Dielectric Relaxation and Molecular Structure. VII. Structure of the Molecules of Diphenylene Dioxide Type

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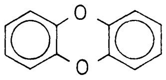
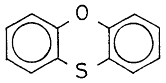
The dielectric constants and losses of diphenylene dioxide, phenoxathiin, thianthrene, xanthene and phenothiazine have been measured in dilute solution of benzene at the millimeter-wave frequency of 100 GHz at 20 °C. Diphenylene dioxide is found to have a very small dielectric relaxation time which is associated with the change in dipole orientation by the intramolecular change (butterfly motion). The dipole moment of this molecule is small but not considered to be zero. Similar to thianthrene, which has a folded structure about the S–S axis, diphenylene dioxide is also folded about the O–O axis or can easily have a folded structure. Phenoxathiin and the other two molecules have a folded structure and the dielectric relaxation times (at 100 GHz) reveal the effect of the butterfly-flapping motion associated with the barrier height for this internal motion.

Both planar and non-planar configurations of diphenylene dioxide have been concluded from measurements of the dipole moments. According to Bennett, Earp and Glasstone[1] it has a planar structure since their measurements indicated a zero moment, while Higasi[2] inferred that it would have a folded structure since its dipoe moment amounts to 0.64 D. The observed difference between ${}_{\infty}P_2$ and R_D may possibly be due to a rather large atomic polarization arising from the vibration of the molecule about the O–O axis. For this reason Smith[3] considered that diphenylene dioxide is planar.

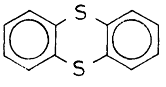
From a recent X-ray crystal analysis[4] it was revealed that the molecule of diphenylene dioxide is not fixed at the coplanar configuration in solid. In addition Davies and Swain[5] discovered a dielectric absorption due to the butterfly-flapping motion for diphenylene dioxide in polystyrene matrix.



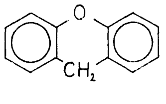
I: Diphenylene dioxide



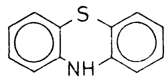
II: Phenoxathiin



III: Thianthrene



IV: Xanthene



V: Phenothiazine

Diphenylene dioxide (I) and related molecules (II), (III), (IV), and (V) were studied in order to obtain further information on the molecular configuration and intramolecular configurational changes.

Experimental

The frequencies of the dielectric measurements are 96.382 GHz (*ca.* 100 GHz) and 1 MHz (for the static value). Pure samples of diphenylene dioxide (mp 119 °C) and phenoxathiin (mp 56.5 °C) were kindly provided by Professor S. Uyeo, Kyoto University. Other compounds were obtained from commercial sources, and were purified by recrystallization. Benzene employed as the solvent was prepared in the usual way. The apparatus and experimental technique for dielectric measurements were the same as those used previously.[6]

TABLE 1. REFRACTIVE INDICES, ABSORPTIONS, DIELECTRIC CONSTANTS AND LOSSES OF DIPHENYLENE DIOXIDE IN BENZENE SOLUTION AT 96.382 GHz (20 °C)

Weight fraction	n	k	ε'	ε''
0.00000	1.5110	0.0022	2.2831	0.0068
0.02126	1.5156	0.0023	2.2970	0.0069
0.05325	1.5200	0.0029	2.3104	0.0087
0.08243	1.5247	0.0030	2.3248	0.0093
0.09217	1.5258	0.0032	2.3281	0.0098

The complex refractive indices $n^*=n-ik$, n and k being the real and imaginary parts, respectively, have been measured for three or four different dilute solutions of the same sample at 20 °C. The dielectric constants ε' and the losses ε'' were obtained from n and k by $\varepsilon'=n^2-k^2$ and $\varepsilon''=2nk$ (Table 1). The slopes of a' and a'' were obtained on the assumption that the linear relationship of ε' and ε'' with the concentration (weight fraction) w_2 exists.

$$\varepsilon' = \varepsilon_1' + a'w_2$$
$$\varepsilon'' = \varepsilon_1'' + a''w_2 \qquad (1)$$

In addition, a_0, a_D and b are the slopes for the static dielectric constant ε_0, the square of refractive index n_D (for the sodium D-line) and the specific volume v against the weight fraction, respectively (Table 2).

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1) G. M. Bennett, D. P. Earp, and S. Glasstone, *J. Chem. Soc.*, 1179 (1934).

2) K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **38**, 331 (1941).

3) J. W. Smith, "Electric Dipole Moments," Butterworths Sci. Publ., London (1955), pp. 244—245.

4) K. Osaki, Kyoto Univ. Private communication.

5) M. Davies and J. Swain, *Trans. Faraday Soc.*, **67**, 1637 (1971).

6) K. Chitoku, K. Higasi, M. Nakamura, Y. Koga, and H. Takahashi, This Bulletin, **44**, 992 (1971).

TABLE 2. SLOPES a_0, a', a'', a_G, a_D, AND b IN BENZENE SOLUTION (20 °C)

Substance	a_0	a'	a''	a_G	a_D	b
Diphenylene dioxide	0.496	0.447	0.038	0.418	0.254	−0.320
Phenoxathiin	1.035	0.521	0.135	0.486	0.380	−0.352
Thianthrene	1.470	0.511	0.111	0.498	0.434	−0.372
Xanthene	1.140	0.367	0.097	0.355	0.266	−0.281
Phenothiazine	3.227	0.676	0.311	0.638	0.480	−0.367

$$\varepsilon_0 = \varepsilon_{10} + a_0 w_2, \quad n_D^2 = n_{1D}^2 + a_D w_2$$
$$v = v_1 + b w_2, \quad \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \tag{2}$$

The total molar polarization of the solute at infinite dilution ($w_2 \rightarrow 0$) is approximately given by Halverstadt and Kumler[7] in the following form:

$${}_\infty P_2 \simeq M_2 \left\{ \frac{3 a_0 v_1}{(\varepsilon_{10}+2)^2} + (v_1+b)\frac{\varepsilon_{10}-1}{\varepsilon_{10}+2} \right\} \tag{3}$$

where M_2 is the molecular weight of the solute. If a_∞ and $\varepsilon_{1\infty}$ are used instead of a_0 and ε_{10}, respectively, the distortion polarization P_A+P_E instead of ${}_\infty P_2$ will be obtained by

$$P_A + P_E \simeq M_2 \left\{ \frac{3 a_\infty v_1}{(\varepsilon_{1\infty}+2)^2} + (v_1+b)\frac{\varepsilon_{1\infty}-1}{\varepsilon_{1\infty}+2} \right\} \tag{4}$$

Similarly, the molecular refraction for the D-line R_D will be given by

$$R_D \simeq M_2 \left\{ \frac{3 a_D v_1}{(n_{1D}^2+2)^2} + (v_1+b)\frac{n_{1D}^2-1}{n_{1D}^2+2} \right\} \tag{5}$$

The atomic polarization P_A will be estimated roughly by $(P_A+P_E)-R_D$ if $R_D \approx P_E$ and $\varepsilon_{10} \approx \varepsilon_{1\infty} \approx n_{1D}{}^2$ (see Appendix 1). Thus we have an estimate for P_A by

$$P_A \simeq M_2 \left\{ \frac{3(a_\infty - a_D) v_1}{(\varepsilon_{10}+2)^2} \right\} \tag{6}$$

The relaxation time of the solute τ is calculated by use of two equations:[8]

$$\tau = \frac{1}{\omega} \frac{a''}{a'-a_\infty} \equiv \tau(1) \tag{7}$$

$$\tau = \frac{1}{\omega} \frac{a_0-a'}{a''} \equiv \tau(2) \tag{8}$$

If one assumes a_∞ to be equal to a_D, the values τ (1) will become much smaller than τ (2); and if a_∞ is given by a_G defined in Eq. (9), τ (1) will become identical with τ (2).

$$a_\infty \simeq a_G \equiv a' - \frac{(a'')^2}{a_0 - a'} \tag{9}$$

Perhaps a_G evaluated from a' and a'' at a very high frequency (100 GHz) would be a good estimate for a_∞ and is often close to a_∞ obtained from Cole-Cole plots. Thus Eq. (4) can be rewritten by using a_G instead of a_∞:

$$P_A + P_E \simeq M_2 \left\{ \frac{3 a_G v_1}{(\varepsilon_1'+2)^2} + (v_1+b)\frac{\varepsilon_1'-1}{\varepsilon_1'+2} \right\} \tag{10}$$

where $\varepsilon_{1\infty}$ is also replaced with ε_1'.

The dipole moment μ is estimated by

$$\mu = \left\{ \frac{9kTM_2}{4N\pi} \left({}_\infty P_2 - (P_A+P_E) \right) \right\}^{1/2} \tag{11}$$

On the assumption that $\varepsilon_{10} \approx \varepsilon_1'$ for non-polar solvents we can obtain approximately

$${}_\infty P_2 - (P_A+P_E) \simeq M_2 \left\{ \frac{3(a_0 - a_\infty) v_1}{(\varepsilon_1'+2)^2} \right\} \tag{12}$$

Therefore

$$\mu^2 \simeq \frac{27kTM_2 v_1}{4N\pi} \frac{a_0 - a_\infty}{(\varepsilon_1'+2)^2} = B^2(a_0 - a_\infty) \tag{13}$$

where

$$B = \left\{ \frac{27kTM_2}{4N\pi d_1} \right\}^{1/2} \frac{1}{(\varepsilon_1'+2)} \tag{14}$$

and d_1 is the density of the solvent. Equations (13) and (14) are equivalent to the corresponding formulae of the previous work[8,9] (see Appendix 2). The relaxation times and polarization data are given in Tables 3 and 4, respectively.

TABLE 3. TWO RELAXATION TIMES $\tau(1)$, $\tau(2)$ AND DIPOLE MOMENTS BASED ON Eqs. (3), (10) AND (11) TOGETHER WITH LITERATURE VALUES. $\tau(1)$ IS OBTAINED ON THE ASSUMPTION OF $a_\infty = a_D$ (20 °C)

Substance	$\tau(1)$ ps	$\tau(2)$ ps	μ D	μ(lit.) D
Diphenylene dioxide	0.3	2.1	0.36	0[a], 0.64[b]
Phenoxathiin	1.6	6.3	0.99	1.09[b], 1.00[c], 0.97[d]
Thianthrene	2.4	14.3	1.37	1.41[e], 1.57[f], 1.70[g]
Xanthene	1.6	13.2	1.13	1.14[h], 1.29[i]
Phenothiazine	2.6	13.6	2.15	2.16[c]
Anthrone(25 °C)	—	21.2	—	3.63[i]
Xanthone(25 °C)	—	21.0	—	2.95[i]

a) Ref. 1.
b) Ref. 2.
c) Ref. 12.
d) Ref. 10.
e) W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, **1**, 337 (1933).
f) I. G. M. Campbell, C. G. Le Fevre, R. J. W. Le Fevre and E. E. Turner, *J. Chem. Soc.*, **1938**, 404.
g) E. Bergmann and M. Tshundnowsky, *Chem. Ber.*, **B65**, 457 (1938).
h) Ref. 15.
i) A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman and Co., San Francisco (1963).

TABLE 4. TOTAL MOLAR POLARIZATION ${}_\infty P_2$, DISTORTION POLARIZATION P_A+P_E OBTAINED FROM Eq. (10) AND MOLECULAR REFRACTION R_D

Substance	${}_\infty P_2$ (cm^3)	P_A+P_E (cm^3)	R_D (cm^3)	P_A (cm^3)	P_A/R_D (%)
Diphenylene dioxide	62.1	59.4	53.2	6.2	11.7
Phenoxathiin	85.7	65.2	60.7	4.5	7.4
Thianthrene	108.8	69.7	66.5	3.2	4.8
Xanthene	85.4	58.8	55.1	3.7	6.7
Phenothiazine	165.7	69.7	63.3	6.4	10.1

Discussion

The dielectric relaxation time of diphenylene dioxide (I) in benzene solution is 2.1 ps (calculated as $\tau(2)$). If $a_\infty \simeq a_D = 0.254$ is assumed, $\tau(1)$ will be only 0.3 ps. In contrast to this, anthrone (VI) and xanthone

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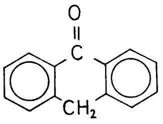
[7] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

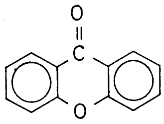
[8] K. Higasi, This Bulletin, **39**, 2157 (1966).

[9] K. Higasi and O. Kiyohara, *Bull. Inst. Appl. Elect.*, **18**, 24 (1966).

(VII) have much larger relaxation times 21.2 and 21.0 ps, respectively, in benzene solution.



VI: Anthrone



VII: Xanthone

The small values observed for τ of diphenylene dioxide are certainly not due to the change of dipole orientation by rotation of the whole molecule.

When there exist two independent paths from the same initial state to the same final state with opposite directions of the molecular dipole, a single relaxation time τ will be observed which is related to the relaxation times τ_m and τ_b for the two individual processes by

$$\frac{1}{\tau}=\frac{1}{\tau_m}+\frac{1}{\tau_b} \tag{15}$$

Suppose that Eq. (15) is valid in this case and some internal process such as the butterfly motion (with a small τ_b value) is considered. If we assume $\tau_m=21$ ps for molecular rotation and $\tau_b=2.5$ ps for butterfly motion, we shall obtain from Eq. (15) $\tau=2.2$ ps which compares well with $\tau(2)=2.1$ ps. This would be an evidence for a slightly folded structure in the equilibrium state.

The dipole moment of diphenylene dioxide is calculated to be 0.36 D from Eqs. (3), (10), and (11). Or, we may calculate it to be 0.38 D from Eq. (A-4) on the basis of the relaxation time $\tau(2)=2.1$ ps. Both values are smaller than 0.64 D obtained from the previous measurement of the static dielectric constant.[2] However, they are not zero so that one may conclude that very likely the molecule of diphenylene dioxide would have a non-planar configuration. At the same time one may notice that the atomic polarization of this molecule is 6.2 cm^3, *i.e.*, about 12% of R_D; diphenylene dioxide has a rather large atomic polarization as Smith[3] pointed out.

The dielectric relaxation time of phenoxathiin is calculated by Eq. (8) to be $\tau(2)=6.3$ ps which compares favorably with 7.0 ps (Hufnagel *et al.*[10]), but is somewhat less than 10 ps given by Anderson and Smyth.[11] These small values of τ for phenoxathiin are related to the butterfly motion. The dipole moments of phenoxathiin in benzene at room temperature from static measurement are 1.09 D (Higasi[2]), 0.97 D (Hufnagel, Klages, and Knobloch[10]) and 1.00 D (Leonard and Sutton[12]). The present work gives the total dipole moment 0.99 D on the basis of Eqs. (3), (10) and (11).

The folded structure of thianthrene has been well established by means of both X-ray crystal analysis[13,14] and dielectric measurements in solution.[3] Anderson and Smyth[11] found the dielectric relaxation time to be 31, 24, and 19 ps at 20, 40, and 60 °C, respectively. In the present experiment, however, it is only 14.3 ps at 20 °C. This seems to indicate the imporatnce of the butterfly motion. Suppose $\tau_m=21$ ps and $\tau_b=50$ ps, τ will be given as 14.8 ps from Eq. (15). It is reasonable to assume a larger τ_b for thianthrene than τ_b of diphenylene dioxide, since thianthrene has a high barrier of inversion by the butterfly motion. The atomic polarization of thianthrene is about 5% of P_E.

From their Kerr effect studies, Aroney, Hoskins, and Le Fevre[15] concluded that the preferred solution-state conformation of xanthene is a slightly folded structure defined by a dihedral angle of 160° (±6°). The dielectric relaxation time of xanthene is somewhat smaller than that of anthrone and of xanthone. Phenothiazine obtained from thianthrene by replacing S by N–H group has also a smaller relaxation time 13.6 ps. In both cases the internal motion process seems to help decrease the relaxation time observed at 100 GHz.

The activation process of butterfly inversion of a folded molecule $C_6H_4{<}\begin{smallmatrix}X\\Y\end{smallmatrix}{>}C_6H_4$ may be described as a change of the valence angles of the central atoms X and Y, that is, from the valence angles, ϕ_X and ϕ_Y, of the folded configuration at an equilibrium state to the valence angles, ψ_X and ψ_Y,[16] at the coplanar configuration. The energy U needed to change the two valence angles from ϕ_X and ϕ_Y to ψ_X and ψ_Y will be approximated by

TABLE 5. DIHEDRAL ANGLES θ, VALENCE ANGLES ϕ, BOND LENGTHS r AND ANGLE BENDING FORCE CONSTANTS H

Atoms X	Atoms Y	θ (°)	ϕ_X (°)	ϕ_Y (°)	r (C–X) Å	r (C–Y) Å	H_{CXC} mdyn/Å	H_{CYC} mdyn/Å
O	O	172[a]	115[a]		1.43[b]		0.30[c]	
O	S	138[d]	118[d]	98[d]	1.40[d]	1.75[d]	0.30[c]	0.157[c]
S	S	128[e]	100[e]		1.773[e]		0.157[c]	
O	C	160[f]	118[d]	109[g]	1.43[b]	1.51[g]	0.30[c]	0.257[h]
S	N	153[i]	100[i]	122[i]	1.77[i]	1.406[i]	0.157[c]	0.20[j]

a) Ref. 4.
b) Ref. 2.
c) Ref. 17.
d) S. Hosoya, *Acta Crystallogr.*, **20**, 429 (1966).
e) Ref. 14.
f) Ref. 15.
g) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. Special Publ., No. 18, (1965).
h) H. Takahashi, *Nippon Kagaku Zasshi*, **83**, 978 (1962).
i) Ref. 19.
j) T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

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[10] V. F. Hufnagel, G. Klages, and P. Knobloch, *Z. Naturforsch.*, **17a**, 96 (1962).

[11] J. E. Anderson and C. P. Smyth, *J. Chem. Phys.*, **42**, 473 (1965).

[12] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948).

[13] H. Lynton and E. G. Cox, *J. Chem. Soc.*, **1956**, 4886.

[14] I. Rowe and B. Post, *Acta Crystallogr.*, **11**, 372 (1958).

[15] M. J. Aroney, G. M. Hoskins, and R. J. W. Le Fevre, *J. Chem. Soc.*, **1969**, 980.

[16] ψ can be obtained from $\cos\psi=1-2(1-\cos\phi)/(1-\cos\theta)$, where θ is the angle between the planes containing the two aromatic rings.

TABLE 6. ACTIVATION ENERGY (U) FOR INVESRION ESTIMATED FROM Eq. (16)

Atoms X	Atoms Y	$\Delta\phi_X$ (°)	$\Delta\phi_Y$ (°)	U kcal/mol	U (literature) kcal/mol
O	O	0.43		0.005	0.29,[2] 0[5]
O	S	15	10	3.9	1.20,[2] 2.63[5]
S	S	17		6.2	5.50,[2] 5.00[5]
O	C	3	2.5	0.2	
S	N	14	6	2.4	2.87[5]

$$U = (1/2)H_{\mathrm{CXC}}r_X^2\Delta\phi_X^2 + (1/2)H_{\mathrm{CYC}}r_Y^2\Delta\phi_Y^2 \qquad (16)$$

$$\Delta\phi_X = \phi_X - \phi_X, \quad \Delta\phi_Y = \phi_Y - \phi_Y$$

where H_{CXC} and H_{CYC} are the angle bending force constants and r_X and r_Y the bond lengths of X and Y atoms, respectively. The literature values of θ, ϕ, r, and H are given in Table 5 and the values U thus estimated in Table 6. For diphenylene dioxide, $\Delta\phi_0=0.43°$, r(C–O)$=1.43$ Å[2] and $H_{\mathrm{COC}}=0.30$ mdyn/Å[17] Eq. (16) gives $U=0.005$ kcal/mol. This is in accordance with the small value 2.5 ps assumed for τ_b. For the inversion barrier of thianthrene we can obtain 6.2 kcal/mol by using the values of $\Delta\phi_S=17°$, r(C–S)$=1.773$ Å[14] and $H_{\mathrm{CSC}}=0.157$ mdyn/Å.[17] The conjugation energy at the coplanar position should decrease these barrier heights, while the viscosity of the solvent would hinder the inversion.

The observed relaxation time for phenoxathiin, 6.3 ps, is close to an average of 2.1 ps (diphenylene dioxide) and 14.3 ps (thianthrene). The inversion barrier of phenoxathiin 3.9 kcal/mol lies between those for the two molecules.

The molecular dipole of phenoxathiin has two components, $\mu_{//}$ directed along the O–S axis for the overall rotation and $\mu_\perp$ perpendicular to the same axis for the butterfly motion. Hence, two dipolar relaxations should be observed; however, the absorption due to the butterfly motion predominates overall rotation since $(\mu_\perp/\mu_{//})^2$ is estimated to be very large, *i.e.*, 12: 1.[5] One can say with certainty that the observed relaxation time at 100 GHz corresponds to that of butterfly motion.

The relaxation time of xanthene is 13.2 ps, which is smaller than that of xanthone and of anthrone by 30—40%. From the analysis of its dipole moment one would expect two dipolar relaxations, the ratio of their intensities $(\mu_\perp/\mu_{//})^2$ being about 1: 20. The observed lowering of the relaxation time might be explained in the following way. The inversion barrier of xanthene is less than 1 kcal/mol and hence the relaxation time associated with the butterfly motion would be similar to τ_b for diphenylene dioxide. If one assumes the relaxation time for the overall rotation to be 20 ps and that for the butterfly motion 2.5 ps, one can estimate $\tau(2)$ obtainable for any frequency for any value of $(\mu_\perp/\mu)^2=C_2$ by using the method given in the preceding paper.[18] The result of calculations for 100 GHz is shown by curve A and that for 10 GHz by curve B in Fig. 1. At the frequency of this experiment, $\tau(2)$ is equal to 13.2 ps for $C_2=0.1$ (*cf.*, 19.4 ps for $C_2=0.1$ at 10 GHz). Consequently, the lowering in relaxation time might be due to the butterfly inversion, although the dipole component associated with this internal process is not significant enough.

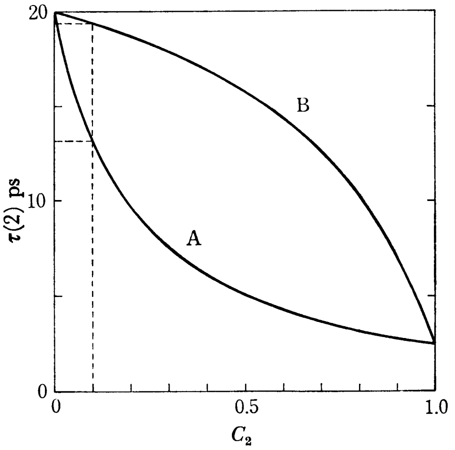

Fig. 1. Dependence of the relaxation time $\tau(2)$ upon the weight of internal process C_2.
A: 100 GHz, B: 10 GHz.

For phenothiazine we find a similar lowering in the relaxation time. Phenothiazine is assumed to have a quasi-equatorial form from X-ray evidence.[19] There are two independent relaxation processes, overall and internal. The dipole component associated with the internal motion is larger than that for xanthene, while the barrier height (see Table 6) for the inversion is found to be much larger. Increase in the above two quantities causes cancellation of the effects so that very likely the relaxation time is lowered to a similar extent to that for xanthene.

Concluding Remarks

1. Atomic polarization as well as the dipole moment of the solute can be obtained from the dilute solution method by use of extended Halverstadt-Kumler equations.
2. Atomic polarization is found to be large for diphenylene dioxide and phenothiazine.
3. Discussion is given for a small but non-zero polarity of diphenylene dioxide. As indicated by X-ray evidence[4] this molecule perhaps is folded about the O–O axis having two shallow potential minima. Or possibly it has one minimum with a very flat potential curve.
4. Thianthrene, phenoxathiin and phenothiazine are folded molecules with two potential minima. Xanthene also has a folded structure either with one potential minimum or two minima.
5. The molecules of $C_6H_4\langle{}^{X}_{X}\rangle C_6H_4$ type have the single relaxation time τ which is related to the relaxation time τ_m and τ_b by Eq. (15).
6. The molecules of $C_6H_4\langle{}^{X}_{Y}\rangle C_6H_4$ type have two

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[17] M. Hayashi, *Nippon Kagaku Zasshi*, **77**, 1804 (1956).

[18] K. Higasi, Y. Koga, and M. Nakamura, This Bulletin, **44**, 988 (1971).

[19] J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, *Chem. Commun.*, **1968**, 1656.

dipolar relaxations. The average relaxation time $\tau(2)$ is a function of $(\mu_{/\!/}/\mu)^2=C_2$ and the frequency of the measurement.[18]

Appendix

I. P_A is obtained by subtracting Eq. (5) from Eq. (4) and neglecting Δ^2.

$$P_A \simeq M_2\left\{\frac{3a_\infty v_1}{(\varepsilon_{1\infty}+2)^2}-\frac{3a_D v_1}{(n_{1D}^2+2)^2}+(v_1+b)\right.$$
$$\left.\times\left[\frac{(\varepsilon_{1\infty}-1)}{(\varepsilon_{1\infty}+2)}-\frac{(n_{1D}^2-1)}{(n_{1D}^2+2)}\right]\right\}$$
$$\simeq M_2\left\{\frac{3[(a_\infty-a_D)(\bar\varepsilon_1+2)-2\Delta(a_\infty+a_D)]v_1}{(\bar\varepsilon_1+2)^3}\right.$$
$$\left.+\frac{6\Delta(v_1+b)}{(\bar\varepsilon_1+2)^2}\right\} \quad \text{(A-1)}$$

where

$$\bar\varepsilon_1=\frac{1}{2}(\varepsilon_{1\infty}+n_{1D}^2) \quad \text{(A-2)}$$

and

$$\Delta=\frac{1}{2}(\varepsilon_{1\infty}-n_{1D}^2) \quad \text{(A-3)}$$

For $n_{1D}{}^2=\varepsilon_{1\infty}$, Eq. (6) follows immediately from (A-1).

II. For dilute solution of a polar molecule in a non-polar solvent, there is a familiar equation between the dipole moment μ and the relaxation time τ.[20]

$$\mu^2=\frac{6750kT}{NC\pi}\,\frac{\varepsilon''}{(\varepsilon'+2)^2}\,\frac{1+(\omega\tau)^2}{\omega\tau} \quad \text{(A-4)}$$

where C is the concentration in mol liter^{-1}. Introducing Eq. (8) for τ in Eq. (A-4) and assuming $\varepsilon'\approx\varepsilon_1'$, we have

$$\mu^2=\frac{6750kT}{N\pi}\,\frac{1}{(\varepsilon_1'+2)^2}\,\frac{(a_0-a')^2+(a'')^2}{a_0-a'} \quad \text{(A-5)}$$

Therefore

$$\mu^2=\frac{27000kT}{4N\pi}\,\frac{1}{(\varepsilon_1'+2)^2}(a_0-a_\infty)=B^2(a_0-a_\infty) \quad \text{(A-6)}$$

where

$$B=\left\{\frac{27000kT}{4N\pi}\right\}^{1/2}\frac{1}{(\varepsilon_1'+2)} \quad \text{(A-7)}$$

The value of B in (A-7) differs from that in Eq. (14) since the concentration of the solute is expressed in units of molar concentration in (A-7) and in units of weight fraction in Eq. (14).[8,9] If $a_D=a_\infty$, then

$$\mu=B(a_0-a_D)^{1/2} \quad \text{(A-8)}$$

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[20] N. E. Hill, W. E. Vaughan, A. H. Price ,and M. Davies, "Dielectric Properties and Molecular Behaviour," Van Nostrand, Rheinhold, London, (1969), p. 289.