

Polarized Vibrational Spectra of *p*-Substituted Nitro and Dinitro *cis*- and *trans*-Stilbenes

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Polarized IR spectra of *p*-nitro and *p,p'*-dinitro derivatives of stilbene were measured in anisotropic (nematic liquid crystalline) solvent. Using the Thulstrup-Eggers stepwise reduction procedure, based on the interactive subtraction of the two polarized IR spectra $A_{||}(\nu)$ and $A_{\perp}(\nu)$, orientational parameters of nearly planar, low symmetry stilbene molecules were determined [1]. Dichroic ratios (subtraction factors), R_u ($u = x, y, z$), of observed vibrational transitions were evaluated and orientational parameters along the out-of-plane axis, K_x , the short in-plane axis, K_y , and the long in-plane axis, K_z , were calculated.

Since the rotation around the double bond changes the molecular geometry, different set of orientation parameters were determined for each molecule (Table 1). The K_z values indicate, as expected, that the *trans*-isomers are better oriented along the long in-plane axis than the *cis*-isomers. In addition, the K_z value for the mono substituted *trans*-stilbene, which is higher than the one for the disubstituted *trans*-stilbene, implies a possible involvement of the nitro groups in dipole-dipole interactions responsible for orientational mechanism of solute molecules in nematic solvent.

Table 1: Orientational parameters of *p*-nitro and *p,p'*-dinitro *cis*- and *trans*-stilbenes.

| Compound | K_x | K_y | K_z |
|--|-------|-------|-------|
| <i>p</i> -nitro- <i>trans</i> -stilbene | 0.139 | 0.287 | 0.574 |
| <i>p</i> -nitro- <i>cis</i> -stilbene | 0.192 | 0.384 | 0.424 |
| <i>p,p'</i> -dinitro- <i>trans</i> -stilbene | 0.150 | 0.383 | 0.467 |
| <i>p,p'</i> -dinitro- <i>cis</i> -stilbene | 0.196 | 0.362 | 0.442 |

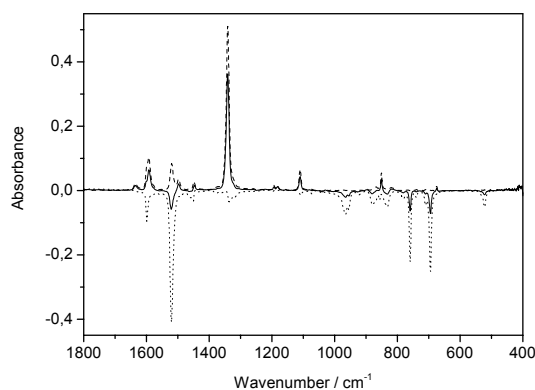


Fig. 1: Polarized IR spectra of *p*-nitro-*trans*-stilbene after reduction by subtraction factors of 0,32 (dashed curve), 1,00 (solid curve) and 2,70 (dotted curve).

Finally, polarized Raman spectra of crystalline stilbene substances were measured and depolarization ratios of selected vibration modes calculated. The values will be compared with those of the parent *trans*-stilbene molecule [2].

[1] M. Rogojerov, G. Keresztury, B. Jordanov, Spectrochim. Acta A 61 (2005) 1661-1670.

[2] G. Baranović, Z. Meić, A.H. Maulitz, Spectrochim. Acta A 54 (1998) 1017-1039.