

On the Determination of Moment of Inertia of Prolate Luminescent Molecules *

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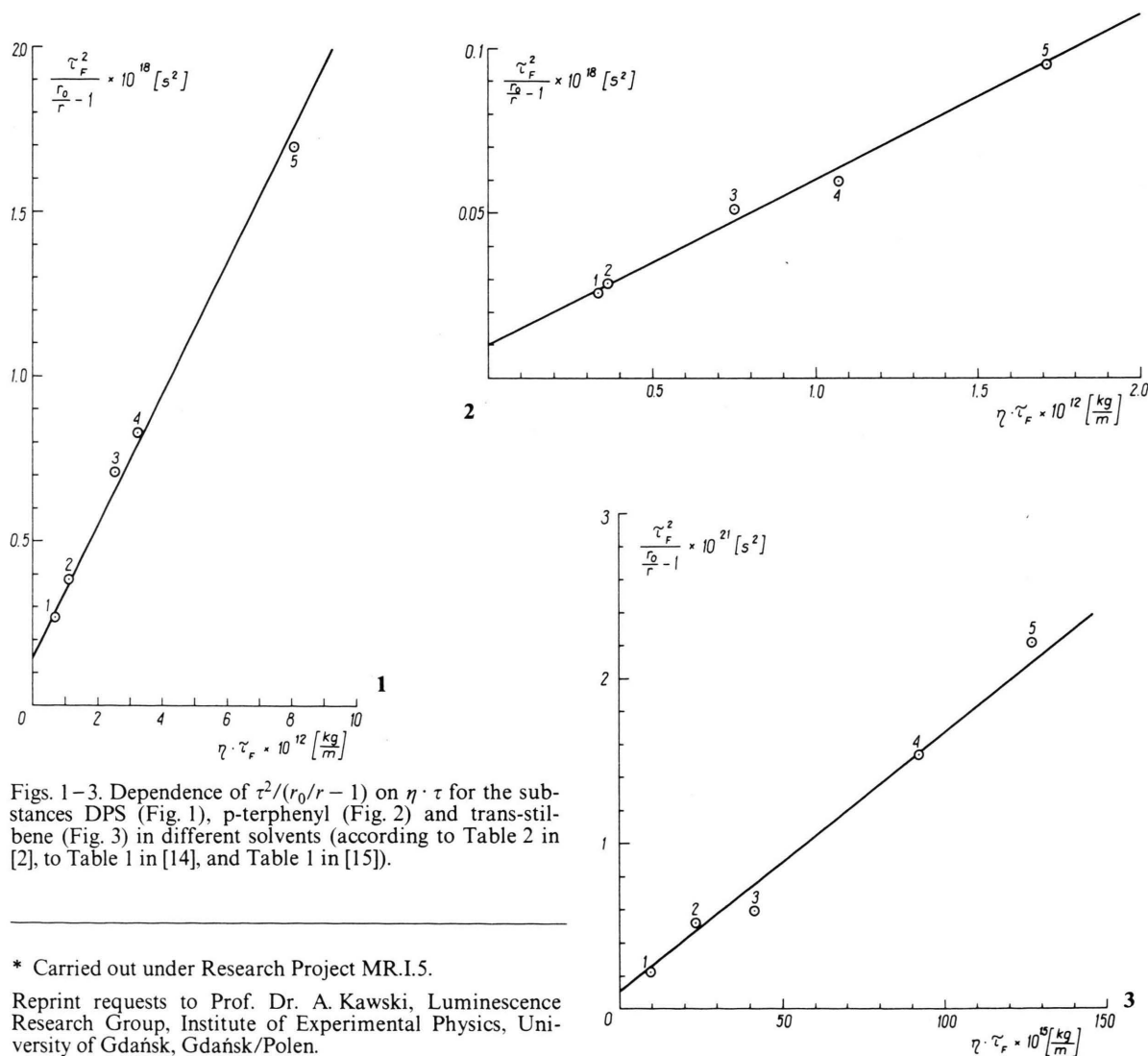
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The possibility to determine simultaneously the effective volume and the molecular moment of inertia on the basis of the generalized equation of the rotational motion of prolate luminescent molecules in solutions is discussed.

As has been shown recently [1, 2], for many luminescent molecules, whose transition moment lies along the long axis, Perrin's linear relation [3] between the inverse of the fluorescence anisotropy and the inverse of the viscosity does not hold, though all theories predict such a linear dependency [4–10]. A similar non-linear relation was observed but not explained by Memming [6] for 3-aminopyrene and by Griebel [11] for p-terphenyl and trans-stilbene. On varying the viscosity by changing the temperature or the solvent, or by mixing two solvents with different viscosities, a distinct change in the mean lifetime τ of the luminescent molecule occurs in most cases, a fact to which no particular significance has been attached so far.

Based on our generalized theory [12] on the rotational Brownian motion of prolate ellipsoidal luminescent mole-



Figs. 1–3. Dependence of $\tau^2/(r_0/r - 1)$ on $\eta \cdot \tau$ for the substances DPS (Fig. 1), p-terphenyl (Fig. 2) and trans-stilbene (Fig. 3) in different solvents (according to Table 2 in [2], to Table 1 in [14], and Table 1 in [15]).

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Table 1.

Compound	r_0	$K \times 10^{18}$ [s ²]	$m \times 10^6$ [kg ⁻¹ · m · s ²]	$I \times 10^{40}$ [kg · m ²] Eq. (5)	$V \times 10^{30}$ [m ³] Eq. (6)
DPS	0.3030	0.15	0.202	36.40	817
p-terphenyl	0.3450	0.01	0.05	2.45	205
trans-stilbene	0.3171	0.0001	0.016	0.0245	65

cules we have obtained the following expression for the fluorescence anisotropy r as a function of viscosity η and mean lifetime τ [13]:

$$r_0/r - 1 = u, \quad (1)$$

where

$$u = \frac{kT}{V} \frac{\tau}{\eta} \left/ \left(1 + A \frac{kT}{V} \frac{\tau}{\eta} \right) \right., \quad (2)$$

$$A = I/6 kT \tau^2. \quad (3)$$

$r_0 = 0.6 \cos^2 \beta - 0.2$ is the fundamental fluorescence anisotropy, $V = (4/3) \pi a^3 \phi$ the effective volume of the luminescent molecule, a its radius, ϕ a fitting parameter dependent on the shape of the molecule and I the effective moment of inertia.

Relation (1) has been shown in [13] to be well fulfilled for a series of oxido-substituted p-oligophenylenes; also effective moments of inertia have been determined therein based on (3) and assuming τ as a mean value in various solvents.

When τ does not change significantly in different solvents, the moment of inertia I determined from (3) is correct. However, if τ changes markedly in different solvents, (1) together with (2) and (3) should be written in the form

$$\frac{\tau^2}{r_0/r - 1} = K + m \eta \tau, \quad (4)$$

where

$$K = I/6 kT, \quad (5)$$

$$m = V/kT. \quad (6)$$

On plotting the left-hand side of (4) vs. $\eta \cdot \tau$ one obtains a straight line, from the slope of which the volume V and from its intersection with the ordinate the moment of inertia I can be found. Figures 1–3 show the experimental results according to (4) for diphenylenestilbene (DPS), p-terphenyl and trans-stilbene. For the two latter luminescent compounds, τ changes very strongly in different solvents [14, 15]. Table 1 summarizes the values of I and V determined by the well fulfilled formula (4).

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