Conformations of Some Substituted Diphenylmethanes and their Dehydrogeno-dimers by Electric Birefringence, Dipole Moment, and Infrared Measurements

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The *meso*- and (±)-diastereoisomers of the chloro-, bromo-, and iodo-derivatives of the ethane [Ph(p-XC_6H_4)CH]$_2$ are prepared by free-radical dimerisation. Their conformations, as well as those of the corresponding monomers Ph(p-XC_6H_4)CH_2, are examined by electric birefringence, dipole moment, and i.r. spectroscopic measurements.

DIPHENYLMETHANE and its mono-substituted derivatives Ph(p-XC_6H_4)CH_2 contain benzylic hydrogen atoms which can be abstracted by the t-butoxyl radical to give the radical Ph(p-XC_6H_4)CH·; the resulting product of dimerisation [Ph(p-XC_6H_4)CH]$_2$, is a heavily substituted ethane capable of existing as the *meso*- or (±)-diastereoisomer when $X \neq H$, which can adopt certain favoured conformations by rotation about the central C–C bond. Here, the conformations of the substituted diphenylmethanes are examined by electric birefringence measurements; further, the identities of (±)- and *meso*-ethanes of the formula [Ph(p-XC_6H_4)CH]$_2$ and the position of the equilibrium (gauche $\rightleftharpoons$ *trans*) for the *meso*-compounds as solutes in dioxan are determined by dipole moment and i.r. spectroscopic measurements.

EXPERIMENTAL

Preparation of Compounds.—The substituted diphenylmethanes were prepared by a reported method [1] except for p-fluorophenyl(phenyl)methane which was obtained by the reduction of p-fluorobenzophenone by hydriodic acid.[2] Since only a barely sufficient quantity of the p-fluorophenyl(phenyl)methane was obtained for physical measurements, dimerisation was not carried out for this compound. The general procedure for dimerisation of diphenylmethane and its derivatives is as follows. The (liquid) substrate and di-t-butyl peroxide in a molar ratio of 2 : 1 were sealed under nitrogen and heated for *ca.* 48 h in the range 120—140°. Any solid product which separated out on cooling was filtered off. The volatile side-products (acetone and t-butyl alcohol) and any unchanged peroxide and substrate were then removed by distillation under reduced pressure, and the residue was worked up to isolate the *meso*- and (±)-dimers.

In the preparation of these compounds it was presumed that the less-soluble, higher-melting isomers had the *meso*- and the lower-melting more soluble isomer the (±)-configuration.

1,2-*Bis*-(p-*bromophenyl*)-1,2-*diphenylethane*.— p-Bromophenyl(phenyl)methane (49·4) gave on reaction with the peroxide (14·6 g) a yellowish solution which on cooling deposited crystals; these were filtered off (15 g). One third were chromatographed on activated alumina with (1 : 1) light petroleum (60—80°)–benzene as eluant to give 2·2 g of meso-1,2-*bis*-(p-*bromophenyl*)-1,2-*diphenylethane*, m.p. 250—251° (from benzene) (Found: C, 63·7; H, 4·3; Br, 32·5. $C_{26}H_{20}Br_2$ requires C, 63·45; H, 4·05; Br, 32·5%). About 0·8 g of the more-soluble (±)-1,2-bis-(p-bromophenyl)-1,2-diphenylethane was obtained mainly

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[1] *Org. Synth.*, 1968, **48**, 27.

[2] C. K. Bradsher and F. A. Vingielle, *J. Org. Chem.*, 1948, **13**, 786.

from the mother liquor. The product had m.p. 200—201° (lit.,[3] 200—201°) (Found: C, 63·8; H, 4·3; Br, 29·7. Calc. for $C_{26}H_{20}Br_2$: C, 63·45; H, 4·05; Br, 32·5%).

1,2-*Bis*-(p-*iodophenyl*)-1,2-*diphenylethane*.—*p*-Iodophenyl-(phenyl)methane (19·0 g) when heated for 48 h with di-t-butyl peroxide (8·4 g) produced a light yellowish solution from which a whitish solid separated out. This was filtered whilst hot (since the substrate is a low-melting solid of m.p. 42—43°). Any further solids which were precipitated on cooling contained essentially the starting material. After several recrystallisations with benzene, *ca.* 1 g of a high-melting product of m.p. 297—298°, presumably the meso-1,2-*bis*-(p-*iodophenyl*)-1,2-*diphenylethane*, was obtained (Found: C, 53·6; H, 3·7; I, 42·0. $C_{26}H_{20}I_2$ requires C, 53·25; H, 3·4; I, 43·35%). Later fractions gave a sample containing mainly (±)-1,2-*bis*-(p-*iodophenyl*)-1,2-*diphenylethane* which had a wide m.p. range. This was passed through a column of activated alumina using (1 : 1) light petroleum (60—80°)-benzene as eluant followed by several recrystallisations from benzene to give white crystals (*ca.* 1 g), m.p. 237—238°. In solution, these crystals had a tendency to turn pink (Found: C, 53·9; H, 3·6; I, 40·2. $C_{26}H_{20}I_2$ requires C, 53·25; H, 3·4; I, 43·35%).

TABLE 1

Polarisations, refractions, dipole moments and molar Kerr constants at 25 °C

Compound	Solvent	$\alpha\varepsilon_1$	β	δ	$_TP$ (cc)	$R_{\text{Dobs.}}$ (cc)	$R_{\text{Dcalc.}}$ (cc)	μ(D) *	$10^{12}{}_{\text{m}}K$
p-Fluorophenyl(phenyl)methane	CCl_4	2·90	−0·444		106·4	55·8	54·8	1·53 ± 0·01	
p-Chlorophenyl(phenyl)methane	CCl_4	3·21	−0·376	88·7	119·9	60·9	59·9	1·65 ± 0·02	159 ± 5
p-Bromophenyl(phenyl)methane	CCl_4	2·68	−0·160	86·1	122·6	64·4	62·8	1·64 ± 0·01	188 ± 12
p-Iodophenyl(phenyl)methane	CCl_4	2·12	−0·010	80·6	120·5	69·4	67·9	1·52 ± 0·03	210 ± 9
meso-1,2-Bis-(*p*-chlorophenyl)-1,2-diphenylethane	Dioxan	0·91	0·158		155·1	118·4	117·5	1·23 ± 0·3	
(±)-1,2-Bis-(*p*-chlorophenyl)-1,2-diphenylethane	Dioxan	3·33	0·135		318·1		117·5	3·07	
meso-1,2-Bis-(*p*-bromophenyl)-1,2-diphenylethane	Dioxan	0·93	0·247		178·4	124·3	123·5	1·53 ± 0·09	
(±)-1,2-Bis-(*p*-bromophenyl)-1,2-diphenylethane	Dioxan	2·66	0·266		305·8	124·5	123·5	2·92 ± 0·09	
meso-1,2-Bis-(*p*-iodophenyl)-1,2-diphenylethane	Dioxan	0·87	0·387		184·5	133·7	133·8	1·47 ± 0·1	
(±)-1,2-Bis-(*p*-iodophenyl)-1,2-diphenylethane	Dioxan	1·97	0·387		290·5	133·7	133·8	2·71 ± 0·09	
Tetraphenylethane	Dioxan	0·75	0·071		127·9	108·5	107·9	0·83 ± 0·1	

* The dipole moments are calculated on the assumption that $_{\text{D}}P = 1{\cdot}05R_{\text{D}}$.

1,2-*Bis*-(p-*chlorophenyl*)-1,2-*diphenylethane*.— *p*-Chlorophenyl(phenyl)methane (46·0 g) and di-t-butyl peroxide (16·6 g) on reaction gave a light yellowish liquid. Crystals were formed only after the reaction mixture had been set aside for half a day; the yield was 12 g. After the removal of the volatile products and unchanged substrate a further crop (1 g) was obtained. The combined crude solid product was run thrice through a column of activated alumina with light petroleum (b.p. 60—80°) as eluant. Repeated recrystallisation from light petroleum finally gave *ca.* 0·8 g of white crystals, presumably the *meso*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethane, m.p. 192—194° (lit.,[4] 191—192°) (Found: C, 77·4; H, 4·9; Cl, 18·3. Calc. for $C_{26}H_{20}Cl_2$; C, 77·4; H, 4·95; Cl, 17·6%). A more soluble, lower melting product (m.p. 176—178°), presumably the (±)-1,2-*bis*-(p-*chlorophenyl*)-1,2-*diphenylethane* (0·1 g), was obtained after great difficulty (Found: C, 77·7; H, 5·2: Cl, 17·6. $C_{26}H_{20}Cl_2$ requires C, 77·4; H, 4·95; Cl, 17·6%).

Apparatus.—Dielectric constants were determined with a heterodyne-beat meter using aural detection.[5] Procedures for density and refractive index measurements were standard,[6] Kerr effects being recorded photometrically.[7] I.r. spectra were obtained with a Perkin-Elmer model 337 instrument.

RESULTS

The dielectric results are summarised in Table 1 and have been calculated where appropriate from the following physical constants for carbon tetrachloride[8] at 25°. $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}58454$; $(n_{\text{D}})_1 = 1{\cdot}4575$, $B_1 = 0{\cdot}083 \times 10^{-7}$, and $_{\text{S}}K_1 = 0{\cdot}888 \times 10^{-14}$. Physical constants for dioxan were determined afresh for each set of measurements. The detailed dielectric results for all the compounds and the i.r. data for *s*-tetraphenylethane and for the *meso*- and (±)-*para*-substituted tetraphenylethanes are deposited as a Supplementary Publication (SUP. no. 20414, 13 pp., 1 microfiche). †

DISCUSSION

Conformations of (p-XC_6H_4)CH_2Ph (X = Cl, Br, or I).—Standard procedures[9] are used to obtain theoretical molar Kerr constants by addition of bond and group polarisability tensors. The calculated molar Kerr constants in carbon tetrachloride solution of various conformations of the family of compounds of formula p-$XC_6H_4CH_2Ph$ where X = Cl, Br, or I are summarised in Table 2.

In these calculations, the bonds of the methane carbon atom have been assumed to be tetrahedral. Any

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[3] H. E. Zimmermann, D. S. Crumrine, D. Dopp, and P. S. Huyffev, *J. Amer. Chem. Soc.*, 1969, **91**, 434.

[4] E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, 1963, **28**, 638.

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

[6] R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953.

[7] H. H. Huang and S. C. Ng, *J. Chem. Soc.* (*B*), 1968, 582.

[8] R. J. W. Le Fèvre and S. C. Solomons, *Austral. J. Chem.*, 1968, **21**, 1706.

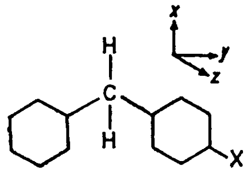
[9] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273.

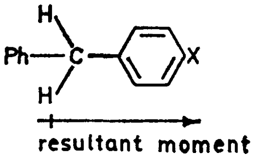
TABLE 2

Summary of molar Kerr constants for various conformations in carbon tetrachloride solution

	θ	0°	10°	20°	30°	40°	60°
p-Chlorophenyl-(phenyl)methane	$10^{12}{}_{m}K$	116	139	163	185	204	226
p-Bromophenyl-(phenyl)methane	$10^{12}{}_{m}K$	141	164	188	211	231	252
p-Iodophenyl-(phenyl)methane	$10^{12}{}_{m}K$	166	135	204	222	239	262

conformer of each of these compounds is defined by the angles of rotation of its aromatic rings. For each individual conformer, the phenyl and the aryl rings are rotated in the same sense as rotation with one of the rings in the opposite sense can be shown by a molecular model to be sterically improbable. The cartesian axes are defined such that the X-axis is taken along a C–H bond, the Y-axis perpendicular to the plane containing the designated H atom, methane carbon atom and the axis of rotation of the aryl ring and the Z-axis in the designated HCC_{Ar} plane. The angle of rotation θ is taken as zero when the aryl ring is coplanar with the designated HCC_{Ar} (or XZ) plane and the line of intersection of the planes of the two rings coincides with the designated C–H bond.





The resultant dipole moment of the molecule as shown in the figure is directed along the C–Ar bond, since the dipole moments of the C–H and C–Ph bonds are approximately equal in magnitude.

The bond and group polarisabilities (in units of 10^{-23} cc) used for the calculation of the values of ${}_{m}K$ of different conformers are tabulated below.

TABLE 3

Anisotropic polarisabilities of bonds and groups

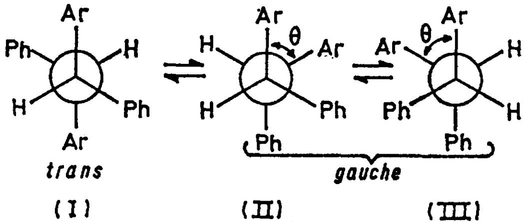
Bond/Group	b_1	b_2	b_3	Ref.
C–H	0·065	0·065	0·065	9
C–C	0·097	0·026	0·026	9
Ph–C	1·210	1·045	0·715	10
BrC_6H_4C	1·710	1·240	0·915	10
ClC_6H_4C	1·550	1·160	0·830	10
IC_6H_4C	2·005	1·551	0·959	10

From Table 2, it can be seen that the experimental molar Kerr constants ($\times 10^{-12}$) of p-chlorophenyl-(phenyl)methane (159), p-bromophenyl(phenyl)methane (188) and p-iodophenyl(phenyl)methane (210) correspond to θ values of *ca.* 18, 20, and 23° respectively. These values are comparable to those determined by Le Fèvre *et al.*[11,12] for the related molecules shown below, converted to conform with our model.

Identity of Diastereoisomers of 1,2-*Bis*-(p-*halogenophenyl*)-1,2-*diphenylethane*.—Heavily substituted ethanes of the general formula $(R^1R^2CH)_2$ where $R^1 = XC_6H_4$, $R^2 = Ph$ and X = Cl, Br, or I may be expected to exist in solution as mobile equilibrium mixtures of certain stable rotamers depicted in (I) to (VI), according to whether they have the *meso*- or (±)-configuration.

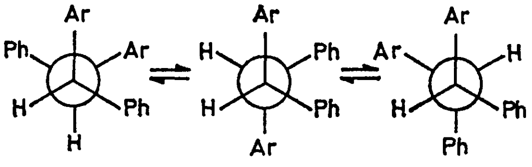
TABLE 4

Solute	Solvent	θ
Diphenylmethane	CCl_4	14°
p-Chlorophenyl(phenyl)methane	CCl_4	22
p-Bromophenyl(phenyl)methane	CCl_4	17
Diphenylacetonitrile	CCl_4	15
4-Benzylpyridine	CCl_4	19
4-Benzylpyridine	Benzene	22



(I) (II) (III)

meso-form



(IV) (V) (VI)

(±)-Form (only one enantiomer shown)

In the preparation of this family of compounds, all the expected *meso* and (±)-diastereoisomers were isolated and their dipole moments measured. The dielectric results (Table 1) show that the lower-melting isomers have consistently and appreciably higher dipole moments than the higher-melting isomers. This finding can be understood in terms of purely steric considerations analogous to those postulated to explain similar results in the case of *meso*- and (±)-1,2-diphenyl-1,2-bis-(4-pyridyl)ethane.[13,14] Thus, with the aid of certain assumptions,[14] it can be shown that the essentially non-polar rotamer (I) predominates in the equilibrium for the *meso*-rotamers and that the highly polar species (VI) is more stable than either (IV) or (V) in the (±) equilibria, and consequently the resulting higher moment of the racemic diastereoisomer in the series can be rationalised. Further information on the rotational isomers of the *meso*-compounds may be obtained from calculations based on Boltzmann statistics:[14] these give the results listed in the following Table, for the percentage number of *gauche*-rotamer (PNg) and the apparent

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[10] L. H. L. Chia, K. K. Chiu, and H. H. Huang, *J. Chem. Soc.* (*B*), 1969, 1120.

[11] M. J. Aroney, R. J. W. Le Fèvre, G. L. D. Ritchie, and A. N. Singh, *J. Chem. Soc.* (*B*), 1965, 5810.

[12] R. J. W. Le Fèvre, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc.* (*B*), 1967, 819.

[13] K. K. Chiu and H. H. Huang, unpublished work.

[14] K. K. Chiu and H. H. Huang, *J. Chem. Soc.* (*B*), 1970, 1142.

energy difference in solution (ΔE) between the *gauche*- and *trans*-rotamers at 25 °C for the three *meso*-compounds, for a range of dihedral angles (θ) [see (II)] since the exact values are now known. The difference in the results for the chloro-derivative on the one hand and the bromo- and iodo-derivatives on the other, is probably more apparent than real and may stem partly from errors arising from technical difficulties in separating rigorously the *meso*-specimens from the racemic.

TABLE 5

Relative abundances of rotamers and their energy differences (for *meso*-compounds)

meso *p,p'*-Derivative of *s*-tetraphenylethane	Dihedral angle (θ) 60° PNg	60° ΔE	70° PNg	70° ΔE	80° PNg	80° ΔE
Chloro	21·0	1·19	23·6	1·10	26·8	1·00
Bromo	32·8	0·83	36·9	0·73	42·0	0·59
Iodo	35·3	0·76	39·3	0·67	44·9	0·53

ΔE in kcal mol^{-1}.

From the Table, it is seen that the *trans*-rotamers emerge as the more stable species, in agreement with our assignments.

Spectroscopic Discussion

Fundamental Vibrational Modes of s-*Tetraphenylethane*.—The likely rotamers for symmetrically substituted ethanes are the *gauche* and the *trans*. In the case of *s*-tetraphenylethane, the *trans* conformer (with C_{2h} symmetry) like any other conformer of this molecule of 48 atoms, would have a total of 138 fundamentals of which exactly half, namely 34 A_u and 35 B_u, are i.r. active, the other 69 modes (36 A_g and 33 B_g) being inactive in the i.r. On the other hand, the 70 A-type and 68 B-type fundamental vibrational modes associated with the *gauche*-rotamer are all i.r.-active.

Examination of the i.r. spectra shows that except for the absorption at 562 cm^{-1} in the solid which is apparently split into two lines at 565 and 566 cm^{-1} in solution probably because one of the two bands is shifted slightly in frequency in the crystalline state so as to blend with the other, no extra bands are present in solution relative to the solid. It appears likely therefore that *s*-tetraphenylethane exists essentially as one conformer (probably the *trans* [14]) in both the solid and solution states. However the possibility of extensive masking as an explanation for the lack of extra lines in solution cannot be precluded with certainty.

meso-1,2-*Bis*-(p-*halogenophenyl*)-1,2-*diphenylethanes*.—In this family of compounds, the point groups to which the *trans* and *gauche* conformers belong are now C_i and C_1 and these give rise for the *trans*-rotamer to 69 A_g and 69 A_u vibrations of which only the A_u are i.r. active, and for the *gauche*-rotamer, the species A in which all the possible 138 vibrations are active in the infrared.

If any of these compounds were to exist entirely in the *trans*-conformation in the solid state and in solution as a dynamic equilibrium mixture of *trans*- and *gauche*-rotamers, then we would expect, in principle, to see many more absorption lines in solution than in the solid. In practice, there would be extensive masking and overlapping absorptions so that one may just be able to see only a few extra absorptions in solution. The i.r. spectra show that indeed, only two or three extra absorptions namely the lines at 815 and 705sh cm^{-1} for the chloro-, 810 and 755sh cm^{-1} for the bromo-, and 809, 750sh, and 617 cm^{-1} for the iodo-compound, are perceptible in solution, suggesting therefore that the *meso*-1,2-bis-(*p*-halogenophenyl)-1,2-diphenylethanes exist in one conformation (probably the *trans*) in the solid state but in two (*trans* and *gauche*) in the solution state. The conformational behaviour of *s*-tetraphenylethane and its 1,2-diphenyl *p,p'*-substituted derivatives thus appears to be very similar to that of 1,2-diphenylethane [15] and its *p,p'*-substituted derivatives in that the non-polar parent compound exists in solution in essentially the *trans*-conformation whereas with their derivatives, the percentage of *gauche* conformer is of the order of 30%. On the other hand, it may be noted that 2,3-dimethyl-2,3-diphenylethane has been shown to exist as a mixture of *trans* and *gauche*-rotamers in solution although it exists essentially as the *trans*-conformer in the solid state.[16] Furthermore the proportion of *gauche*-rotamer [17] in solution of its *p,p'*-substituted derivatives is *ca.* 67%.

Comparison of Spectra of meso- *and* (±)-*Compounds*.—Comparison of the solid-state i.r. spectra of the *meso*- and (±)-compounds shows that in general there are more absorption lines in the (±)- than in the *meso*-compound. This is consistent with the existence of only the *trans*-rotamer in the *meso*-compound in the solid state in which only the A_u modes are i.r.-active whereas in the racemic compounds, the maximum number of the A modes are active.

An additional point of interest is that the spectra of all the *meso*-compounds reveal a prominent line at 910 cm^{-1} which is weak and diffuse in all the (±)-compounds. They may be taken as an indication of the internal consistency of our assignment of the compounds to the *meso* and racemic configurations.

Finally, the *extra* absorptions in the solution spectra of the *meso*-compounds are generally also found in the spectra of the racemic compounds occurring with greater intensity in the latter: 810 and 755 cm^{-1} in the bromo-, 809, 750sh, and 617 cm^{-1} in the iodo-, and 815 cm^{-1} in the chloro-compound.

The evidence in this section taken as a whole therefore lends further support to our assignment of the higher-melting isomer to the *meso* and the lower-melting to the (±) configurations.

We thank Mrs. H. K. Tong for microanalyses.

[1/2048 *Received, 4th November*, 1971]

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[15] K. K. Chiu, H. H. Huang and (in part) L. H. L. Chia, *J.C.S. Perkin II*, 1972, 286.

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

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