Relaxation Time Studies of Excited Oxido-Substituted p-Oligophenylenes in Different Solvents*

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Effective volumes, moments of inertia and Debye relaxation times in the excited state were determined for some oxido-substituted p-oligophenylenes by the method of fluorescence depolarization in nonpolar and polar solvents of different viscosities.

1. Introduction

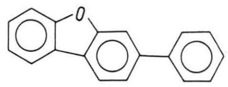
Oxido-substituted p-oligophenylenes derivatives of dibenzofuran, are bridge-substituted prolate oligophenylenes. Orthosubstitution leads to the bridging of two phenyl rings and constrains the molecule in the planar configuration. For example, dioxido-p-terphenyl and trioxido-p-quaterphenyl have highly resolved vibronic spectra in n-hexane at 77 K [1]. The long-wave absorption and fluorescence spectra of p-oligophenylenes are intense and long-axis polarized [2].

These compounds of various lengths, having relatively short mean lifetimes, are particularly useful for investigations of rotational motions in liquid solutions. The aim of this work is to study the relaxation times of these luminescent molecules in nonpolar and polar solvents of different viscosities, and to find their effective volumes and moments of inertia.

2. Experimental

Oxido-substituted p-oligophenylenes (I–V):

I



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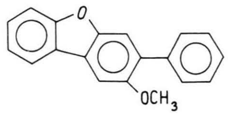

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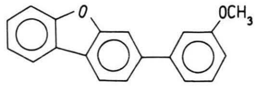

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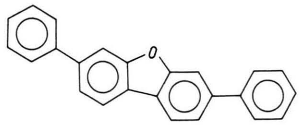

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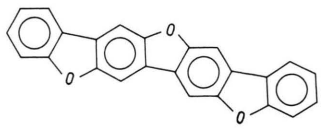

were synthesized by Wirth et al [3]. The fluorescence anisotropy r and the mean lifetimes τ_F were measured photoelectrically [4–6] in different (spectrograde) pure solvents. The accuracy of the τ_F determination by phase measurements was ± 0.1 °.

The absorption and fluorescence spectra and the quantum yields of the compounds examined in different solvents will be comprised in a separate paper. The viscosities of the solvents were determined by means of a Höppler viscosimeter.

3. The Debye Relaxation Time of Excited Molecules

In a liquid medium, the anisotropy of the transition dipole moment of a molecular system excited by linearly polarized light decays as a result of the Brownian rotational motion (depolarization). Assuming prolate ellipsoidal luminescent molecules, the fluorescence anisotropy r as a function of the viscosity η is given by the expression [7]

$$\frac{r_0}{r} - 1 = U\,, \tag{1}$$

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Table 1. Fluorescence anisotropies r and mean decay times τ_F (in ηs) of oxido-substituted-p-oligophenylenes in solvents

No.	Solvent	Viscosity $\eta \times 10^3$ [kg m^{-1} s^{-1}] at 296.5 K	Solute I			Solute II		
			r (322.5) [a]	τ_F (313) [a]	r_0 0.2992	r (342.5)	τ_F (313)	r_0 0.3078
1	n-hexane	0.32	0.0061	1.31	V [b]	0.0067	1.29	V
2	chloroform	0.54	0.0145	0.97	200	0.0157	1.16	237
3	benzene	0.66	0.0114	1.20		0.0113	1.37	
4	cyclohexane	1.01	0.0129	1.34	A	0.0134	1.39	A
5	dioxane	1.45	0.0174	1.38	0.01	0.0212	1.48	0.009
6	n-butanol	2.60	0.0216	1.44	I [c]	0.0247	1.45	I
7	n-heptanol	4.52	0.0394	1.44	4.6	0.0458	1.48	4.6
8	ethylene glycol	17.15	0.1342	1.33		0.1435	1.46	
9	propylene 1,2-glycol	45.88	0.1990	1.35	χ^2 [d]	0.2004	1.46	χ^2
10	cyclohexanol	61.92	0.1674	1.22	25.2991	0.1849	1.40	24.1874

[a] Excitation wavelengths in nm; [b] Effective volume V in 10^{-30} m^3; [c] Effective moment of inertia I in 10^{-40} kg · m^2; [d] Mean

where

$$U = \frac{\dfrac{kT}{V} \cdot \dfrac{\tau_F}{\eta}}{1 + A \dfrac{kT}{V} \dfrac{\tau_F}{\eta}}, \tag{2}$$

$$A = \frac{I}{6 k T \tau_F^2}. \tag{3}$$

$r_0 = 0.6 \cos^2 \beta - 0.2$ is the fundamental fluorescence anisotropy, τ_F the mean lifetime, β the angle between the absorption and fluorescence dipoles, $V = (4/3)\, \pi a^3 \varphi$ the effective volume and φ a fitting parameter dependent on the shape of the luminescent molecule, I is the effective moment of inertia.

With increasing η, (1) changes into the known Perrin equation [8] with linear dependence of $1/r$ upon $1/\eta$.

For rigid spherical molecules Debye [9] has derived the following relation for the relaxation time:

$$\tau_D = 3\, V\eta / kT, \tag{4}$$

where V may be here expressed as $(4/3)\, \pi a^3 \psi$ with ψ being a fitting parameter.

Debye's theory [9], as well as that of Perrin [8] and ours [7], describes the friction of molecules with the surroundings by the macroscopic viscosity η, applying Stokes' law for the friction forces acting on the sphere or the ellipsoide. The introduction of an internal (microscopic) molecular viscosity might be more proper, a suitable definition, however, has not been formulated as yet. The parameter ψ has been found to be a function of the dimensions and shape of the solute molecule [10]. It depends in general on the ratio of the solute-to-solvent molecular volumes and tends to unity when the volume of the solute molecules exceeds significantly that of the solvent. In such cases, the solute molecule behaves as a macroscopic particle satisfying (4) [10, 11].

If the factors φ and ψ are dropped in (2) and (4), we obtain for ellipsoidal prolate molecules

$$\tau_D = 3\, \tau_F \left(\frac{r}{r_0 - r} - A \right). \tag{5}$$

4. Results and Discussion

The values of r and τ_F measured in solvents of different viscosities are listed in Table 1, the values r_0 and V being found from the linear Perrin dependence of $1/r$ versus $1/\eta$ in the range of high viscosities. Mention should be made that for the examined solute substances the mean lifetime in chloroform is markedly lower than that in other solvents (solute IV is an exception). This is due to the heavy atom (chlorine) effect causing an enhancement in the probability of the S–T transition, which means a decrease in τ_F of state S_1. A similar effect was observed with p-terphenyl in chloroform [4].

The value of A could be found by fitting the combined relations (1) and (2). The values obtained of different viscosities η and other parameters.

Solute III			Solute IV			Solute V		
r (322)	τ_F (313)	r_0 0.3091	r (343)	τ_F (333)	r_0 0.3521	r (356)	τ_F (333)	r_0 0.2526
0.0069	1.27	V 290	0.0250	0.90	V 498	0.0093	1.78	V 567
0.0156	1.05		0.0351	0.97		0.0236	1.27	
0.0136	1.21		0.0407	0.91		0.0228	1.33	
0.0184	1.25	A 0.007	0.0521	0.99	A 0.04	0.0195	1.78	A 0.0145
0.0224	1.46		0.0616	1.00		0.0480	1.32	
0.0324	1.42	I 3.3	0.0796	1.05	I 9.3	0.0299	2.00	I 11.5
0.0573	1.39		0.1219	1.03		0.0674	1.72	
0.1575	1.52		0.2531	0.95		0.1223	1.85	
0.2171	1.47	χ^2 5.5147	0.2964	1.08	χ^2 1.3063	0.1831	1.87	χ^2 17.4285
0.2041	1.38		0.2868	1.02		0.2325	1.41	

squares deviation of experimental points from the best fitted curve.

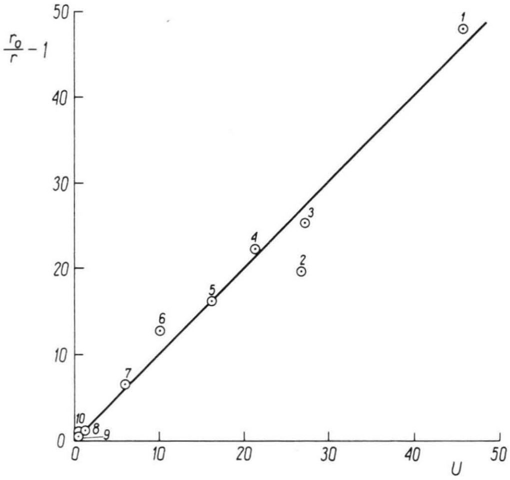

Fig. 1

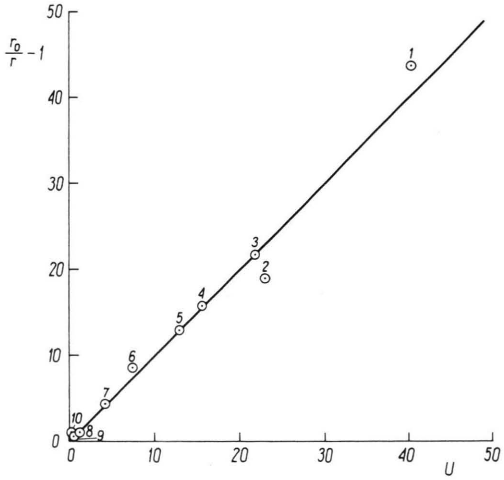

Fig. 3

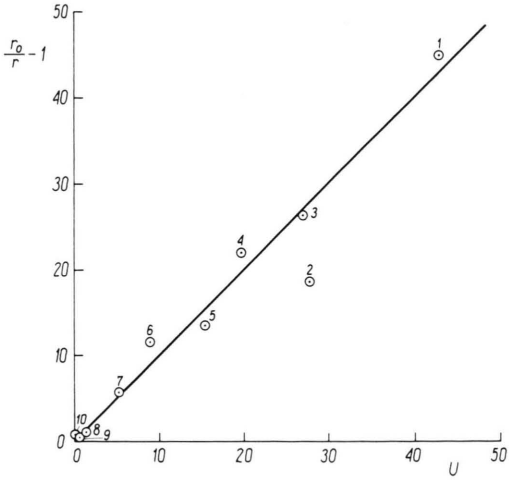

Fig. 2

Figs. 1–3. Dependence of $(r_0/r) - 1$ on the function U for substances I (Fig. 1), II (Fig. 2) and III (Fig. 3) in different solvents (according to Table 1).

for r_0, V, A and the moment of inertia I are given in Table 1 also.

The values of $r_0/r - 1$ should be correlated to the values U, calculated with the parameters A, V, η and the measured τ_F values corresponding to (2), by a straight line with 45° declination for all measured compounds.

This correlation is shown in Figs. 1–3 for the compounds I–III. A stronger deviation is found in Chloroform only.

The compound V, having stronger variations of τ_F in different solvents, gives a larger scattering of the experimental points around the correlation line. That may be explained by the microviscosity of the solvation shell around the luminescent centers. An other reason may be association effects as known in n-butanol [12–14], which may account for the difference between experiment and theory (see point 6 in Figs. 1–3 p.e.). Thus, specific (chemical) interactions in liquids may be the main reason for the deviation of the experimental points from the linear correlation corresponding to (1), (2).

The Debye relaxation time of the excited molecules may be elucidated from expression (5). Equation (4) implies that the relaxation time τ_D is proportional to the molecular volume and macroscopic viscosity of the solvent. A trouble with depolarisation effects by energy transfer can be neglected considering the small concentrations. Table 1 summarizes also effective moments of inertia I of some molecules carrying three or four phenyl rings, determined from the values of A and τ_F. They are nearly equal for substances I–III, but markedly higher for IV and V. The volume of compound IV is smaller than that of V, which is consistent with the structural model of these molecules. The values V, I and τ_D for the substances investigated refer undoubtedly not only to the luminescent molecule itself but also to its solvation shell.

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