

1092. *Molecular Polarisability. The Conformations of Certain Diphenyl- and Triphenyl-methanes as Solutes in Non-polar Media*

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Dipole moments and molar Kerr constants are reported for triphenylmethane as a solute in carbon tetrachloride (*ca.* 0 D and 13.7×10^{-12}), in cyclohexane (*ca.* 0 D and 18.2×10^{-12}), and in benzene (*ca.* 0 D and 12.5×10^{-12}), and for triphenylchloromethane (1.91 D and -142×10^{-12}), diphenylmethane (*ca.* 0.2 D and 14.0×10^{-12}), diphenylchloromethane (1.82 D and -49.2×10^{-12}), diphenylbromomethane (1.86 D and -18.7×10^{-12}), and diphenyldichloromethane (2.28 D and -33.0×10^{-12}) as solutes in carbon tetrachloride. The data are analysed to provide information on the preferred molecular conformations. It is shown that there is no solute-solvent association in triphenylmethane-benzene mixtures.

THIS work is concerned with the experimental estimation of the dipole moments and the electric birefringences of a number of diphenyl- and triphenyl-methanes examined as solutes at high dilution in non-polar media, and with the analysis of these data to yield information on the preferred molecular conformations. Observations and results are summarised under usual ^{1,2} headings in Tables 1 and 2.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were commercial samples which were purified immediately before use to give: triphenylmethane, m. p. 94°; triphenylchloromethane, m. p. 112°; diphenylmethane, b. p. 120°/*ca.* 10 mm.; diphenylchloromethane, b. p. 159°/*ca.* 12 mm.; diphenylbromomethane, m. p. 45°; diphenyldichloromethane, b. p. 172°/*ca.* 16 mm. The experimental techniques, symbols used, and methods of calculation have been described before.^{1,2} The Kerr constants were measured photometrically as in ref. 3. Precautions were taken to minimise the access of atmospheric moisture during the measurements but, despite this, difficulty was experienced in maintaining a constant high voltage across the electrodes of the Kerr cell with some solutions of the halogeno-derivatives. This is reflected in a greater than normal scatter of points in the plot of B_{12} against solute concentration. In the case of triphenylbromomethane satisfactory results could not be obtained.

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

	ϵ_1	d_1	$(n_1)_D$	$10^7 B_1$	$10^{12} K_1$
Carbon tetrachloride.....	2.2270	1.58454	1.4575	0.070	0.00749
Cyclohexane	2.0199	0.77389	1.4235	0.059	0.0147
Benzene	2.2725	0.87378	1.4973	0.410	0.0756

The nuclear magnetic resonance spectra recorded for this work were taken on a Varian A-60 spectrometer operating at 60 Mc./sec.

Previous Measurements.—Dipole moment determinations already recorded in the literature are listed in McClellan's Tables.⁴ Diphenylbromomethane alone has not previously been measured, and the other solutes, triphenylmethane excepted, have not been examined before in carbon tetrachloride solution. An earlier estimate⁵ of the molar Kerr constant of triphenylmethane in carbon tetrachloride ($+8.3 \times 10^{-12}$) is lower than that now found (photometrically) in Table 2.

¹ R. J. W. Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953.

² C. G. Le Fèvre and R. J. W. Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (b) Ch. XXXVI in "Physical Methods of Organic Chemistry," ed. A. Weissberger, Interscience, New York and London, 3rd edn., vol. 1, p. 2459.

³ R. J. W. Le Fèvre and G. L. D. Ritchie, *J.*, 1963, 4933.

⁴ A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco and London, 1963.

⁵ M. J. Aroney and R. J. W. Le Fèvre, *J.*, 1960, 3600.

TABLE I

Incremental Kerr effects, refractive indices, dielectric constants, and densities for solutions at 25°

<i>Triphenylmethane in carbon tetrachloride</i>							
$10^5 w_2$		3175	4352	5094		6089	
$10^{11} \Delta B$		150	198	242		265	
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0.457$.							
<i>Triphenylmethane in cyclohexane</i>							
$10^5 w_2$	2350	2394	3295	3311	4367	4526	
$10^{11} \Delta B$	54	54	—	102	—	128	
$10^4 \Delta n$	28	—	—	39	—	52	
ϵ^{25}	2.0286	2.0286	2.0319	2.0324	2.0361	2.0361	
d_4^{25}	0.77820	0.77831	—	0.77988	—	0.78196	
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0.269$; $\Sigma \Delta n / \Sigma w_2 = 0.117$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.367$; $\Sigma \Delta d / \Sigma w_2 = 0.181$.							
<i>Triphenylmethane in benzene</i>							
$10^5 w_2$	1766	2359	2824	$10^5 w_2$	2067	2089	2445
$10^4 \Delta n$	14	18	22	ϵ^{25}	2.2779	2.2779	2.2784
d_4^{25}	0.87613	0.87694	0.87756	whence $\Sigma \Delta \epsilon / \Sigma w_2 = 0.252$; $\Delta B = 0$ for solutions up to concn. $w_2 = 0.02600$.			
whence $\Sigma \Delta n / \Sigma w_2 = 0.078$; $\Sigma \Delta d / \Sigma w_2 = 0.134$.							
<i>Triphenylchloromethane in carbon tetrachloride</i>							
$10^5 w_2$	1151	1482	1785	2088	2950		
$-10^{11} \Delta B$	75	63	83	103	150		
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -5.01$.							
$10^5 w_2$	485	963	1557	1853	2520	3180	
$10^4 \Delta n$	12	22	40	47	62	79	
ϵ^{25}	2.2423	2.2589	2.2783	2.2891	2.3104	2.3328	
d_4^{25}	1.58196	1.57953	1.57668	1.57489	1.57162	1.56808	
whence $\Sigma \Delta n / \Sigma w_2 = 0.248$; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.31$; $\Sigma \Delta d / \Sigma w_2 = -0.516$.							
<i>Diphenylmethane in carbon tetrachloride</i>							
$10^5 w_2$	1766	3223	4424	5181	5989	7592	
$10^{11} \Delta B$	124	218	313	368	427	512	
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0.696$.							
$10^5 w_2$	1257	2107	2749	3782	5128	6574	
$10^4 \Delta n$	—	41	53	73	100	129	
ϵ^{25}	2.2354	2.2405	2.2435	2.2489	2.2544	2.2620	
d_4^{25}	1.57354	1.56626	1.56071	1.55221	1.54072	1.52863	
whence $\Sigma \Delta n / \Sigma w_2 = 0.195$; $\Delta \epsilon = 0.664 w_2 - 2.09 w_2^2$; $\Sigma \Delta d / \Sigma w_2 = -0.857$.							
<i>Diphenylchloromethane in carbon tetrachloride</i>							
$10^5 w_2$	578	1087	1526	2046	2636	3158	
$-10^{11} \Delta B$	114	225	323	476	606	720	
$10^4 \Delta n$	—	—	30	40	51	61	
ϵ^{25}	2.2487	2.2683	2.2837	2.3042	2.3272	2.3459	
d_4^{25}	1.58124	1.57823	1.57565	1.57275	1.56923	1.56627	
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -2.23$; $\Sigma \Delta n / \Sigma w_2 = 0.194$; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.77$; $\Sigma \Delta d / \Sigma w_2 = -0.579$.							
<i>Diphenylbromomethane in carbon tetrachloride</i>							
$10^5 w_2$	456	961	1370	2150	2337	2837	3563
$-10^{11} \Delta B$	—	58	107	133	157	—	181
$10^4 \Delta n$	—	—	—	40	44	—	57
ϵ^{25}	2.2421	2.2592	2.2724	2.2974	2.3041	2.3202	—
d_4^{25}	1.58340	1.58227	1.58105	—	—	1.57804	—
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0.664$; $\Sigma \Delta n / \Sigma w_2 = 0.191$; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.30$; $\Sigma \Delta d / \Sigma w_2 = -0.238$.							
<i>Diphenyldichloromethane in carbon tetrachloride</i>							
$10^5 w_2$	1067	1587	2556	3378	4224	5566	
$-10^{11} \Delta B$	137	176	314	427	517	674	
$10^4 \Delta n$	20	30	50	65	80	107	
ϵ^{25}	2.2781	2.3022	2.3463	2.3860	2.4253	2.4904	
d_4^{25}	1.58028	1.57836	1.57464	1.57148	1.56816	1.56293	
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -1.22$; $\Sigma \Delta n / \Sigma w_2 = 0.192$; $\Sigma \Delta \epsilon / \Sigma w_2 = 4.71$; $\Sigma \Delta d / \Sigma w_2 = -0.388$.							

TABLE 2

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°)

Solute	Solvent	$\alpha\epsilon_1$	β	γ	δ	∞P_2 (c.c.)	R_D (c.c.)	μ^* (D)	$10^{12}\infty(mK_2)$
Triphenylmethane	CCl ₄	0.746 †	-0.439 †	0.175 †	6.53	83.7 †	80.6 †	0	13.7
"	C ₆ H ₁₂	0.367	0.234	0.082	4.56	82.9	81.1	0	18.2
"	C ₆ H ₆	0.252	0.153	0.052	0	82.1	80.2	0	12.5
Triphenylchloro- methane	CCl ₄	3.31	-0.326	0.170	-71.6	165.5	86.1	1.91	-142
Diphenylmethane	CCl ₄	0.664	-0.541	0.134	9.94	59.3	55.3	0.2	14.0
Diphenylchloro- methane	CCl ₄	3.77	-0.365	0.133	-31.9	131.7	60.4	1.82	-49.2
Diphenylbromo- methane	CCl ₄	3.30	-0.150	0.131	-9.49	138.5	64.2	1.86	-18.7
Diphenyldichloro- methane	CCl ₄	4.71	-0.245	0.132	-17.4	174.8	65.6	2.28	-33.0

* Calculated assuming ${}_D P = 1.05 R_D$. † From ref. 5. ‡ Calculated from the densities and refractive indexes listed in ref. 5.

DISCUSSION

Triphenylmethane.—For an axially symmetric configuration of triphenylmethane, the molecular polarisability ellipsoid is specified by the semi-axes $b_1 \neq b_2 = b_3$, where b_1 is located along the symmetry axis and b_2 and b_3 lie in a plane normal to this direction. It follows also that $\mu_1 = \mu$ (observed), $\mu_2 = \mu_3 = 0$, so that the molar Kerr constant can be expressed in terms of the optical polarisabilities through the relationships: ²

$${}_m K = 2\pi N(\theta_1 + \theta_2)/9 \quad (1)$$

$$\theta_1 = 2{}_D P(b_1 - b_2)^2/45kT{}_E P$$

$$\theta_2 = 2\mu(\text{obs.})^2(b_1 - b_2)/45k^2T^2$$

where θ_1 and θ_2 are the anisotropy and dipole terms, respectively, ${}_D P$ the distortion polarisation, and ${}_E P$ the electronic polarisation. The molar Kerr constant can thus be computed for any conformational model of triphenylmethane from a knowledge of $\mu(\text{obs.})$, the ratio ${}_D P/{}_E P$, and the polarisability tensor specifications (b_i) for that model. The electron polarisation is calculable as 78.0 c.c. ($= R_\infty$) from the refractivity data of ref. 6. However, the distortion polarisation, and hence the dipole moment, cannot be estimated with certainty. If, for example, ${}_D P = 1.05 R_D$, then μ in each case is zero (see Table 2). In the subsequent calculations we assume that $\mu(\text{triphenylmethane}) = 0$ D, or, alternatively, 0.3 D, and the ratio ${}_D P/{}_E P$ is, respectively, 1.1 or 1.05 (this is sufficiently precise for the present purpose). The molecular polarisabilities* were computed by the procedure outlined on pp. 2483—2486 of ref. 2b, using the following bond and group parameters: ^{2,5} $b_L(\text{C}_6\text{H}_5) = b_T(\text{C}_6\text{H}_5) = 10.56$; $b_V(\text{C}_6\text{H}_5) = 6.72$; $b_L(\text{C-C}) = 0.99$; $b_T(\text{C-C}) = b_V(\text{C-C}) = 0.27$; $b_L(\text{C-H}) = b_T(\text{C-H}) = b_V(\text{C-H}) = 0.64$. The individual conformations of triphenylmethane are defined geometrically by α ($\angle \text{C}_{Ar}-\text{C}-\text{C}_{Ar}$ which we assume to be tetrahedral) and by angles of rotation ϕ of the phenyl groups from a structure (having $\phi = 0^\circ$) in which the planes of the benzene rings intersect along the three-fold symmetry axis (see Figure 1). Thus, we can write:

$$b_1(\text{Ph}_3\text{CH}) = 3\{[b_L(\text{C}_6\text{H}_5) + b_L(\text{C-C}) + \Delta b/3] \cos^2(180 - \alpha) + [b_T(\text{C}_6\text{H}_5) \cos^2 \phi + b_V(\text{C}_6\text{H}_5) \sin^2 \phi + b_T(\text{C-C})] \sin^2(180 - \alpha)\} + b_L(\text{C-H}) \quad (2)$$

$$b_2(\text{Ph}_3\text{CH}) = b_3(\text{Ph}_3\text{CH}) = \{3[\Sigma b(\text{C}_6\text{H}_5) + \Sigma b(\text{C-C})] + \Sigma b(\text{C-H}) + \Delta b - b_1(\text{Ph}_3\text{CH})\}/2 \quad (3)$$

* Polarisability semi-axes of bonds or groups, b_L , b_T , or b_V , or of molecules, b_1 , b_2 , or b_3 , are quoted throughout in \AA^3 (10^{-24} c.c.) units.

⁶ G. G. Kikina, Ya. K. Syrkin, and E. A. Shott-L'vova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1954, 563.

Kikina *et al.*⁶ showed that an apparent exaltation of molecular refraction of 1.97 c.c. arises from inter-ring conjugation in triphenylmethane. From this the exaltation in the total polarisability (Δb) is calculable as 2.34 \AA^3 . We assume, in equation (2), that an additional polarisability component, $\Delta b/3$, is directed along each $C_{Ar}-C$ axis. Theoretical values of the principal polarisabilities and of the molar Kerr constants for the various conformations of triphenylmethane are shown in Table 3. The plot of ${}_mK(\text{calc.})$ against ϕ is shown in Figure 2. The experimental molar Kerr constants of Table 2 correspond to the following values of ϕ : $54^\circ \pm 3^\circ$ (in carbon tetrachloride); $57^\circ \pm 3^\circ$ (in cyclohexane);

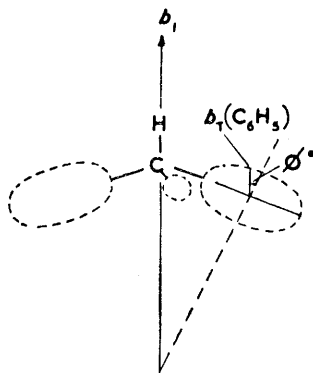


FIGURE 1

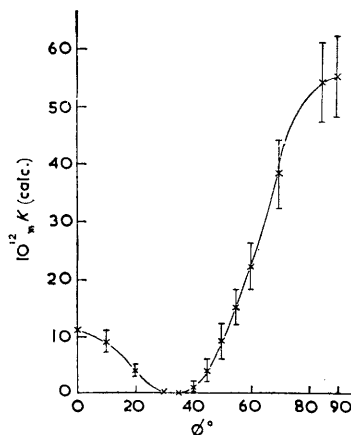


FIGURE 2

$53^\circ \pm 3^\circ$ (in benzene). We have assumed that the triphenylmethane solute molecules are in an "inert" solvent environment. This is reasonably the case with cyclohexane and carbon tetrachloride, but it has been claimed from light-scattering evidence⁷ and from cryoscopic measurements⁸ that triphenylmethane associates with benzene. This

TABLE 3

Calculated polarisability semi-axes and molar Kerr constants for conformations of triphenylmethane

ϕ	b_1	$(b_2 = b_3)$	θ_1	${}_mK^*$	$(\theta_1 + \theta_2)^\dagger$	${}_mK^\dagger$	${}_mK(\text{mean})$
0	33.63	29.37	2.15×10^{-35}	9.1×10^{-12}	3.06×10^{-35}	12.9×10^{-12}	$(11 \pm 2) \times 10^{-12}$
10	33.30	29.54	1.68	7.1	2.49	10.5	9 ± 2
20	32.42	29.98	0.71	3.0	1.26	5.3	4 ± 1
30	31.06	30.66	0.02	0.1	0.11	0.5	0.3 ± 0.2
35	30.25	31.06	0.08	0.4	-0.11	-0.5	0.0 ± 0.5
40	29.39	31.49	0.52	2.2	0.00	0.0	1 ± 1
45	28.50	31.93	1.40	5.9	0.52	2.2	4 ± 2
50	27.61	32.38	2.70	11.4	1.45	6.1	9 ± 3
55	26.75	32.81	4.36	18.3	2.74	12.4	15 ± 3
60	25.94	33.22	6.30	26.5	4.29	18.0	22 ± 4
70	24.58	33.90	10.32	43.4	7.65	32.2	38 ± 6
85	23.46	34.46	14.38	60.5	11.13	46.8	54 ± 7
90	23.39	34.49	14.64	61.6	11.36	47.8	55 ± 7

* Calculated on the basis that $\mu(\text{Ph}_3\text{CH}) = 0$ and hence the θ_2 term is also zero. † Calculated assuming that $\mu(\text{Ph}_3\text{CH}) = 0.3 \text{ D}$.

type of complex formation, by π -hydrogen bonding, is well known in the case of chloroform.⁹ The n.m.r. spectra of triphenylmethane in benzene, carbon tetrachloride, and cyclohexane show that the central proton signal (a singlet at $\tau = 4.50$ — 4.55 , using

⁷ P. Bothorel, *Compt. rend.*, 1958, **246**, 3452.

⁸ V. M. Kravechenko, *Doklady Akad. Nauk S.S.S.R.*, 1951, **76**, 847.

⁹ W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

tetramethylsilane as internal reference) is effectively invariant, and this is strong evidence against benzene-triphenylmethane association. It had been concluded earlier,¹⁰ from infrared spectral evidence, that triphenylmethane "gave no indication of hydrogen bonding to strong proton acceptors."

Triphenylchloromethane.—Molar Kerr constants computed for conformations of triphenylchloromethane having ring rotations ϕ equal to 0, 53, or 90° are listed in Table 4. The C-Cl bond polarisability semi-axes were taken² as $b_L(\text{C-Cl}) = 3.18$, $b_T(\text{C-Cl}) = b_V(\text{C-Cl}) = 2.20$. The experimental value, ${}_{\infty}(\text{m}K_2) = -142 \times 10^{-12}$, is in good agreement with that predicted for $\phi = 53^\circ$. It appears that the substitution of the central proton of triphenylmethane by chlorine does not result in any appreciable change in the orientations of the phenyl groups.

TABLE 4

Calculated polarisability semi-axes and molar Kerr constants for conformations of triphenylchloromethane

ϕ	b_1	$(b_2 = b_3)$	$10^{12} \text{m}K$
0°	35.91	29.89	260
53	29.38	33.15	-145
90	25.68	35.01	-354

Diphenylmethane.—Conformations of this molecule are described with reference to a model [structure (A)] in which both phenyl groups are coplanar with $\text{C}_{\text{Ar}}\text{-C-C}_{\text{Ar}}$, *i.e.*, $\psi = \psi' = 0^\circ$. Structure (B) has each phenyl group perpendicular to the $\text{C}_{\text{Ar}}\text{-C-C}_{\text{Ar}}$ plane, *i.e.*, $\psi = \psi' = 90^\circ$; (C) is generated from (A) by ring rotations of 41° in the same sense, *i.e.*, $\psi = \psi' = +41^\circ$; (D) has one phenyl group in the $\text{C}_{\text{Ar}}\text{-C-C}_{\text{Ar}}$ plane and the other other perpendicular to this plane, *i.e.*, $\psi = 0^\circ$, $\psi' = 90^\circ$. The calculated values, given in Table 5, were derived on the assumption that the central carbon atom is tetrahedral, that there is negligible polarisability exaltation [$R_D(\text{obs.}) = 55.3 \text{ c.c.}$; $R_D(\text{calc.}) = 55.5 \text{ c.c.}$],¹¹ and that there is a permanent electric moment directed along the X-direction in Figure 3 (for diphenylmethane $R_1 = R_2 = \text{H}$) and equal in magnitude to 0 D or, alternatively, to 0.3 D.

The observed molar Kerr constant (14.0×10^{-12}) agrees with that calculated for structure (C) in which $\psi = \psi' = 41^\circ$. Alternative forms involving equal ring rotations

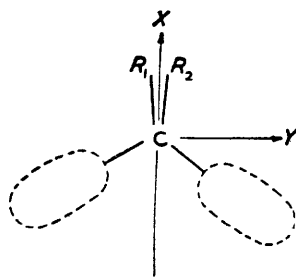


FIGURE 3

TABLE 5

Calculated polarisability semi-axes and molar Kerr constants for conformations of diphenylmethane

Structure	$b_1(\text{calc.})$	Direction cosines with			$\text{m}K^*$	$\text{m}K^\dagger$	$\text{m}K(\text{mean})$
		X	Y	Z			
$\psi = \psi' = 0$ (A)	$b_1 = 23.42$	+1	0	0	35.4	37.6	36.5 ± 1.1
	$b_2 = 23.90$	0	+1	0			
	$b_3 = 15.26$	0	0	+1			
$\psi = \psi' = 90^\circ$ (B)	$b_1 = 18.30$	+1	0	0	8.3	4.1	6.2 ± 2.1
	$b_2 = 21.34$	0	+1	0			
	$b_3 = 22.94$	0	0	+1			
$\psi = \psi' = 41^\circ$ (C)	$b_1 = 21.22$	+1	0	0	14.1	13.9 _s	14.0 ± 0.1
	$b_2 = 23.73$	0	+0.920	+0.391			
	$b_3 = 17.64$	0	-0.391	+0.920			
$\psi = 0^\circ, \psi' = 90^\circ$ (D)	$b_1 = 19.73$	+0.846	+0.532	0	10.4	10.0	10.2 ± 0.2
	$b_2 = 23.75$	-0.532	+0.846	0			
	$b_3 = 19.10$	0	0	+1			

* Calculated assuming $\mu(\text{Ph}_2\text{CH}_2) = 0$. † Calculated assuming $\mu(\text{Ph}_2\text{CH}_2) = 0.3 \text{ D}$.

¹⁰ A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.

¹¹ A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

from (A) but of opposite senses, *i.e.*, $\psi = -\psi'$, are sterically improbable. Conformation (D), which is analogous to that proposed¹² for diphenyl ether, also appears unlikely on the basis of these calculations. If the angle $C_{Ar}-C-C_{Ar}$ is increased to 114° , the calculated molar Kerr constant for (D) is even lower $[(9.5 \pm 0.4) \times 10^{-12}]$.

Diphenylchloromethane, Diphenylbromomethane, and Diphenyldichloromethane.—Polarisability semi-axes and molar Kerr constants have been computed for conformations analogous to (A) and (C) of diphenylmethane, and for intermediate structures having $\psi = \psi'$. In the calculations we assume a tetrahedral central carbon atom, negligible exaltation, $b_L(C-Br) = 4.65$; $b_T(C-Br) = b_V(C-Br) = 3.08$,² and that the electric moment in diphenyldichloromethane acts along the *X*-axis in Figure 3 ($R_1 = R_2 = Cl$) while in diphenylchloromethane and diphenylbromomethane it is directed along C-Cl and C-Br, respectively.

TABLE 6

Calculated polarisability semi-axes and molar Kerr constants for conformations of diphenylchloromethane, diphenylbromomethane, and diphenyldichloromethane

		Direction cosines with				
	$\psi = \psi'$	$b_i(\text{calc.})$	<i>X</i>	<i>Y</i>	<i>Z</i>	mK
Diphenylchloromethane	0	$b_1 = 25.33$	+0.998	0	+0.059	-90.6×10^{-12}
		$b_2 = 25.46$	0	+1	0	
		$b_3 = 17.44$	-0.059	0	+0.998	
"	33	$b_1 = 23.81$	+0.991	-0.120	+0.053	-49.5
		$b_2 = 25.44$	+0.096	+0.935	+0.341	
		$b_3 = 18.99$	-0.090	-0.333	+0.939	
"	90	$b_1 = 20.14$	+0.996	0	-0.092	75.0
		$b_2 = 22.90$	0	+1	0	
		$b_3 = 25.19$	+0.092	0	+0.996	
Diphenylbromomethane	0	$b_1 = 26.45$	+0.995	0	+0.096	-75.1
		$b_2 = 26.34$	0	+1	0	
		$b_3 = 18.67$	-0.096	0	+0.995	
"	38	$b_1 = 24.51$	+0.972	-0.220	+0.088	-17.4
		$b_2 = 26.40$	+0.162	+0.889	+0.428	
		$b_3 = 20.55$	-0.172	-0.402	+0.900	
"	90	$b_1 = 21.16$	+0.990	0	-0.140	102
		$b_2 = 23.78$	0	+1	0	
		$b_3 = 26.53$	+0.140	0	+0.990	
Diphenyldichloromethane	0	$b_1 = 27.19$	+1	0	0	239
		$b_2 = 27.02$	0	+1	0	
		$b_3 = 19.68$	0	0	+1	
"	50	$b_1 = 24.19$	+1	0	0	-30.2
		$b_2 = 27.13$	0	+0.803	+0.596	
		$b_3 = 22.57$	0	-0.596	+0.803	
"	90	$b_1 = 22.07$	+1	0	0	-210
		$b_2 = 24.46$	0	+1	0	
		$b_3 = 27.36$	0	0	+1	

From a comparison of the calculated molar Kerr constants of Table 6 with those derived from experiment (in Table 2) we conclude that the solute molecules in carbon tetrachloride have apparent conformations defined by $\psi = \psi' = ca. 33^\circ$ (diphenylchloromethane), *ca.* 38° (diphenylbromomethane), and *ca.* 50° (diphenyldichloromethane).

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¹² Y. Morino, cited by K. Higasi in "Dielectric Relaxation and Molecular Structure," Monograph Series of the Research Institute of Applied Electricity, No. 9, Hokkaido University, Sapporo, Japan, 1961.