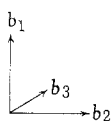
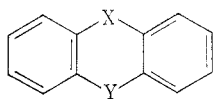


THE CONFIGURATION OF DIPHENYLENE DIOXIDE (DIBENZO-*p*-DIOXIN)

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Among heterocyclic compounds of general formula (I) the degree of folding about the X . . . Y line is dependent on the nature of the atoms X and Y.¹ Recently we have undertaken a systematic study of the preferred solute configurations and conformations of such molecules by analysis of their electric dipole moments and molar Kerr constants.^{2,3} From these data estimates of the dihedral angle ϕ may be obtained provided the anisotropic electron polarizabilities of the component units



C_6H_4 , $C_{ar}-X$, and $C_{ar}-Y$ are known.⁴ The $C_{ar}-X$ bond polarizabilities† differ considerably from the corresponding C (aliphatic)-X parameters, e.g. $b_L(C_{ar}-S) = 4.74$, $b_T(C_{ar}-S) = 0.60$, $b_V(C_{ar}-S) = 1.06$ (in thianthren)⁵ whilst $b_L(C-S) = 1.88$, $b_T(C-S) = 1.69$ (in dimethyl sulphide).⁶ The purpose of the present work is to specify the solution-state configuration of diphenylene dioxide (dibenzo-*p*-dioxin) (I; $X = Y = O$) and thence to derive, from the experimental molar Kerr constant, the principal polarizability semi-axes for the $C_{ar}-O$ bond appropriate to this type of molecule.

Experimental

Diphenylene dioxide (m.p. 119–120° from ethanol) was prepared from *o*-chlorophenol, anhydrous potassium carbonate, and copper powder using the method of Gilman and Dietrich.⁷

The apparatus, techniques, methods of calculation, and symbols have previously been described.^{8–11} Experimental results for solutions are shown in Tables 1 and 2.

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† Polarizabilities are quoted throughout in 10^{-24} c.c. units.

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Discussion

Neither the present, nor the previously reported¹²⁻¹⁵ measurements of dielectric constants can be used to distinguish dipole moments in the range from 0 to 0.63 D for diphenylene dioxide, since the atomic polarization component in ${}_D P$ cannot be estimated with certainty, and ${}_O P$ may have possible values from 0 to 8.2 c.c. An

TABLE I
INCREMENTAL KERR CONSTANTS, DIELECTRIC CONSTANTS,
DENSITIES, REFRACTIVE INDEXES, AND DIELECTRIC LOSS
TANGENTS OF SOLUTIONS AT 25°

<i>Diphenylene Dioxide in Carbon Tetrachloride</i>					
$10^5 w_2$	740	1173	1738	2462	3143
$10^{10} \Delta B$	17	25	34	51	63
$10^4 \Delta \epsilon$	66	106	160	225	284
$-10^5 \Delta d$	328	507	747	1059	1356
$10^4 \Delta n$	15	24	40	54	72
<i>Diphenylene Dioxide in Benzene</i>					
$10^5 w_2$	686	1416	2346	2887	3430
$10^{10} \Delta B$	8	15	22	27	33
$10^4 \Delta \epsilon$	33	70	114	141	168
$10^5 \Delta d$	174	361	596	732	871
$10^4 \Delta n$	6	13	22	26	31
$10^3 \Delta \tan \delta^a$	—	0.00	—	0.17	0.40
<i>Diphenylene Dioxide in Cyclohexane</i>					
$10^5 w_2$	2137	4263			
$10^3 \Delta \tan \delta^a$	0.00	0.00			

^a Measurements at 9400 MHz.

TABLE 2
DIELECTRIC POLARIZATIONS, DIPOLE MOMENTS, AND MOLAR KERR CONSTANTS OF DIPHENYLENE
DIOXIDE
(from observations on solutions at 25°)

Sol-vent	$\alpha \epsilon_1$	β	γ	δ	${}_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) ^a	$10^{12} {}_\infty ({}_m K_2)$
CCl ₄	0.909	-0.273	0.152	24.9	60.7	53.6	0.46	42(±3)
C ₆ H ₆	0.489	0.291	0.060	2.39	61.5	53.2	0.52	39(±3)

^a Calculated on the basis that ${}_D P = 1.05 R_D$.

X-ray study by Wood, McCale, and Williams,¹⁶ in 1941, showed, using symmetry considerations, that the molecule is most likely planar in the crystal state. The existence of small, real moments can be detected by microwave absorption measure-

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ments.¹⁷ Accordingly, solutions of diphenylene dioxide in benzene and in cyclohexane have been examined; the results are shown in Table 1. The observed incremental loss tangents $\Delta \tan \delta$ are very small in benzene and zero in cyclohexane. The values in cyclohexane are the more significant since there is less likelihood of solute-solvent interactions. We conclude therefore that diphenylene dioxide is in fact non-polar and hence has a configuration indistinguishable from planar. The experimental $_{\infty}K_2$ values are qualitatively in accord with a non-polar structure in which the anisotropy term θ_1 must be positive while the dipole term θ_2 is zero; the latter would have a negative value for $\mu \neq 0$ and $140^\circ < \phi < 180^\circ$.

From the molar Kerr constant in carbon tetrachloride we can extract estimates of the anisotropic polarizabilities of the $C_{ar}-O$ bonds appropriate for this type of molecule on the basis that (a) diphenylene dioxide is planar and (b) the angles $C_{ar}-C_{ar}-O$ are 120° . Since scattered light data are not available the principal molecular polarizabilities (b_i) cannot be directly obtained. We therefore adopt the alternative procedure of finding that set of C-O bond semi-axes which, in combination with the C_6H_4 group values³ [$b_L(C_6H_4) = b_T(C_6H_4) = 9.85$, $b_V(C_6H_4) = 6.14$], leads to a calculated $_mK$ in agreement with that observed. Le Fèvre *et al.*¹⁸ have recorded the C(aliphatic)-O bond axes as $b_L(C-O) = 0.89$, $b_T(C-O) = b_V(C-O) = 0.46$. These are not applicable as such to diphenylene dioxide but must be corrected to allow for delocalizations of the oxygen lone-pair electrons into the aromatic rings. The overall molecular polarizability exaltation resulting from such interactions, $\sum \Delta b_i (= 2.03)$, is derived from $\Delta_E P = 0.95 \Delta R_D$ where $\Delta R_D = R_D(\text{obs.}) - R_D$ [calculated¹⁹ as $2R_D(C_6H_4) + 4R_D(C(\text{aliphatic})-O)$]. We regard $\sum \Delta b/4$ as a polarizability exaltation increment directed along each C-O bond axis i.e. in the direction of maximum electromeric shift. The C(aliphatic)-O bond semi-axes are now corrected to give $b_L(C_{ar}-O) = 1.40$, $b_T(C_{ar}-O) = b_V(C_{ar}-O) = 0.46$. Additivity of the $C_{ar}-O$ link values with those of the C_6H_4 group leads to the calculated molecular polarizabilities $b_1 = 22.23$, $b_2 = 23.60$, $b_3 = 14.12$, and thence to $\theta_1 = 10.13 \times 10^{-35}$ and to $_mK(\text{calc.}) = 42.6 \times 10^{-12}$, which is in good agreement with the measured value (in CCl_4).

Acknowledgment

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