Conformations of Some Phenyl-substituted Ethane Derivatives as Solutes

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The electric dipole moments of 1,2-diphenyltetrachloroethane and of three 2,3-di-(p-halogenophenyl)2,3-dimethylbutanes have been measured in carbon tetrachloride at temperatures from −20 to 45°. Molar Kerr constants and dipole moments in benzene are also reported for these compounds as well as the related molecules 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane, p-bromocumene, p-fluorocumene, and 2,3-dimethyl-2,3-diphenylbutane. Conformational analysis of the results shows that substitution of two phenyl groups for the hydrogen atoms in tetrachloroethane has little effect on the relative stabilities of the rotational isomers in solution. Substitution of p-halogenophenyl groups for the two Cl or Br atoms in 2,3-dihalogeno-2,3-dimethylbutane reduces (a) the ΔE (solution) value almost to zero, thereby altering the gauche : trans isomeric ratio; and (b) the dihedral angle θ from about 70 to 65°.

MONO-, DI- and POLY-SUBSTITUTED ethanes in which the substituent is an atom, alkyl group, or a simple polar group have been extensively studied in relation to the rotational isomerism existing in them.[1,2] However, little is known about the steric effect of the phenyl group on the configurations of such rotational isomers. This paper provides polarisation and electric birefringence data on some phenyl-substituted ethanes and their conformations are discussed in terms of considerations based on molecular polarity and polarisability. A few structurally related molecules furnishing additional information have been included.

EXPERIMENTAL

Solutes.—The preparations of 1,2-diphenyltetrachloroethane, 2,3-dimethyl-2,3-di-p-bromophenylbutane, 2,3-dimethyl-2,3-di-p-chlorophenylbutane, 2,3-dimethyl-2,3-di-p-fluorophenylbutane, and 2,3-dimethyl-2,3-diphenylbutane have been described.[3] 1,1,2,2-Tetrachloroethane, 1,1,2,2-tetrabromoethane, p-bromocumene, and p-fluorocumene were commercial samples which after fractional distillation had n_D^{20} 1·4940 (lit.,[4] 1·4940), 1·6378 (lit.,[5] 1·6380), 1·5362 (lit.,[5] 1·5363), and 1·4713 (lit.,[6] 1·4712) respectively. All were freshly purified before measurement.

The apparatus,[7-9] procedures, and methods of treating the polarisation and electric birefringence data[10] have been

described. The symbols and equations used with Tables 2 and 3, which contain the results are summarized in ref. 11. Measurements were carried out with benzene and carbon tetrachloride solution and over a range of temperatures with the latter. The physical constants for the solvents are in Table 1.

TABLE 1

Carbon tetrachloride

Temp.	−20° *	25°	45°
ε_1	2·3112	2·2270	2·1893
d_1	1·67372	1·58454	1·54518
$(n_1)_D$	—	1·4575	1·4462
$10^7 B_1$	—	0·083	—
$10^{14} s K_1$	—	0·888	…

Benzene at 25°

ε_1	d_1	$(n_1)_D$	$10^7 B_1$
2·2725	0·87378	1·4973	0·410

* Values at −20° and 45° were calculated from the relevant equations given by R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 1953, pp. 46, 53.

Previous Measurements.—The dipole moments of the aryl substituted ethanes and of the cumenes have not been reported before. The moments of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane compare favourably

[1] S. Mizushima, 'Structures of Molecules and Internal Rotation,' Academic Press, New York, 1954.
[2] N. Sheppard, in 'Advances in Spectroscopy,' vol. 1, ed. H. W. Thompson, Interscience Publishers, New York, 1959.
[3] H. H. Huang and P. K. K. Lim, *J. Chem. Soc.* (C), 1967, 2432.
[4] J. Timmermans, 'Physico-chemical Constants of Pure Organic Compounds,' Elsevier Publishing Co., Amsterdam, vol. 1, 1950; vol. 2, 1965.

[5] I. Heilbron, J. W. Cook, and H. M. Bunbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.
[6] Aldrich Chemical Company Inc., 1966, Catalogue 12.
[7] H. H. Huang and E. P. A. Sullivan *Austral. J. Chem.*, 1968, 1721.
[8] H. H. Huang and S. C. Ng, *J. Chem. Soc.* (B), 1968, 583.
[9] L. H. L. Chia, Ph.D. Thesis, University of Singapore, 1969.
[10] R. J. W. Le Fèvre, (a) Dipole Moments, 3rd edn., Methuen, London, 1953, ch. 2; (b) *Adv. Phys. Org. Chem.*, 1965, **3**, 1.
[11] R. J. W. Le Fèvre and A. Sundaram, *J. Chem. Soc.*, 1962, 1494.

TABLE 2

Incremental refractive indices, dielectric constants, and densities of carbon tetrachloride solutions containing weight fractions w_2 of solute at 45°

1,1,2,2-Tetrachloro-1,2-diphenylethane

$10^5 w_2$	528	1004	1547	1978	2575
$10^4 \Delta\varepsilon$	272	524	803	1017	1339
$-10^5 \Delta d$	62	138	218	254	347
$10^4 \Delta n^2$	29	58	87	113	148

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5.18$, $\Sigma\Delta d/\Sigma w_2 = -0.134$, $\Sigma\Delta n^2/\Sigma w_2 = 0.570$

2,3-Dimethyl-2,3-di-p-bromophenylbutane

$10^5 w_2$	514	1083	1319	1543	1881	2063	2532
$10^4 \Delta\varepsilon$	169	339	416	479	604	640	767
$-10^5 \Delta d$	—	74	102	142	—	174	234
$10^4 \Delta n^2$	—	52	61	—	87	107	133

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3.12$, $\Sigma\Delta d/\Sigma w_2 = -0.085$, $\Sigma\Delta n^2/\Sigma w_2 = 0.496$

2,3-Dimethyl-2,3-di-p-chlorophenylbutane

$10^5 w_2$	315	604	1162	1646
$10^4 \Delta\varepsilon$	124	243	470	660
$-10^5 \Delta d$	165	352	607	832
$10^4 \Delta n^2$	—	32	58	87

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4.02$, $\Sigma\Delta d/\Sigma w_2 = -0.525$, $\Sigma\Delta n^2/\Sigma w_2 = 0.519$

2,3-Dimethyl-2,3-di-p-fluorophenylbutane

$10^5 w_2$	489	938	1521	1971	2583
$10^4 \Delta\varepsilon$	193	354	589	746	974
$-10^5 \Delta d$	297	620	944	1194	1601
$10^4 \Delta n^2$	12	23	49	78	96

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3.81$, $\Sigma\Delta d/\Sigma w_2 = -0.621$, $\Sigma\Delta n^2/\Sigma w_2 = 0.344$

At 25°

1,1,2,2-Tetrachloro-1,2-diphenylethane

$10^5 w_2$	529	1078	1519	2016	2537
$10^4 \Delta\varepsilon$	291	588	843	1129	1431
$-10^5 \Delta d$	62	151	228	309	404
$10^4 \Delta n^2$	29	62	88	111	143

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5.58$, $\Sigma\Delta d/\Sigma w_2 = -0.150$, $\Sigma\Delta n^2/\Sigma w_2 = 0.564$

2,3-Dimethyl-2,3-di-p-bromophenylbutane

$10^5 w_2$	540	1147	1749	2227	2526
$10^4 \Delta\varepsilon$	188	401	609	785	885
$-10^5 \Delta d$	53	117	174	219	243
$10^4 \Delta n^2$	29	64	99	123	134

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3.50$, $\Sigma\Delta d/\Sigma w_2 = -0.098$, $\Sigma\Delta n^2/\Sigma w_2 = 0.548$

2,3-Dimethyl-2,3-di-p-chlorophenylbutane

$10^5 w_2$	423	899	1329	1812
$10^4 \Delta\varepsilon$	183	390	573	791
$-10^5 \Delta d$	216	458	668	934
$10^4 \Delta n^2$	—	47	73	99

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4.34$, $\Sigma\Delta d/\Sigma w_2 = -0.510$, $\Sigma\Delta n^2/\Sigma w_2 = 0.542$

2,3-Dimethyl-2,3-di-p-fluorophenylbutane

$10^5 w_2$	475	1033	1395	1931
$10^4 \Delta\varepsilon$	198	432	588	807
$-10^5 \Delta d$	321	681	936	1301
$10^4 \Delta n^2$	18	38	50	73

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4.19$, $\Sigma\Delta d/\Sigma w_2 = -0.670$, $\Sigma\Delta n^2/\Sigma w_2 = 0.370$

At -20°

2,3-Dimethyl-2,3-di-p-bromophenylbutane

$10^5 w_2$	307	356	468	531	665	731
$10^4 \Delta\varepsilon$	128	149	203	235	278	309
$-10^5 \Delta d$	50	—	86	105	135	138

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4.26$, $\Sigma\Delta d/\Sigma w_2 = -0.189$

TABLE 2 (Continued)

1,1,2,2-Tetrachloro-1,2-diphenylethane

$10^5 w_2$	386	414	565	625	719	809
$10^4 \Delta\varepsilon$	259	288	396	422	486	572
$-10^5 \Delta d$	92	98	125	149	190	206

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 6.89$, $\Sigma\Delta d/\Sigma w_2 = -0.245$

Incremental Kerr effects, refractive indices, dielectric constants, and densities of benzene solutions containing weight fractions w_2 of solute at 25°

1,1,2,2-Tetrachloro-1,2-diphenylethane

$10^5 w_2$	870	1801	2166	2803	3450
$10^4 \Delta\varepsilon$	295	574	682	895	1096
$10^5 \Delta d$	290	620	735	1010	1217
$10^4 \Delta n$	5	13	22	16	24
$10^4 \Delta n^2$	15	39	48	66	72
$10^{11} \Delta B$	791	1613	2526	1896	3133

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3.19$, $\Sigma\Delta d/\Sigma w_2 = 0.349$, $\Sigma\Delta n^2/\Sigma w_2 = 0.22$, $\Sigma\Delta n/\Sigma w_2 = 0.073$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 8.98$

2,3-Dimethyl-2,3-di-p-fluorophenylbutane

$10^5 w_2$	519	936	1312	1857	2238
$10^4 \Delta\varepsilon$	98	206	279	387	469
$10^5 \Delta d$	98	193	259	369	445
$10^4 \Delta n$	—	1	1	1	—
$10^{11} \Delta B$	—	475	611	867	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2.10$, $\Sigma\Delta d/\Sigma w_2 = 0.199$, $\Sigma\Delta n/\Sigma w_2 = 0.003$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 4.76$

2,3-Dimethyl-2,3-diphenylbutane

$10^5 w_2$	1109	2109	3045	4006	5036
$10^4 \Delta\varepsilon$	31	36	62	80	98
$10^5 \Delta d$	100	227	323	427	555
$10^4 \Delta n$	6	14	18	—	34
$10^4 \Delta n^2$	18	42	54	—	102
$10^{11} \Delta B$	40	70	110	—	170

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.20$, $\Sigma\Delta d/\Sigma w_2 = 0.107$, $\Sigma\Delta n/\Sigma w_2 = 0.064$, $\Sigma\Delta n^2/\Sigma w_2 = 0.191$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 0.34$

2,3-Dimethyl-2,3-di-p-bromophenylbutane

$10^5 w_2$	881	952	1688	2409	2871	3585
$10^4 \Delta\varepsilon$	175	—	330	460	569	692
$10^5 \Delta d$	291	—	609	882	994	1271
$10^4 \Delta n$	5	—	11	17	21	25
$10^4 \Delta n^2$	15	—	33	51	63	75
$10^{11} \Delta B$	—	671	1131	1674	2017	2492

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1.95$, $\Sigma\Delta d/\Sigma w_2 = 0.353$, $\Sigma\Delta n^2/\Sigma w_2 = 0.21$, $\Sigma\Delta n/\Sigma w_2 = 0.069$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 6.94$

2,3-Dimethyl-2,3-di-p-chlorophenylbutane

$10^5 w_2$	791	1216	1671	1911	2717	4353
$10^4 \Delta\varepsilon$	160	263	372	422	660	1063
$10^5 \Delta d$	195	284	395	457	641	1038
$10^4 \Delta n$	5	9	13	14	—	—
$10^4 \Delta n^2$	15	27	39	42	57	90
$10^{11} \Delta B$	634	924	1293	1482	—	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2.32$, $\Sigma\Delta d/\Sigma w_2 = 0.238$, $\Sigma\Delta n^2/\Sigma w_2 = 0.213$, $\Sigma\Delta n/\Sigma w_2 = 0.056$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 7.75$

p-Fluorocumene

$10^5 w_2$	1094	2241	3195	4311	5324
$10^4 \Delta\varepsilon$	248	475	708	961	1187
$10^5 \Delta d$	38	115	174	263	321
$-10^4 \Delta n$	15	24	36	45	54
$-10^4 \Delta n^2$	5	8	12	15	18
$10^{11} \Delta B$	573	1191	1783	2262	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2.21$, $\Sigma\Delta d/\Sigma w_2 = 0.056$, $\Sigma\Delta n^2/\Sigma w_2 = -0.108$, $\Sigma\Delta n/\Sigma w_2 = -0.036$, $\Sigma 10^7 \Delta B/\Sigma w_2 = 5.36$

TABLE 2 (*Continued*)

p-Bromocumene

$10^5 w_2$	1227	2306	3521	4956	5601
$10^4 \Delta\epsilon$	248	470	748	1057	1191
$10^5 \Delta d$	330	616	968	1366	1549
$10^4 \Delta n$	3	5	10	15	16
$10^4 \Delta n^2$	9	15	30	45	48
$10^{11} \Delta B$	1097	2107	3352	4731	5262

whence $\Sigma\Delta\epsilon/\Sigma w_2 = 2.11$, $\Sigma\Delta d/\Sigma w_2 = 0.274$,
$\Sigma\Delta n^2/\Sigma w_2 = 0.083$, $\Sigma\Delta n/\Sigma w_2 = 0.028$,
$\Sigma 10^7 \Delta B/\Sigma w_2 = 9.39$

1,1,2,2-Tetrachloroethane

$10^5 w_2$	1295	2219	3102	4174	5549
$10^4 \epsilon$	274	410	599	767	1073
$10^5 \Delta d$	510	862	1243	1647	2216
$10^4 \Delta n$	1	1	1	1	1
$-10^{11} \Delta B$	245	463	599	791	1056

whence $\Sigma\Delta\epsilon/\Sigma w_2 = 1.92$, $\Sigma\Delta d/\Sigma w_2 = 0.396$,
$\Sigma\Delta n/\Sigma w_2 = 0.003$, $\Sigma 10^7 \Delta B/\Sigma w_2 = -1.93$

1,1,2,2-Tetrabromoethane

$10^5 w_2$	1059	2067	3276	4407	5006
$10^4 \Delta\epsilon$	95	162	263	350	403
$10^5 \Delta d$	653	1319	2078	2801	3202
$10^4 \Delta n$	6	11	14	21	23
$10^4 \Delta n^2$	13	27	36	57	63
$-10^{11} \Delta B$	98	211	335	418	430

whence $\Sigma\Delta\epsilon/\Sigma w_2 = 0.80$, $\Sigma\Delta d/\Sigma w_2 = 0.636$,
$\Sigma\Delta n^2/\Sigma w_2 = 0.124$, $\Sigma\Delta n/\Sigma w_2 = 0.047$,
$\Sigma 10^7 \Delta B/\Sigma w_2 = -0.94$

with literature values,[12] though that of the latter compound has not been measured in benzene. No previous measurement of the molar Kerr constant of any of the above compounds can be found.

such molecules can be regarded as a mixture of staggered *gauche*- (I) and *trans*- (II) rotamers. Three physical
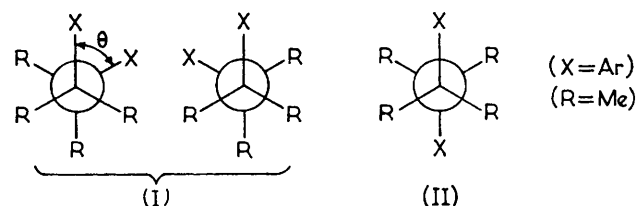
quantities associated with those molecules are of special interest: (*a*) the dihedral angle θ between the planes containing the central C–C bond and the halogen atoms. Any configuration of this type of molecule (without regard for the disposition of the phenyl ring) is defined by θ; (*b*) the *gauche* : *trans*-isomeric ratio; (*c*) the energy difference between the *gauche*- and *trans*-conformers. We shall consider these quantities in greater detail below.

The Dihedral Angle and gauche : trans-*Isomeric Ratio.* —If we set the origin of θ at the *cis*-form with C_{2v} symmetry, then the *trans*-conformation with C_{2h} symmetry is attained when θ reaches 180°. In order to determine θ it is necessary [13] to compute both the molar Kerr constant and dipole moment of a given molecular configuration as a function of θ and thence of the mixture of rotamers using the experimental $_mK$ and μ to evaluate the proportion of *gauche*-conformer when θ is allowed to

TABLE 3

Polarisations, refractions and dipole moments at infinite dilution in carbon tetrachloride solutions

	Temp.	$\alpha\epsilon_1$	β	P_2 (c.c.)	R_D (c.c.)	R_D(calc.)	$\mu(D)$
1,1,2,2-Tetrachloro-1,2-diphenylethane	−20°	6.89	−0.146	279.3	—		2.85 ± 0.06
	25	5.58	−0.095	253.3	80.4	79.5	2.87 ± 0.03
	45	5.18	−0.086	247.4	81.2		2.92 ± 0.01
2,3-Dimethyl-2,3-di-*p*-bromophenylbutane	−20	4.26	−0.133	242.8	—		2.45 ± 0.04
	25	3.50	−0.062	224.1	96.6	94.3	2.45 ± 0.01
	45	3.12	−0.055	213.6	94.9		2.45 ± 0.04
2,3-Dimethyl-2,3-di-*p*-chlorophenylbutane	25	4.34	−0.322	215.7	88.4	88.6	2.45 ± 0.02
	45	4.02	−0.340	212.2	89.2		2.49 ± 0.02
2,3-Dimethyl-2,3-di-*p*-fluorophenylbutane	25	4.19	−0.423	193.3	78.5	78.3	2.33 ± 0.01
	45	3.81	−0.402	186.2	77.3		2.35 ± 0.03

TABLE 4

Polarisations, refractions, dipole moments and molar Kerr constants at infinite dilution in benzene solution at 25°

	$\alpha\epsilon_1$	β	γ	δ	P_2 (c.c.)	R_D (c.c.)	R_D(calc.)	$\mu(D)$ *	$10^{12}{}_\infty(_mK_2)$
1,1,2,2-Tetrachloro-1,2-diphenylethane ...	3.19	0.400	0.048	21.9	257.8	79.6	79.5	2.92	508
2,3-Dimethyl-2,3-di-*p*-bromophenylbutane	1.95	0.404	0.029	16.9	225.6	94.8	94.3	2.48	497
2,3-Dimethyl-2,3-di-*p*-chlorophenylbutane	2.32	0.272	0.037	18.9	210.4	87.4	88.6	2.40	433
2,3-Dimethyl-2,3-di-*p*-fluorophenylbutane	2.10	0.227	0.002	11.6	180.5	—	78.3	2.19	236
1,1,2,2-Tetrachloroethane	1.91	0.454	0.002	−4.7	91.6	30.6	30.7	1.70	−64
1,1,2,2-Tetrabromoethane	0.80	0.728	0.032	−2.3	84.4	41.6	42.2	1.41	−64
p-Bromocumene	2.11	0.314	0.019	22.9	125.5	48.9	48.2	1.90	340
p-Fluorocumene	2.21	0.064	0.007	15.1	101.6	40.5	40.2	1.70	136
2,3-Dimethyl-2,3-diphenylbutane	0.20	0.122	0.043	0.90	80.3	78.8	78.03	0	29.4

* μ is calculated on the basis that $_DP = 1.05 R_D$.

DISCUSSION

2,3-Dimethyl-2,3-di-(p-halogenophenyl)*butanes.*— These belong to the class of ethanes which can be described by the general formula $X–CR_2–CR_2–X$. An assemblage of

vary over a range of values. The results of such calculations are summarised in Table 5. In these computations the benzene ring is considered to be a rigid unit unable to rotate about its 1,4-axis. Examination of the steric

[12] A. L. McClellan, ' Tables of Experimental Dipole Moments,' W. H. Freeman and Co., San Francisco, 1963.

[13] L. H. L. Chia, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc.* (B), 1969, 608.

situation in a model of the 2,3-di-(p-halogenophenyl)-2,3-dimethylbutane molecule suggests that the preferred orientation of the phenyl ring is such that the plane of each phenyl ring is parallel with the line joining the centres of the two methyl carbons attached to the same

TABLE 5

θ	0°	50°	60°	70°	80°	180°
			Bromo-compound			
$10^{12}{}_{m}K$ (calc.)	1391	979	791	611	—	77.9
% gauche	31.9	46.5	58.7	78.6	—	—
μ(calc.) D	3.67	3.32	3.17	3.00	—	0
% gauche	47.7	58.0	63.5	71.0	—	—
			Chloro-compound			
$10^{12}{}_{m}K$ (calc.)	1070	743	630	517	—	62.2
% gauche	36.7	54.4	65.3	81.5	—	—
μ(calc.) D	3.48	3.15	3.01	2.85	—	0
% gauche	50.5	61.4	67.3	75.2	—	—
			Fluoro-compound			
$10^{12}{}_{m}K$ (calc.)	584	442	390	337	283	36
% gauche	36	49	56	67	81	—
μ(calc.) D	3.25	2.95	2.82	2.66	2.49	0
% gauche	47.0	57.3	62.5	70.1	80.2	—

carbon atom linked to the phenyl ring. The planes of the two phenyl rings are considered to be parallel to, but not coplanar with, each other in a fashion similar to the molecular configuration obtaining in bibenzyl,[14,15] as shown in (III). We have accordingly adopted this
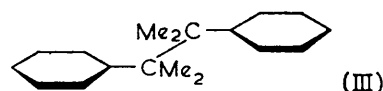
configuration for all the Kerr constant calculations for both the gauche- and trans-conformers, assuming tetrahedral angles at the aliphatic carbon atoms. The aryl group attached to an ethane carbon is treated as a single $C–C_6H_4$–halogen unit with the component of polarisability b_1 along the 1,4-axis; b_2 in the plane of the ring but perpendicular to b_1; and b_3 orthogonal to both b_1 and b_2. These components are equal to $b_i(C_6H_5 \cdot CH_3) - 4b_i(C–H) + b_i$ (C–halogen) where $i = 1$, 2, or 3. They have values $b_1 = 1.710$, $b_2 = 1.240$, and $b_3 = 0.910$ (in 10^{-23} c.c units) when the halogen is bromine; $b_1 = 1.550$, $b_2 = 1.160$, and $b_3 = 1.025$ for chlorine; and $b_1 = 1.237$, $b_2 = 1.025$, and $b_3 = 0.695$ for fluorine. The Ph·CH$_3$ polarisabilities used are from ref. 16 and the C–halogen values from ref. 17. For the calculation of dipole moments [13] it is assumed that the trans-conformer has zero moment, and that the moment of the gauche-conformer is given by $\mu_g = 2\mu_0 \sin 70 \cos\left(\dfrac{\theta}{2}\right)$. The dipole moment ($\mu_0$) of the group CR_2X is taken along the C–X bond with values given by the measured moments of the p-halogenocumenes (Table 4), except for p-chlorocumene. In this case, difficulties in purifying the p-chlorocumene

prevented us from obtaining a reliable experimental moment. However, the correct value is estimated with some confidence to be ca. 1.85 D from the existing data on p-halogenotoluenes, p-halogenoethylbenzenes, and the two p-fluoro- and p-bromo-cumenes measured in this work. When the $_mK$ and μ(calc.) values in Table 5 are plotted against the dihedral angle θ, it is seen that two curves are obtained which intersect at a point consistent with a mixture containing 67% of the gauche-conformer (with θ 65°) and 33% of the trans-form for the bromo-compound. For the chloro-compound, the isomeric gauche : trans ratio is 68 : 32 with $\theta = 63°$, but for the fluoro-compound the ratio indicated is about 74 : 26 with $\theta = 76°$. From an examination of the Leybold models of these molecules it appears unlikely that the halogen atoms, situated as they are at the para-positions of the phenyl rings, can exert any steric influence either on each other or on the methyl groups. Nor is the mutual halogen–dipolar electrostatic interaction, even if this is not negligible, likely to vary significantly with different halogen atoms since the C–halogen bonds have essentially the same group moment. Consequently, θ should be independent of the halogen. This conclusion, based on qualitative reasoning, is, within the experimental errors, substantiated by the above results for the bromo- and chloro-compounds though apparently not in the case of the fluoro-compound. However, it is possible that the discrepancy in the fluoro-compound does not reflect a real effect, but rather may be the result of the inapplicability of the C–F bond polarisabilities used. The validity of this conclusion is strengthened by further analysis of the dipole moment data below which show that the fluoro-compound gives essentially the same results as the chloro- and bromo-analogues. No significant improvement in the above-noted discrepancy is obtained by using alternative C–F bond polarisabilities derived from fluorobenzene.[18]

It can also be shown qualitatively that the value of ca. 65° for θ is plausible. Although the dihedral angle θ is usually in the region of 60°, some molecules show larger values, e.g., 1,2-dichloroethane [1] has $\theta = 71°$. In the analogous molecules 2,3-dichloro-2,3-dimethylbutane and 2,3-dibromo-2,3-dimethylbutane the measured moments at different temperatures indicate a μ_g value of ca. 3.33 D for both these molecules,[19] corresponding to a dihedral angle of ca. 70°. This suggests that the resultant interaction between the methyl group and the halogen atom is negligible. In the case of the 2,3-di(halogenophenyl)-2,3-dimethylbutanes the dipolar repulsions responsible for the widening of the dihedral angle to 70° in the 2,3-dihalogeno-2,3-dimethylbutanes are now considerably reduced since the centres of the dipoles are further apart. In addition, steric repulsions between the methyl and the bulky p-halogenophenyl

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groups will cause θ to become smaller although this will be counterbalanced to some extent by the repulsions between the two *p*-halogenophenyl groups. The net result of these effects however, would be to reduce θ and we should therefore expect lower dihedral angles for the 2,3-di-(*p*-halogenophenyl)-2,3-dimethylbutanes than for the corresponding 2,3-dihalogeno-2,3-dimethylbutanes. Hence a θ of *ca.* 65° is not unreasonable for the phenyl-substituted compounds.

Energy Difference between the gauche- *and* trans-*conformers.*—The solution energy difference ΔE_s between *gauche-* and *trans*-conformers can be obtained from equation (1)[1] where N_g and N_t are the numbers of

$$N_g/N_t = 2 \exp\left(-\Delta E_s/\boldsymbol{R}T\right) \qquad (1)$$

molecules in the *gauche-* and *trans*-conformations respectively. The ratio $N_g : N_t$ can be obtained from the measured moment if the dihedral angle is known. Table 6 lists the ΔE_s (benzene) values calculated from

TABLE 6

ΔE (benzene) (kcal./mole) for $\mu_g = \mu(\theta = 60\text{—}70°)$

|	
2,3-Dibromo-2,3-dimethylbutane	1·62—1·53
2,3-Dichloro-2,3-dimethylbutane	1·09—0·97
2,3-Di-(*p*-bromophenyl)2,3-dimethylbutane ...	0·08—(—0·12)
2,3-Di(chlorophenyl)-2,3-dimethylbutane	0·10—0·10
2,3-Di-(*p*-fluorophenyl)2,3-dimethylbutane ...	0·11—(—0·07)

the experimental moments and equation (1) for the 2,3-di-(*p*-halogenophenyl)-2,3-dimethylbutanes, the 2,3-dihalogeno-2,3-dimethylbutanes being included for comparison.

As expected the calculated ΔE_s values are practically constant and essentially zero for all three 2,3-di-(*p*-halogenophenyl)-2,3-dimethylbutanes. The fact that ΔE_s is practically zero implies that there should be no significant variation in dipole moment with temperature. The experimental data in Table 3 with CCl_4 as solvent confirm this expectation.

A further consequence of the virtually zero ΔE_s values is that the moments of the 2,3-di-(*p*-halogenophenyl)-2,3-dimethylbutanes calculated on the basis of free rotation about the central C–C bond, are only *ca.* 0·1 D higher than the observed values, in contrast to observations[20] on other molecules of the type R_2XC–CXR_2 where the difference is usually substantially greater. From current theory[1] it can be shown that observed moments can be greater or smaller than the values calculated for free rotation depending on the parameters θ and ΔE_s. Thus it would be incorrect to assume that if the observed moment of a compound of the type under discussion is close to that calculated for free rotation, hindered rotation must necessarily be ruled out.

1,2-Diphenyltetrachloroethane.—By analogy with 1,1,2,2-tetrachloroethane,[21,22] the diphenyl-substituted

compound can be regarded as a mixture of *trans-* (IV) and *gauche-* (V) conformers. The moments of this compound at different temperatures in carbon tetrachloride solution (Table 3) show an apparent tendency to increase slightly with a rise in temperature. Application of the Lennard-Jones and Pike method[23] to the experimental data then yields a ΔE_s value of 0·3 kcal./mole and a μ_g value of 3·96 D for the *gauche*-conformer (V).

(IV)　　　　　(V)
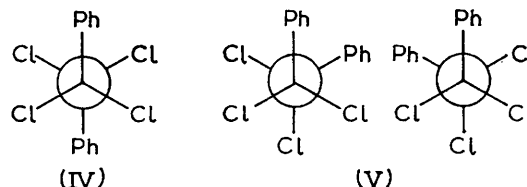
In principle, it is also possible to regard this molecule as a dehydrogeno-dimer of benzylidene chloride[12] ($\mu = 2\cdot05$ D). Assuming that the effective moment of the $-PhCl_2$ moiety is equal to that of benzylidene chloride, and that it acts along the bisector of the Cl–C–Cl angle in the Cl–C–Cl plane, one can calculate ΔE_s from equation (1). In both benzene and carbon tetrachloride solution this model leads to ΔE_s *ca.* —0·34 kcal./mole when θ = 60 and —0·50 kcal./mole when θ is assumed to be 65°, *i.e.*, it suggests that the *gauche*-conformer is more stable than the *trans*. However, the precise direction of action of the dipole moment of benzylidene chloride is uncertain and there may be deviations of the bond angles from tetrahedral symmetry. Consequently it is difficult to decide how much significance should be attached to these results. What appears to be certain from both approaches is that ΔE_s has a value near zero and therefore the *gauche* proportion is in the region of 70%.

It is interesting to compare these results with those of 1,1,2,2-tetrachloroethane obtained from various physical methods. Its ΔE values in the gas phase[24,25] have been shown to be about 0 kcal./mole but the corresponding value in the liquid[21] is —1·1 kcal./mole. The large difference between the liquid and gas values of ΔE can be attributed to stabilisation of the *gauche*-conformer by intermolecular electrostatic interaction in the condensed phase.

A point of considerable interest is that ΔE in the vapour state is much lower than that obtained for 1,2-dichloroethane. To explain this, Miyagawa[26] suggested that as observed in related molecules such as CH_2Cl_2 the angle between the two C–Cl bonds attached to the same carbon atom is greater than the usual tetrahedral angle. This will have the effect of simultaneously stabilising the *gauche*-conformation and making the *trans*-conformation less stable, for the C–Cl azimuthal angles will be greater than 60° in the *gauche-* and less

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than 60° in the *trans*-conformation. The effect on the *trans*-conformation is particularly great as a given increase in the angle Cl–C–Cl will be doubly effective in decreasing each azimuthal angle. Thus a slight increase in the Cl–C–Cl angle would satisfactorily account for the low ΔE_v value. This effect may also be present in 1,2-diphenyltetrachloroethane. It is possible to estimate the ΔE_s (benzene) value of 1,1,2,2-tetrachloroethane, subject to the uncertainties mentioned in connection with the tetrachlorodiphenyl compound, by the methods discussed earlier with 2,3-dimethyl-2,3-di-(*p*-halogenophenyl)-butanes. If we assume that the appropriate group moment μ_0 is 1·4 D (*i.e.*, between the values of methylene dichloride and chloroform) and lies along the bisector of the Cl–C–Cl angle, for azimuthal angles between 60 and 65° ΔE_s is 0·23—0·15 kcal./mole. These values are comparable with those found for 1,2-diphenyltetrachloroethane and suggest that the diphenyl compound is not significantly different from the 1,1,2,2-tetrachloroethane molecule as regards the relative stabilities of the rotational isomers.

Additional Kerr Constant Results.—Following our birefringence measurements on the tetrahalogeno-substituted compounds, our attention was drawn to the apparent inapplicability of the usual C–halogen bond polarisabilities where two such bonds are attached to the same carbon atom, *e.g.*, in benzylidene chloride and benzotrichloride.[27] In view of these discrepancies, we have not attempted to extract more detailed information concerning molecular parameters from our Kerr constant results on the tetrahalogeno-compounds. The observed molar Kerr constant, however, is still useful in providing qualitative information on *gauche–trans* mixtures. According to Kerr effect theory, the predominant

contribution to the molar Kerr constant is the dipole term. The anisotropic terms for both the *trans*- and the *gauche*-conformers are small. Thus the large positive $_mK$ value of 508×10^{-12} observed indicates a large dipole term for the 1,2-diphenyltetrachloro-compound which in turn implies that a large proportion of the molecules exist in the polar *gauche*-form. In the analogous tetrachloro- and tetrabromo-ethane molecules, the observed molar Kerr constants are negative and of a reasonable magnitude (-64×10^{-12}). Kerr effect theory would require a positive (and usually small) value for θ_1 the anisotropy term. Thus for $_mK$'s of -64×10^{-12}, the dipole term must be definitely negative and sufficiently large to offset the contribution of the positive term θ_1. This could arise if both molecules exist in solution as the more polar *gauche*-form or as mixtures of *trans*- and *gauche*-conformers with the latter predominating.

In the case of 2,3-dimethyl-2,3-diphenylbutane, the non-polar character of this molecule has been confirmed by the dielectric polarisation results. The observed $_mK$ of 27 (in 10^{-23} c.c. units) when compared with the values of 30·5 and 22·9 calculated for the *trans*- and *gauche*-conformers respectively based on the same dibenzyl type model used in the calculations for the 2,3-dimethyl-2,3-di-(*p*-halogenophenyl)butanes, is again qualitatively consistent with that expected for a mixture of *trans*- and *gauche*-conformers in solution.

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