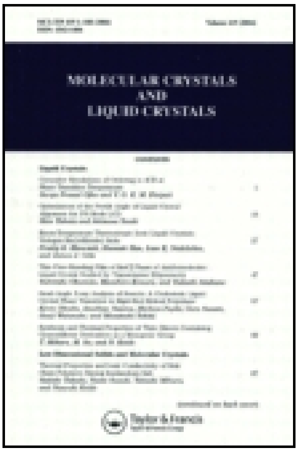

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# The Rotation Mobility of the Guest Molecules and its Reactivity in the Thermal Reaction in the Solid Matrix

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# THE ROTATION MOBILITY OF THE GUEST MOLECULES AND ITS REACTIVITY IN THE THERMAL REACTION IN THE SOLID MATRIX

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Abstract Characteristic times of the thermal reaction and the molecular rotation for the guest molecules have been measured in polystyrene films. Rotation mobility of molecules was determined from the relaxation of the light induced optical anisotropy of the photoselected samples. Close agreement of the activation energies and characteristic times of thermal reaction and molecular rotation was observed. By the comparison of the induced optical anisotropy of the initial and photoconverted molecules the angles of the rotation of the molecular dipole transition moment in the instant of the elementary act of the photochemical conversion were determined.

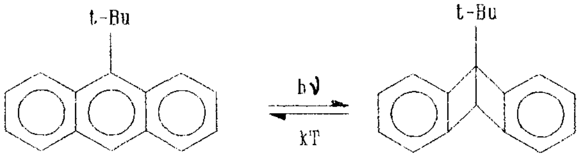
## INTRODUCTION

The molecular rotation mobility is known to correlate with the reactivity of molecules[1,2]. Commonly the molecular rotation mobility is measured by the spin label and fluorescent methods. As a result the correlation between molecular rotation and reaction of different molecules is considered. Photoselection makes it possible to investigate molecular rotation and reaction of the same molecules simultaneously.

Photoselection means that under irradiation of polarized light only preferably oriented molecules undergo photochemical reaction. As a result the macroscopic optical anisotropy of the sample appears[3,4]. The dark relaxation of this anisotropy is used for the determination of the rotation mobility of the molecules[5]. Comparison of the light induced optical anisotropy of the initial and photoconverted molecules allows to measure the rotations movements of molecules at the moment of the elementary act of the chemical reaction.

## EXPERIMENTAL RESULTS AND DISCUSSION

Light induced optical anisotropy of samples were observed in the course of the following reactions carried out in polystyrene films under irradiation of polarized light:



I II

III IV

R = 3 - pyrenil

photoisomerisation of 9-tert-butylanthracene (I) in its Dewar isomer (II)and photoisomerisation of pyrazolidone-(3)-azomethine imine (III) in aziridine (IV) (Figure 1).

The kinetics of the thermal relaxation of optical anisotropy of 9-tert-butylanthracene presented on Figure 2. The magnitudes of characteristic times for molecular rotation were calculated due to method developed earlier[6,7] and presented in Table 1.

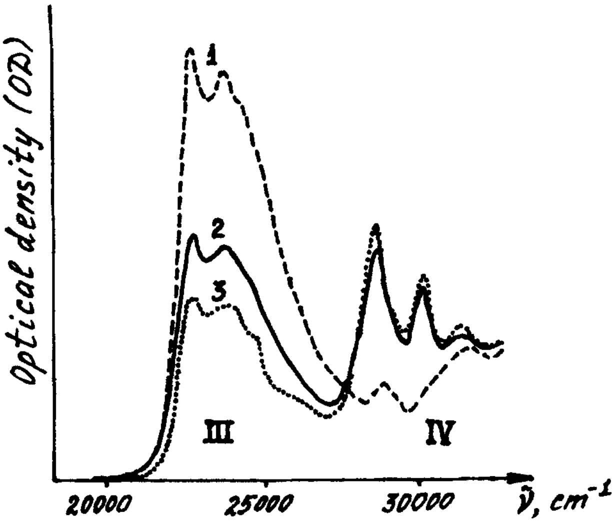


FIGURE 1 The spectra of III and IV in polystyrene film at room temperature: 1 - before irradiation, 2 and 3 - after irradiation with polarized light: polarizations of irradiating and probing light beams are mutually perpendicular (2) or parallel (3).

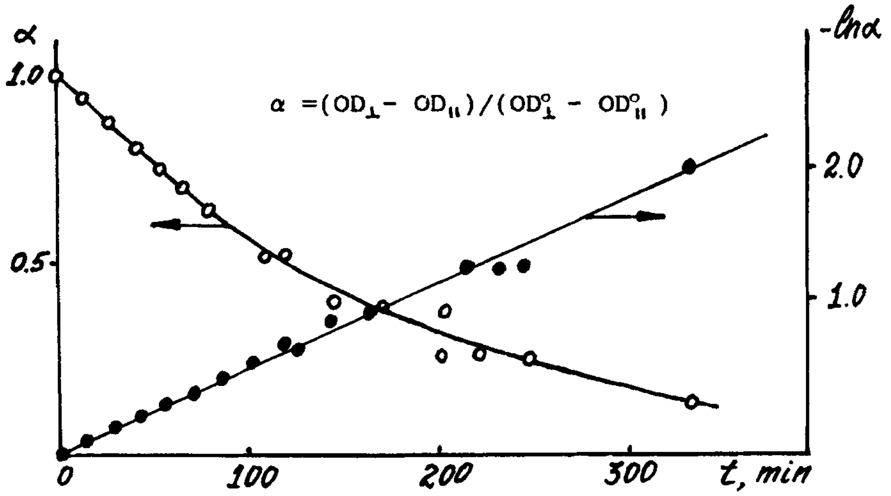


FIGURE 2 The dark relaxation of the light induced optical anisotropy of 9-tert-butylanthracene in polystyrene at 293 K.

The effective activation energies have been evaluated from the Arrhenius plots in the temperature range 293-323K ( Table 1).

TABLE 1 Characteristic times and effective activation energies for thermal reaction and molecular rotations.

| Compound | $\tau_{ROT}\ 10^{-4}$ (sec) | $\tau_{REACT} 10^{-4}$ (sec) | $E_{ROT}$ (kcal/M) | $E_{REACT}$ (kcal/M) |
|---|---|---|---|---|
| I[7] | (1.4÷2.0) | (2.0÷2.6) | 25±3 | 22.1±0.3 |
| IV | (2.1÷3.4) | (4.0÷7.1) | 19±2 | 17±2 |

A good agreement of characteristic times for thermal reaction and molecular rotation was observed (Table 1). Presumably, the thermal reaction as well as the thermal rotation of the guest molecules in polystyrene are determined by the same properties of the surroundings.

Comparative analysis of light induced optical anisotropy of the initial and photoconverted molecules allowed to measure the angles of the rotation of the molecular dipole transition moment (θ) in the instant of the elementary act of the chemical conversion for photoisomerisation of III and IV. For the experimental determination of θ the equation was derived:

$$(OD_{\parallel}-OD_{\perp})^{B} = R(OD_{\perp}-OD_{\parallel})^{A}$$

were $R=P_2(\cos\theta)[(\epsilon_z-\epsilon_x)\epsilon]^{B}/[(\epsilon_z-\epsilon_x)\epsilon]^{A}$, $P_2(\cos\theta)=(3\cos^2\theta-1)/2$, $\epsilon_z$, $\epsilon_x$ - the principle values of extinction coefficient tensor, $\epsilon=(\epsilon_z+2\epsilon_x)/3$.

The magnitudes of θ, calculated from the experimental data are presented in Table 2.

TABLE 2 Obtained magnitudes of θ

| Temperature T, K | Processes III→IV | IV→III |
|---|---|---|
| 77 | 0÷8° | - |
| 293 | 20±3° | 30±2° |

We associate the transition moments in this molecules with the pyrenil group. The fact, that the low temperature magnitude of $\theta$ is smaller then the "high" temperature one, shows that the photochemical reaction at the temperature of boiling nitrogen occurs without restructuring of the immediate environment of pyrenil fragment. It is agreed with kinetic nonequivalency of molecules observed in course of low temperature photochemical reaction. The 293 K reactions include the rotation of pyrenil group and associate with the rearrangement of polymer chains in the molecular surrounding medium.

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## REFERENCES

1. A.Griva, L.Denisova, and E.Denisov, Dokl.Acad.Nauk SSSR (russian), 232, 1343 (1977).
2. G.Lazarev and Y.Lebedev, Khimicheskaya fizika (russian), 7,1159 (1988).
3. A.Albrecht, J.Chem.Phys., 27, 1413 (1957),
4. J.Michl and E.W.Thulstrup, Spectroscopy with polarized light( VCH Inc, 1986), Chapter 4.
5. J.Lombardi and A.Albrecht, J.Chem.Phys., 40, 1148 (1968).
6. V.Minaylov, A.Vorobiev and V.Gurman, Khimicheskaya fizika (russian), 12, 496 (1993)
7. V.Minaylov, A.Vorobiev and V.Gurman, Khimicheskaya fizika (russian), 12, 504 (1993)