The Conformation of Triphenylbismuthine and Tris-(*p*-chlorophenyl)-bismuthine in Benzene Solution

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Molar Kerr constant, dipole moment, and dielectric relaxation measurements of $(p\text{-}C_6H_4Cl)_3Bi$ in benzene solution indicate a C–Bi–C bond angle of 93° and an average rotation (in the same sense) of each C_6H_4Cl group about its C–Bi bond of 45° from a model in which the aromatic planes intersect along the symmetry axis. A similar configuration in solution is likely in the case of Ph_3Bi, for which a C–Bi–C bond angle of 94° has been reported in the solid state.

PREVIOUSLY[1] we reported the dipole moment and molar Kerr constant of triphenylbismuthine in benzene (0 D † and $7{\cdot}2 \times 10^{-12}$ respectively) and interpreted the data in terms of a molecular model having the three C–Bi bonds coplanar and each C–Bi–C bond angle equal to 120°. This configuration about the Bi atom was based on a crystal-structure determination by Wetzel[2] and seemed consistent with the zero dipole moment measured. However more recently Hawley and Ferguson[3] have shown from three-dimensional *X*-ray data that triphenylbismuthine is pyramidal in the solid state with a mean C–Bi–C bond angle of 94°. Hence in order to clarify the conformation in solution we have measured the dielectric loss of triphenylbismuthine in benzene, as well as the dipole moment, Kerr effect, and dielectric loss of tris-(*p*-chlorophenyl)bismuthine, also in benzene.

EXPERIMENTAL

Materials, Apparatus, etc.—Triphenylbismuthine was recrystallized from benzene. Commercial tris-(*p*-chlorophenyl)bismuthine was not further purified. Thiophen-free benzene, as solvent, was dried (Na) before use. Static electric dipole moments, electric birefringences, and incremental dielectric loss tangents were measured with apparatus and procedures previously described.[4-8]

RESULTS

Triphenylbismuthine.—Dielectric relaxation measurements for weight fractions up to 0·05 indicate that $10^3\Delta$ *tan* δ is $0{\cdot}00 \pm 0{\cdot}04$ (at 3·109 GHz) and $0{\cdot}00 \pm 0{\cdot}06$ (at 9·400 GHz). These results confirm that Ph_3Bi is non-polar in benzene solution as reported earlier.[1] If a relaxation time of *ca.* 50×10^{-12} s is assumed, the maximum probable error in the dipole moment is 0·2 D. The Kerr constant of Ph_3Bi was originally determined with a visual apparatus, so photoelectric techniques were used to check the earlier measurements. *B* was again found to be indistinguishable from the solvent and the resulting value of δB_1 $(0{\cdot}0 \pm 0{\cdot}1)$ leads to an experimental molar Kerr constant of $(7 \pm 8) \times 10^{-12}$.

*Tris-(*p*-chlorophenyl)bismuthine.*—The static dipole moment measurements indicate a polar structure for this solute in benzene and this is confirmed by the moment obtained from dielectric loss measurements (Table 1). The difference between μ(static) and μ(loss) is equivalent to *ca.* 60 cm³ and could arise from experimental error and/or high atomic polarization. The apparent absence of such atomic polarization in Ph_3Bi may not be significant since the higher polarity of the C_6H_4Cl group than Ph could lead to a greater atomic contribution to the polarization if ' flapping ' occurs about the Bi–C bond. There is also the possibility of significant solute–benzene interactions in these molecules and the true molecular moments may differ somewhat from the measured values. Consideration of probable errors leads to a molar Kerr constant of $(27 \pm 10) \times 10^{-12}$ for $(p\text{-}C_6H_4Cl)_3Bi$ in benzene.

TABLE 1

Incremental dielectric constants, densities, refractive indices, Kerr constants, and loss tangents for solutions of tris-(*p*-chlorophenyl)bismuthine in benzene at 25 °C

10^5w_2	702	1149	1644	2021	2684
$10^4\Delta\varepsilon$	128	195	262	343	465
$10^5\Delta d$	319	515	758	951	1243
$10^4\Delta n$	5	8	15	20	26
$-10^{10}\Delta B$	121	156	206	212	251
10^5w_2	702	1149	1497	1644	2021
$10^3\Delta \tan\delta$ (3·109 GHz)	1·319	1·851	2·574	2·638	3·276
$10^3\Delta \tan\delta$ (9·400 GHz)	0·703	1·250	1·407	1·563	1·798
10^5w_2	2072	2684	2770	3952	
$10^3\Delta \tan\delta$ (3·109 GHz)	3·531	4·552	4·722	6·806	
$10^3\Delta \tan\delta$ (9·400 GHz)	1·719	2·032	2·188	3·126	

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}70$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}462$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}090$; $\Sigma\Delta B/\Sigma w_2 = -0{\cdot}115$; $\psi^{3\cdot109} = \Sigma\Delta \tan\delta^{3\cdot109}/\Sigma w_2 = 0{\cdot}169$; $\psi^{9\cdot400} = \Sigma\Delta \tan\delta^{9\cdot400}/\Sigma w_2 = 0{\cdot}085$; $\alpha\varepsilon_1 = 1{\cdot}70$; $\beta = 0{\cdot}529$; $\gamma = 0{\cdot}060$; $\delta = -0{\cdot}280$; ${}_\infty P_2 = 261{\cdot}0$ cm³; $R_D = 113{\cdot}8$ cm³; μ(static) = 2·63 D (assuming ${}_DP = 1{\cdot}05R_D$); ${}_\infty({}_mK_2) = -27{\cdot}6 \times 10^{-12}$; μ(loss) = 2·0 D; $\tau = 72 \times 10^{-12}$ s.

DISCUSSION

The zero moment of Ph_3Bi may be due either to a planar C_3Bi nucleus or to each Ph–Bi group being effectively non-polar. The latter possibility is strongly favoured by the experimental moment of 2·6 D for $(p\text{-}C_6H_4Cl)_3Bi$. Further, nuclear quadrupole resonance spectra of ^{209}Bi have shown[9] that there is little change in configuration about the bismuth atom in the series Ph_3Bi,

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† 1 D = $3{\cdot}336 \times 10^{-30}$ C m.

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$(p\text{-}C_6H_4Cl)_3Bi$, and $(p\text{-}C_6H_4Br)_3Bi$. In terms of electron pair moments the resultant of the three Bi–C bonding electron pairs is equal in magnitude but opposite in direction to that of the bismuth lone pair. Thus, if it is assumed that the C–Bi–C bond angle is the same in both molecules and that μ ($Bi\text{–}C_6H_4\text{–}Cl$) is 1·59 D (the experimental value for chlorobenzene [10]), then the calculated value of the C–Bi–C angle from dipole moment data alone is 93°. This is in good agreement with the crystal structure of Ph_3Bi in which this angle lies between 92 and 96°, the mean being 94°.[3]

Using a C–Bi–C angle of 93° and previously reported polarisability data † for chlorobenzene ($b_1 = 14{\cdot}78$, $b_2 = 12{\cdot}55$, $b_3 = 8{\cdot}21$),[10] the C–H bond ($b_L = b_T = b_V = 0{\cdot}65$),[11] and the C–Bi bond ($b_L = 1{\cdot}87$, $b_T = b_V = 2{\cdot}99$),[1] we can calculate [6] ${}_mK_2$ for various average angles of rotation of the C_6H_4Cl groups in $(p\text{-}C_6H_4Cl)_3Bi$. In each calculated structure the C_6H_4Cl groups are rotated (in the same sense to preserve C_3 symmetry) through angles ϕ from a model having $\phi = 0°$, in which the C_6H_4Cl planes intersect along the symmetry axis. The calculated ${}_mK_2$ values (Table 2) are sensitively dependent upon ϕ and agreement between observed and calculated ${}_mK_2$ is achieved only for $\phi = 45 \pm 1°$. In Table 2 polarisabilities of the C–Bi bond derived from the empirical rule of Le Fèvre [1,12] have been used, but if this bond is assumed to be isotropic ($b_L = b_T = b_V = 2{\cdot}62$), the mean rotation ϕ emerges as $44 \pm 1°$. Thus for $(p\text{-}C_6H_4Cl)_3Bi$ in benzene solution we may conclude that on average the C_6H_4Cl rings are rotated through $45 \pm 2°$.

Table 2 also shows values of ${}_mK_2$ calculated for Ph_3Bi in a similar way. Because this molecule is non-polar ${}_mK_2$ is much less sensitive to changes in ϕ and comparison with the experimental value only allows us to exclude structures in which ϕ is smaller than 9° or greater than 77°. In the solid state Ph_3Bi possesses no overall symmetry owing to unequal rotations of the phenyl rings about the C–Bi bonds.[3] Such a distortion, attributable to crystal packing, seems unlikely in dilute solution where C_3 symmetry is to be expected. On this basis and from use of $(p\text{-}C_6H_4Cl)_3Bi$ as a guide it appears probable that ϕ for Ph_3Bi would be close to 45°.

TABLE 2

Calculated molecular polarisabilities and molar Kerr constants for triphenylbismuthine and tris-(*p*-chlorophenyl)bismuthine

	Ph_3Bi			$(p\text{-}C_6H_4Cl)_3Bi$		
$\phi°$	b_1	$b_2 = b_3$	$10^{12}{}_mK_2$	b_1	$b_2 = b_3$	$10^{12}{}_mK_2$
0	39·66	33·71	17·7	45·68	39·32	506
15	39·12	33·98	13·2	45·06	39·63	429
30	37·64	34·72	3·7	43·39	40·47	227
45	35·62	35·73	0·0	41·11	41·61	−38
60	33·60	36·74	4·9	38·82	42·75	−292
75	32·12	37·48	14·4	37·15	43·59	−471
90	31·58	37·75	19·0	36·54	43·89	−534

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† The polarisability semi-axis 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 10^{-24} cm^3 units.

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