasing ability to interact in the order dibutyl < diethyl ether, are consistent with the idea of interaction.

Earp and Glasstone,⁶ studying the molecular polarisation of mixtures of ethers and polyhalogenated hydrocarbons, suggested that the differences between calculated and measured values were due to compound formation. The calculated equilibrium constants (K) for the association of the components for these complexes showed a marked drift with change of concentration if any ratio other than 1 : 1 was assumed for their compositions. Although the actual values of K perhaps ought to be treated with caution, their relative values are very interesting. Thus, the bonding between ethers and chloroform or pentachloroethane (hydrogen-bonding) appeared to be much stronger than with carbon tetrachloride, although interaction was still discernible in this case.

The order dibutyl > diethyl ether obtained by Earp and Glasstone for chloroform is opposite to that obtained by us for carbon tetrachloride. This is not necessarily inconsistent since the hydrogen bonding effect of chloroform, whilst still depending on the electron density at the oxygen atom, is stronger and is less likely to be influenced by steric hindrance.

These workers also showed that carbon tetrabromide interacts very strongly with ethers. This result is similar to that found by us for amines.⁵ The apparent total polarisation of pyridine in mixtures of benzene and carbon tetrabromide rises very rapidly at

⁶ Earp and Glasstone, *J.*, 1935, 1709, 1720.

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low concentrations of carbon tetrabromide and is non-linear, suggesting that the bonding is quite strong, *i.e.*, a large proportion of the pyridine is complexed.

Figs. 1 and 2 show how the apparent total molar polarisation at infinite dilution of pyridine and diethyl ether (data taken from Table 2), respectively, changes in mixtures of benzene with carbon tetrabromide and carbon tetrachloride. The similarity is at once evident.

Earp and Glasstone⁶ also showed that acetone can interact with polyhalogenated hydrocarbons, and it is interesting to record here some values for the dipole moments of

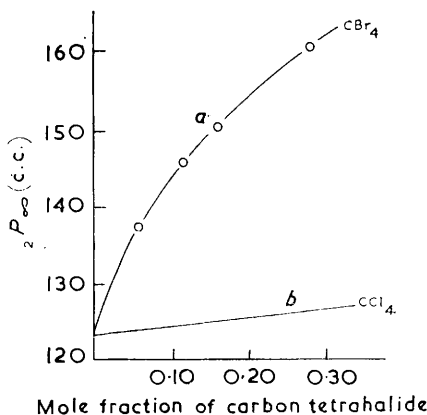


FIG. 1. Dependence of ${}_2P_\infty$ of pyridine on the mole fraction of (a) CBr_4 and (b) CCl_4 in mixtures of pyridine + carbon tetrahalide + benzene.

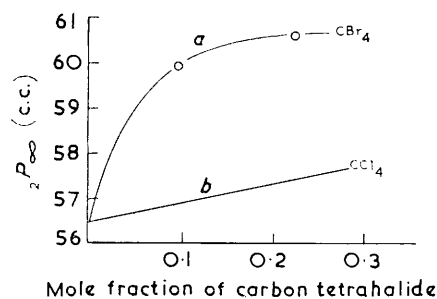


FIG. 2. Dependence of ${}_2P_\infty$ of diethyl ether on the mole fraction of (a) CBr_4 and (b) CCl_4 in mixtures of diethyl ether + carbon tetrahalide + benzene.

esters in benzene and carbon tetrachloride. The $\Delta\mu$ values suggest that interaction may occur between esters and carbon tetrachloride.

TABLE 4.

Dipole moments and $\Delta\mu$ values of esters in benzene and carbon tetrachloride.*

	μ_B (D)	μ_{CT} (D)	$\Delta\mu$ (D)
Methyl propionate	1.69	1.74	0.05
Ethyl acetate	1.81	1.87	0.06
Ethyl benzoate	1.88	1.99	0.11
Propyl acetate	1.78	1.91	0.13

* Values taken from Wesson's "Tables of Electric Dipole Moments."

In an oxygen compound where there is very little steric hindrance and high electron density at the oxygen atom, the interaction is likely to be most pronounced, resulting in a considerable increase in apparent total polarisation. The enormous increase in apparent total polarisation of 4-methylpyridine 1-oxide (91.8 c.c.), three times the R_D values for the compound in benzene, fits in very well with the idea of this type of interaction.⁴

TABLE 5.

Dipole moments and $\Delta\mu$ values of sulphides in benzene and carbon tetrachloride.

	μ_B (D)	μ_{CT} (D)	$\Delta\mu$ (D)
Diallyl sulphide	1.33	1.39	0.06
Dimethyl sulphide	1.46	1.55	0.09

Sulphur Compounds.—The data are recorded in Table 5. The $\Delta\mu$ values again suggest that interaction occurs and the higher value for dimethyl sulphide is consistent with its lower steric hindrance compared with diallyl sulphide. However, steric hindrance in

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both these compounds is relatively small, so that the low $\Delta\mu$ values indicate that interaction is weaker than with ethers or amines.

Phosphorus Compounds.—In view of what has been said about steric hindrance in diphenyl ether, a value of $\Delta\mu = 0.11D$ for triphenylphosphine seems, at first sight, to be rather high. However, the alkylphosphines—unlike the alkyl ethers—react rapidly with carbon tetrachloride to produce what has been described as a quaternary phosphonium salt.⁷ The interaction in these is, therefore, extremely strong in comparison with those of the alkyl ethers, and it is not surprising that triphenylphosphine—unlike diphenyl ether—also exhibits a tendency to interact.

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⁷ Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1508.
