A Study of Rotational Isomerism in 1,2-Diphenylethane, its *pp'*-Disubstituted Derivatives (Cl, Br, and CN), 2,3-Diphenylbutane, and its *pp'*-Dibromo-substituted Derivatives, by Infrared and Raman Spectroscopy and Molecular Polarisability Measurements

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An examination of the Raman spectra of 1,2-diphenylethane, 1,2-di-(*p*-chlorophenyl)ethane, *meso*-2,3-diphenylbutane, and its *pp'*-dibromo-derivative reveals the general absence of corresponding frequencies from the i.r. spectra of the solids. This fact, taken together with the general appearance of certain extra bands in the i.r. and Raman spectra of various solutions, strongly suggests the existence of only the *trans*-rotamer in the solid phase but of a dynamic equilibrium mixture of both *trans*- and gauche-rotamers in solution. This conclusion is also considered to be essentially true in the case of 1,2-diphenylethane, notwithstanding the lack of extra bands in the i.r. spectra of its solutions. The relatively weak intensities of the bands attributed to the gauche-rotamers suggest that in these compounds the proportion of the gauche-rotamer is appreciably less than that of the *trans* in solution. The greater number of absorption bands observed in the i.r. spectra of the racemic (±) than in that of the corresponding solid *meso*-compound, is in accord with predictions based on simple selection rules. The dihedral angles of some of the gauche-rotamers are determined by molecular polarisability measurements.

In this paper the conformations of 1,2-diphenylethanes and 2,3-diphenylbutanes are examined by i.r. and Raman spectroscopy and molecular polarisability measurements.

EXPERIMENTAL

The following compounds have been studied: 1,2-diphenylethane, 1,2-di-(*p*-chlorophenyl)ethane, 1,2-di-(*p*-bromophenyl)ethane, 1,2-di-(*p*-cyanophenyl)ethane, *meso*-2,3-diphenylbutane, (±)-2,3-diphenylbutane, *meso*-2,3-di-(*p*-bromophenyl)butane and (±)-2,3-di-(*p*-bromophenyl)-butane. With the exception of 1,2-diphenylethane which was a commercial specimen, all the compounds were prepared by free-radical dimerisation.[1] In addition to these compounds which were all examined spectroscopically, the moments of *p*-bromotoluene, *p*-chlorotoluene, and *p*-bromoethylbenzene were measured to facilitate discussion on the conformations of the two 1,2-di-(*p*-halogenophenyl)-ethanes and *meso*-2,3-di-(*p*-bromophenyl)butane whose electric birefringences were also determined.

The apparatus,[2] procedures, and methods of treating the polarisation and electric birefringence data have been described.[3] The dielectric results are summarised in Tables 1 and 2. The presentation of selected i.r. and Raman data follows an earlier pattern [4] in Tables 3—4 and in the Figure. I.r. spectroscopic data were obtained with the Perkin-Elmer

Table 1

Incremental electric birefringences, dielectric constants, densities, and refractive indices for solutions of weight fractions w_2 at 25 °C

1,2-Di-(*p*-bromophenyl)ethane [a]

10^5w_2	1015	1426	1794	2274	2763	3600
$10^{11}\Delta B$	521	765	901	1184	1508	1919
$10^4\Delta n$	21	29	36	46	55	71

$$\text{whence } \frac{10^7\Sigma\Delta B}{\Sigma w_2} = 5{\cdot}28 \qquad \frac{\Sigma\Delta n}{\Sigma w_2} = 0{\cdot}200$$

1,2-Di-(*p*-chlorophenyl)ethane [a]

10^5w_2	610	1260	1634	2039	2550	3623
$10^{11}\Delta B$	396	—	1026	1177	1591	2217
$10^4\Delta B$	11	26	32	39	51	63

$$\text{whence } \frac{10^7\Sigma\Delta B}{\Sigma w_2} = 6{\cdot}13 \qquad \frac{\Sigma\Delta n}{\Sigma w_2} = 0{\cdot}185$$

p-Bromotoluene [a]

10^5w_2	1554	3944	4780	6143	7478	8616
$10^4\Delta\varepsilon$	670	1699	2063	2641	3217	3697
$-10^5\Delta d$	325	810	973	1256	1518	1733
$10^4\Delta n^2$	50	143	158	205	252	305

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 4{\cdot}30 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = -0{\cdot}203 \qquad \frac{\Sigma\Delta n^2}{\Sigma w_2} = 0{\cdot}342$$

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[1] H. H. Huang and P. K. K. Lim, *J. Chem. Soc.* (*C*), 1967, 2432.

[2] H. H. Huang and E. P. A. Sullivan, *Austral. J. Chem.*, 1968, **21**, 1721.

[3] (*a*) R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953; (*b*) C. G. Le Fèvre and R. J. W. Le Fèvre, 'Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 3rd edn., vol. 1, p. 2459.

[4] L. H. L. Chia and H. H. Huang, *J. Chem. Soc.* (*B*), 1970, 1695.

TABLE 1 (*Continued*)

p-Chlorotoluene[a]

10^5w_2	1629	2723	4260	5588	6969	8564
$10^4\Delta\varepsilon$	928	1566	2418	3164	3933	4795
$-10^5\Delta d$	1228	1984	3155	4127	5174	6344
$10^4\Delta n^2$	44	85	129	155	202	240

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 5{\cdot}65 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = -0{\cdot}740 \qquad \frac{\Sigma\Delta n^2}{\Sigma w_2} = 0{\cdot}288$$

meso-2,3-Di-(*p*-bromophenyl)butane[a]

10^5w_2	504	1047	1537	1876	2006	3054	4070
$10^4\Delta\varepsilon$	60	130	171	225	261	377	485
$-10^5\Delta d$	20	67	85	137	171	213	290
$10^4\Delta n^2$	—	35	79	97	111	167	208
10^5w_2	1139	1377	1738	2075	2478	3375	
$10^{11}\Delta B$	467	584	739	886	1067	1466	
$10^4\Delta n$	21	23	31	36	43	59	

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 1{\cdot}21 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = -0{\cdot}070 \qquad \frac{10^7\Sigma\Delta B}{\Sigma w_2} = 4{\cdot}28$$

$$\frac{\Sigma\Delta n^2}{\Sigma w_2} = 0{\cdot}513 \qquad \frac{\Sigma\Delta n}{\Sigma w_2} = 0{\cdot}175$$

p-Bromomethylbenzene[a]

10^5w_2	1452	2747	3431	5080	6102
$10^4\Delta\varepsilon$	617	1163	1444	2129	2562
$-10^5\Delta d$	414	760	957	1459	1744
$10^4\Delta n^2$	47	91	111	164	193

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 4{\cdot}21 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = -0{\cdot}284 \qquad \frac{\Sigma\Delta n^2}{\Sigma w_2} = 2{\cdot}0322$$

meso-2,3-Di-(*p*-bromophenyl)butane[b]

10^5w_2	1149	2099	3252	4408	5737
$10^4\Delta\varepsilon$	75	164	239	323	417
$10^5\Delta d$	402	766	1175	1591	2095
$10^4\Delta n^2$	27	45	63	87	111

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 0{\cdot}73 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = 0{\cdot}362 \qquad \frac{\Sigma\Delta n^2}{\Sigma w_2} = 0{\cdot}200$$

p-Bromoethylbenzene[b]

10^5w_2	1071	2107	3282	4504	6503
$10^4\Delta\varepsilon$	266	554	851	1143	1645
$10^5\Delta d$	329	650	1008	1363	2012
$10^4\Delta n^2$	9	18	27	39	54

$$\text{whence } \frac{\Sigma\Delta\varepsilon}{\Sigma w_2} = 2{\cdot}55 \qquad \frac{\Sigma\Delta d}{\Sigma w_2} = 0{\cdot}307 \qquad \frac{\Sigma\Delta n^2}{\Sigma w_2} = 0{\cdot}084$$

[a] In carbon tetrachloride. [b] In benzene.

337 instrument, and the Raman spectra with the Jarell–Ash 25—300 He–Ne laser spectrometer for solids and the Cary 81 instrument with a Toronto type mercury arc light source for solutions.

RESULTS AND DISCUSSION

Spectroscopic Discussion.—The fundamental vibrations for the likely rotamers (*trans* and gauche) of 1,2-diphenylethane and *meso*-2,3-diphenylbutane are summarised in Table 5. These are representative of the other molecules studied in this work except the (±)-compounds. From Table 5 it is clear that all the fundamental vibrations are active in the i.r. for the gauche-rotamer whereas only about half are active in the case of the *trans*-rotamer. As with all large molecules overlapping and masking would considerably reduce the actual number of fundamentals observed.

Comparison of the solid-state i.r. and Raman spectra of 1,2-diphenylethane, 1,2-di-(*p*-chlorophenyl)ethane, *meso*-2,3-diphenylbutane, and *meso*-2,3-di-(*p*-bromophenyl)-butane shows that except for a few coincident bands due probably to accidental degeneracy, the Rule of Mutual Exclusion for centrosymmetric molecules holds true here, indicating the existence of the compounds in the *trans*-conformation in the solid, a conclusion already supported by *X*-ray crystallographic evidence[5] in the case of 1,2-diphenylethane.

With the exception of 1,2-diphenylethane, the solution spectra of the three 1,2-di-(*para*-substituted phenyl)-ethanes and the *meso*-2,3-substituted butanes reveal certain absorption bands (see Figure and Tables 3—4) which are absent from the spectra of the potassium bromide pressed-disc samples, Nujol mulls, and hexachlorobutadiene mulls. These extra absorption bands in solution (printed in italics in the Tables) strongly point to the presence of the gauche-rotamer in solution in addition to the *trans* and most of them probably arise from a mixture of fundamental modes including the central C–C stretching. The relative intensities of the extra bands in the solution spectra are consistent with the evaluation from electric dipole moment measurements[6] that the *trans* : gauche ratio in solution is 63 : 36 in the case of the 1,2-di-(*para*-substituted phenyl)ethanes, and 84 : 16 (this work) for *meso*-2,3-di-(*p*-bromophenyl)-butane. The absence of extra bands from the solution spectra of 1,2-diphenylethane suggests the possibility of a substantial difference in the gauche : *trans* isomeric ratio between this compound (in which the proportion of the gauche-rotamer is too low to be detected by the i.r. spectrometer) and its *pp*′-disubstituted derivatives. This observation can be explained in terms of Onsager's model[7,8] according to which a 1,2-diphenylethane molecule having essentially zero moment (whether *trans* or gauche) is not subject to any significant dielectric energy change when the dielectric constant of its surrounding medium is increased, whereas the polar gauche-rotamer of the *pp*′-disubstituted derivative should be appreciably stabilised by this effect.

Dipole Moment and Kerr Constant Results.—In principle, the dihedral angle θ of the gauche-conformer of a symmetrically substituted ethane exhibiting rotational isomerism can be determined from dipole moment and electric birefringence measurements.[9] If the origin of θ is set at the *cis*-form so that the *trans*-conformation is attained when θ reaches 180°, the proportion of the gauche-conformer can be evaluated as a function of θ based independently on the experimental ${}_mK$ and μ. Thus two separate plots of gauche-percentage population ($X\%$) against θ are obtained, which should intersect at a point giving the X and θ values simultaneously satisfying both the observed dipole moment and molar Kerr constant of the equilibrium mixture.

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[5] C. J. Brown, *Acta Cryst.*, 1964, **7**, 97.

[6] K. K. Chiu, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc.* (*B*), 1970, 304.

[7] L. Onsager, *J. Amer. Chem. Soc.*, 1963, **58**, 1456.

[8] N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288.

[9] L. H. L. Chia, K. K. Chiu, and H. H. Huang, *J. Chem. Soc.* (*B*), 1969, 1117.

TABLE 2

Polarisations, refractions, dipole moments, and Kerr constants at infinite dilution

Solute	Solvent	Temp./°C	$\alpha\varepsilon_1$	β	δ	γ	${}_2P$/cm^3	R_D/cm^3	μ/D	$10^{12}{}_mK$
1,2-Di-(*p*-bromophenyl)-ethane	CCl_4	25	2·27 [a]	−0·018 [a]	63·6	0·137	143·0 [a]	75·2 [a]	1·77 ± 0·04 [a]	192 ± 6
1,2-Di-(*p*-chlorophenyl)-ethane	CCl_4	25	3·16 [a]	−0·319 [a]	73·8	0·127	144·7 [a]	69·5 [a]	1·87 ± 0·02 [a]	164 ± 6
meso-2,3-Di-(*p*-bromophenyl)butane	CCl_4	25	1·21	−0·044	51·5	0·120	117·7	87·1 (85·1)	1·19 ± 0·03	170 ± 4
	C_6H_6	25	0·73	0·415			124·1	86·3	1·31 ± 0·03	
p-Bromotoluene	CCl_4	25	4·30	−0·128			113·3	39·7 (38·9)	1·87 ± 0·01	
p-Chlorotoluene	CCl_4	25	5·65	−0·467			109·8	36·0 (36·1)	1·88 ± 0·01	
p-Bromoethylbenzene	CCl_4	25	4·21	−0·179			122·5	44·2 (43·6)	1·93 ± 0·01	
	C_6H_6	25	2·55	0·351			129·8	43·2	2·03 ± 0·01	

[a] Taken from K. K. Chiu, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc.* (*B*), 1970, 307.

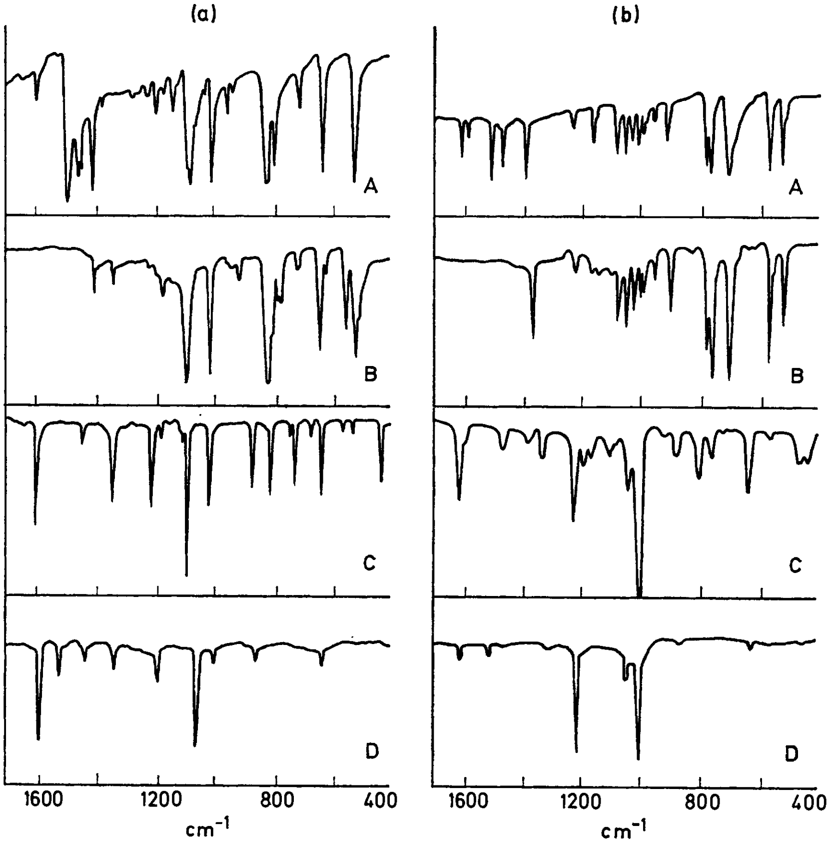
TABLE 3

I.r.* and Raman * spectra of 1,2-diphenylethane and *meso*-2,3-di-(*p*-bromophenyl)butane in the solid state and in solution (cm^{-1})

1,2-Diphenylethane			*meso*-2,3-Di-(*p*-bromophenyl)butane			
KBr disc	Raman (solid)	Raman (CCl_4)	KBr disc	Raman (solid)	Raman ($CHCl_3$)	I.r. (CS_2)
1605(16)	1605(15)			1592(63)	1600(7) p	
1585(4)	1585(7)	1595(15) dp	1490(62)			X
		1527(7) p			*1515*(9) p	
1495(26)				1465(20)		
1455(32)			1455(29)			X
	1438(6)	1432(4) pp	1405(34)			1400(17)
1385(1)			1375(26)			1375(19)
	1350(8)			1350(13)	1350(3)	
1340(2)				1330(9)		
	1335(8)	1337(5) p	1325(5)			1322(2)
	1208(23)			1300(4)		
1200(1)		*1195*(14) p	1275(5)			1275(2)
1180(4)	1184(6)		1230(1)			1230(2)
	1160(11)	1160(5) dp?		1215(69)	1225(41) p	
1145(10)				1184(11)	1184(7)	
1080(½)			1178(2)			1180(4)
1064(24)				1145(3)		
1029(20)	1032(28)		1105(20)			1103(13)
	1020(19)	1025(14) p	1078sh(19)	1077(60)	1085(14) p	1078sh(40)
	1000(79)	997(39) p	1069(56)			1072(44)
983(3)			1058(18)			1058(19)
910(7)				1020(60)	1020(10) p	
	850(21)	842(9) p	1010(61)			1012(62)
840(2)			1000(36)			1000(26)
†			960(14)			959(6)
752(48)	740(17)			868(21)	870(4)	
698(63)			825(63)	830(10)	X	827(67)
623(2)	622(23)		777(33)	783(80)	X	777(20)
	618(8)	617(4) dp?				*745*(6)
580(7)						*727*(8)
†	532(5)		719(31)	720(14)	X	*719*(21)
520(29)				665(43)	X	
503(13)			633(4)	630(40)	X	633(½)
	468(10)		603(30)			606(21)
	352(4)					*568*
	243(28)			545(6)	550(2)	
	222(5)		532(55)			531
	145(29)			478(8)	480(5)	
				425(13)	X	
				375(30)	X	
				339(45)	X	
				305(15)	X	
				220(71)	X	

? Uncertainty in genuine character and/or intensity. X masking by background or solvent. p, polarised line; dp, depolarised line; pp, partly polarised. † Possible masking by neighbouring absorption. Italics denote extra frequencies as observed in solution.

* Spectra obtained below 1700 cm^{-1}. The numbers in parentheses after each wave number correspond approximately to the peak heights and thus give some idea of the *relative* intensities of the different bands.



Spectra of (a) 1,2-di-(*p*-chlorophenyl)ethane and (b) *meso*-2,3-diphenylbutane; A, i.r. spectra as KBr disc; B, i.r. spectra in CS_2; C, Raman spectra of solid; D, Raman spectra in CCl_4 and $CHCl_3$ respectively

TABLE 4

I.r. absorption frequencies (cm^{-1})

1,2-Di-(*p*-bromophenyl)ethane		1,2-Di-(*p*-cyanophenyl)ethane	(±)-2,3-Diphenylbutane		(±)-2,3-Di-(*p*-bromophenyl)butane	
KBr disc	CS_2	KBr disc	liquid film		KBr disc	
1445(23)	X	3060(4)	3080(19)	1155(6)	3070(4)	1010(44)
1405(18)	1400(32)	3045(5½)	3060(25)	1075(16)	3030(6)	990sh(17)
1395(19)	1395(10)	2955(2)	3030(37)	1045(10)	3008(7)	950(12)
1345(6)?	1340(6)	2935(6)	2970(41)	1025(32)	2960(26)	880(4)
1228(1)	1228(8)	2865(3)	2930(34)	1005(9)	2890(13)	835sh(18)
	1213(4)	2230(56)	2880(34)	990(7)	2870(13)	820(52)
	*1200*10)	1940(3)	1940(5)	960(4)	1885(9)	782sh(5)
1180(8)	1180(13)	1820(1)	1880(4)	905(10)	1770(2)	772(25)
	1142(3)	1605(45)	1800(3)	835(4)	1630(5)	731(6)
1110(7)		1505(53)	1690(11)	800(4)	1590(15)	719(37)
1100sh(10)	1100sh(13)	1460(14)	1610(31)	763(50)	1490(38)	665(2)
	1092(27)	1420(16)	1590(48)	700(60)	1440(25)	650(28)
1072(45)	1074(70)	1410(16)	1500(54)	650(6)	1400(30)	635(16)
	1013(71)	1320(2)	1460(23)	620(3)	1370(20)	600(4)
1007(46)		1295(12)	1380sh(17)	602(2)	1280(6)	585(3)
962(13)	960sh(5)	1270(3)	1320(7)	590(5)	1220(3)	565(5)
940(8)	947(7)	1200(7)	1260(10)	550(38)	1178(6)	549(45)
	918(11)	1178(36)	1180(5)	525(6)	1120(4)	530(35)
852(14)	X	1150sh(2)		490(3)	1105(27)	485(5)
818(43)	820sh(71)	1095(8)			1070(43)	440(8)
					1045(20)	
792(35)	795sh(39)	1025(27)				
	775(22)	955(8)				
748(22)	762(39)	860(39)				
	711(14)	837(62)				
	*608*sh(20)	768(1)				
603(27)	601(31)	730(3)				
	538(37)	685(3)				
	518(51)	648(8)				
503(27)	500(32)	*572*(8) *				
485(32)	X	562(65)				
		490(7)				

* Observed in C_6H_6, $CHCl_3$, and MeCN solution only.

The results of such calculations for the molecules 1,2-di-(*p*-chlorophenyl)ethane, 1,2-di-(*p*-bromophenyl)-ethane, and *meso*-2,3-diphenylbutane are summarised in Table 6.

TABLE 5

Fundamental vibrations for the rotamers

Conformation	Vibrational species	Activity I.r.	Activity Raman	No. of non-phenyl modes	No. of phenyl modes	No. of fundamentals
		1,2-Diphenylethane				
trans (C_{2h})	A_g	ia	p *	6	20	26
	A_u	a	v	4	10	14
	B_g	ia	dp	3	10	13
	B_u	a	v	5	20	25
gauche (C_2)	A	a	p *	10	30	40
	B	a	dp	8	30	38
		meso-2,3-Diphenylbutane				
trans (C_i)	A_g	ia	p *	18	30	48
	A_u	a	v	18	30	48
gauche (C_1)	A	a	p *	36	60	96

a = Active; ia = inactive; p = polarised; p* = partly polarised; dp = depolarised; v = forbidden.

TABLE 6

Calculated dipole moments and molar Kerr constants, with corresponding gauche-conformer percentage population, for various dihedral angles

θ	0°	50°	60°	70°	80°	90°	180°
			1,2-Di-(*p*-bromophenyl)ethane				
$\mu(\theta)$	3·51	3·18	3·04	2·88	2·69	2·48	0
$X\%$	25·4	31·0	33·9	37·8	43·2	50·9	—
$10^{12}{}_{\mathrm{m}}K$ (calc.)	1430	831	633	441	272	—	71
$X\%$	8·9	15·9	21·5	32·6	60·1	—	—
			1,2-Di-(*p*-chlorophenyl)ethane				
$\mu(\theta)$	3·53	3·2	3·06	2·89	2·71	2·49	0
$X\%$	28·1	34·2	37·3	41·9	47·6	56·4	—
$10^{12}{}_{\mathrm{m}}K$ (calc.)	1260	719	546	379	232	—	54
$X\%$	9·2	16·6	22·4	33·8	61·9	—	—
			meso-2,3-Di-(*p*-bromophenyl)butane				
$\mu(\theta)$	3·63	3·29	3·14	2·97	2·78	2·56	0
$X\%$	10·8	13·1	14·4	16·0	18·4	21·7	—
(Assuming free aryl ring rotations)							
$10^{12}{}_{\mathrm{m}}K$ (calc.)	1479	865	664	471	298	—	65
$X\%$	7·3	13·0	17·3	25·6	44·6	—	—
(Assuming restricted aryl ring rotations)							
$10^{12}{}_{\mathrm{m}}K$ (calc.)	1397	931	774	617	473	—	80
$X\%$	6·8	10·5	12·8	16·6	24·9	—	—

In the calculation of the molar Kerr constants of the various conformations, the Cartesian axes to which the bond or group moments and polarisabilities are resolved are: the X-axis along the C–C bond, Y-axis perpendicular to one of the C–C–X planes, and Z-axis perpendicular to both these axes but lying in the plane containing C–C–X. Further, the aryl rings are assumed to be freely rotating about their respective $C-C_{Ar}$ bond although an additional set of calculations was carried out in the case of *meso*-2,3-di-(*p*-bromophenyl)butane with the assumption that the aryl rings are parallel to, but not coplanar with, each other as in the case of solid 1,2-diphenylethane.[5] The bond and group polarisabilities [10-12] (in units of 10^{-24} cm^3) used are as in Table 7. The polarisabilities of the group $C-C_6H_4-Y$ (Y = Cl or Br) treated as a single unit in the calculations, are given by the relation (1) where $i = 1, 2,$ or 3. If the aryl

$$b_i(C-C_6H_4-Y) = b_i(PhMe) - 4b_i(C-H) + b_i(C-Y) \quad (1)$$

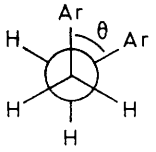
group is freely rotating, its transverse and vertical polarisability semi-axes, b_T and b_V should be related by (2). It is assumed that the *trans*-conformer has zero

$$b_T = b_V = (b_2 + b_3)/2 \quad (2)$$

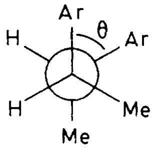
moment and that the moment of the gauche-conformer is given by the equation $\mu(\theta) = 2\mu_0 \sin 70 \cos \theta/2$ where μ_0 is taken along the C–X bond with values given by the measured moments of the *p*-halogenotoluenes (Table 2). Table 6 shows that the apparent θ and $X\%$ values are: (76 ± 2°; 45 ± 2) for 1,2-di-(*p*-chlorophenyl)ethane; (74 ± 2°; 40 ± 2) for 1,2-di-(*p*-bromophenyl)ethane; and (50 ± 1°, 13 ± 1; or 69 ± 1°, 16 ± 1) for *meso*-2,3-di-(*p*-bromophenyl)butane (II). For the last compound the second result, θ = 69 ± 1, $X\%$ = 16 ± 1, is more reasonable than the alternative as it lies between those of 2,3-dimethyl-2,3-di-(*p*-halogenophenyl)butane (III) (θ = *ca.* 65°) and 1,2-di-(*p*-halogenophenyl)ethane (I) (θ = *ca.* 75°).

TABLE 7

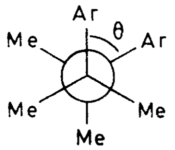
Bond/group	b_1	b_2	b_3	Ref.
C–H	0·65	0·65	0·65	10
C–C	0·97	0·26	0·26	10
C–Cl	4·1	1·8	1·8	11
C–Br	5·7	2·6	2·6	11
PhMe	14·05	12·40	9·10	12



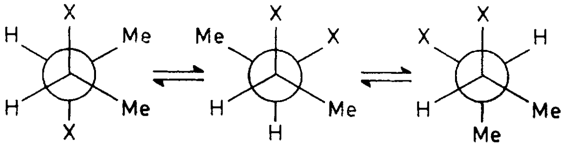
(I)



(II)



(III)



(IV) (V) (VI)

(X = Ph or *p*-BrC$_6$H$_4$) only one enantiomer shown.

Racemic (±)-2,3-*Diphenylbutane and Racemic* (±)-2,3-*Di*-(p-*bromophenyl*)*butane*.—The probable rotamers of these compounds are depicted by the Newman

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[10] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273.

[11] M. L. Kemp and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 3463.

[12] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.*, 1967, 1295.

projections (IV)—(VI). Two points of interest arise from the i.r. spectra of the above compounds. First, as expected from symmetry considerations, the solid-state and solution i.r. spectra are virtually identical whereas the solid-state i.r. spectra of the corresponding *meso*-compounds consist of fewer absorption bands than those of the solid (±)-2,3-di-(*p*-bromophenyl)butane and liquid (±)-2,3-diphenylbutane. Also, since all the rotational isomers of these racemic diastereoisomers belong to the same point-group as the gauche-rotamer of the *meso*-compound, namely C_1, many if not all of their vibrational frequencies should coincide. Thus, the fact that the extra bands in the solution i.r. spectra of the *meso*-compounds [835, 620, and 550 cm^{-1} for *meso*-2,3-diphenylbutane and 727 and 568 cm^{-1} for *meso*-2,3-di-(*p*-bromophenyl)butane] do have coincident frequencies in the corresponding racemic diastereoisomers confirms their gauche-origin (*cf.* Tables 3—4 and Figure).

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