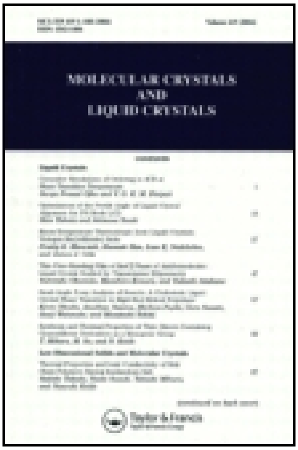

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On the Spectroscopic and Nonlinear Optical Properties OF 3-(1,1-Dicyanoethenyl)-1-Phenyl-4,5-Dihydro-1H-Pyrazole (DCNP)

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ON THE SPECTROSCOPIC AND NONLINEAR OPTICAL PROPERTIES OF 3-(1,1-DICYANOETHENYL)-1-PHENYL-4,5-DIHYDRO-1H-PYRAZOLE (DCNP)

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Abstract Dispersion of the vectorial part of DCNP molecular second order hyperpolarizability $\beta_{CT}(-2\omega;\omega,\omega)$ was calculated from solvatochromic method supplemented with a separately measured ground state dipole moment of DCNP and from quantum-mechanical calculations basing on two-level model. Photoconductivity and pyroelectric properties of DCNP combined with large electrooptic coefficient observed in this material may be useful in formation of transient gratings.

Keywords: nonlinear optics, 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole, electrooptic, solvatochromism, dipole moments, hyperpolarizability

INTRODUCTION

3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (hereafter DCNP) has been reported as an excellent electrooptic organic crystal [1] with a reduced half-wave voltage of 370 V at 632.8 nm wavelength. Such a very high figure of merit of linear electrooptic (Pockels) effect in this crystal is the result of favourable (parallel) molecular packing in a unit cell and a large resonance enhancement of a molecular second order hyperpolarizability $\beta(-2\omega;\omega,\omega)$. In this paper we focused our attention on spectroscopic properties of the molecule of DCNP in order to determine its second-order nonlinear optical susceptibility by a solvatochromic method [2] and quantum mechanical calculations.

SOLVATOCHROMIC METHOD

Solvatochromic method is based on the effect of a solvent on the position, shape and intensity of absorption and emission bands of molecules with respect to their vapor-phase properties. Among many methods employed to quantitatively describe these solvatochromic shifts[3] we adopted the modified Abe's theory [3-5] which derives a formula linking the angular frequency of the S_0 - S_1 electronic transition of the molecule in the solvent ω^{s}_{eg} and in diluted vapor ω_{eg} with refractive index of the solvent n and its dielectric constant ε:

$$\hbar(\omega^{s}_{eg} - \omega_{eg}) = -\frac{1}{4\pi\varepsilon_0 a^3}[2(\mu^{u}_{e} - \mu^{u}_{g})\mu^{u}_{g}(\frac{\varepsilon - 1}{\varepsilon - 2} - \frac{n^2 - 1}{n^2 + 2}) + [(\mu^{u}_{e})^2 - (\mu^{u}_{g})^2]\frac{n^2 - 1}{n^2 + 2}] \quad (1)$$

Solvatochromic shifts depend on such molecular properties as molecular dipole moments in the first excited (μ^{u}_{e}) and the ground (μ^{u}_{g}) states. (The index u refers to the solute). In Equation (1) **a** is a radius of a spherical cavity occupied by the molecule in the solvent. From the measurements of ω^{s}_{eg} for several solvents of different polarities such molecular parameters as ω_{eg} , μ_e and μ_g can in principle be determined, providing the cavity radius is known. A reasonable approximation for **a** is [3]

$$a = r_u + \tfrac{1}{2}\cdot r \quad (2)$$

for $\frac{1}{2} r_u \langle r \langle 2 r_u$, where

$$r_u = (\frac{3M_u}{4\pi N_A \rho_u})^{1/3} \text{ and } r = (\frac{3M}{4\pi N_A \rho})^{1/3} \quad (3)$$

describe the spherical radii of the solute r_u (r_{DCNP} = 4.099A as estimated using data from the paper of Allen et al. [1]) and solvent r molecules, respectively. M, ρ and N_A denote molecular weights, densities and Avogadro's number, respectively. The considerable errors in determination of ω_{eg} , μ_e and μ_g are due to uncertainty of estimation of **a** and some assumptions made in the course of derivation of Eq. (1) (μ_e and μ_g should be parallel, S_0 - S_1 transition well separated in energy from other ones, reorientation of the solvent dipoles upon excitation neglectable).

The quantum-mechanical two-state model for the vectorial part of the second order susceptibility β_{CT} of a molecule[6] with the dominating lowest electronic state (intra-CT transition) of a large oscillator strength predicts:

$$\beta_{CT} = \frac{3}{2\varepsilon_0\hbar^2}\cdot\Delta\mu\cdot\mu^2_{eg}\cdot\frac{\omega^2_{eg}}{(\omega^2_{eg} - 4\omega^2)(\omega^2_{eg} - \omega^2)} \quad (4)$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference between the excited and ground state dipole moment, μ_{eg} is the transition dipole moment between the ground and the excited state and ω_{eg} is the transition frequency, ε_0 is the vacuum permittivity and ħ is the Planck's constant h/2π. The vector component of the molecular hyperpolarizability $\beta_{CT} = \beta_z$ is related to tensor coefficients by the formula:

$\beta_z = \beta_{zzz} + \frac{1}{3}\sum_i (\beta_{zii} + 2\beta_{iiz})$ where the z-axis is along the direction of the dipole moment.

The frequency of the transition ω^s_{eg} and the transition dipole moment μ_{eg} can be determined from uv-visible absorption spectrum of the substance in solution. Calculating the area under the absorption band, one can determine μ_{eg} [7]:

$$\int_{\mathrm{CT\,band}} E\,d\omega = \frac{2\pi^2\omega^s_{eg} N_A f^2}{3\ln 10\,\varepsilon_0\, c\, h\, n} \cdot \mu^2_{eg} \tag{5}$$

wher E is the molar absorbance and c is the speed of light. In the above expression we used a correction factor [8]:

$$\frac{f^2}{n} = \frac{(n^2+2)^2}{9n} \tag{6}$$

where f is a local-field factor (in Lorentz approximation) which accounts for the influence of the dense medium on the absorption process. The procedure described gives the absolute value of the transition dipole moment thus insertion of this value into Eq. (4) yields an upper limit for β_{CT}.

The presented approach, which is in fact essentially the same as presented by Bosshard et al. [8] can be used to establish the dispersion of second order molecular hyperpolarizability β_{CT}. It has been argued [8] that the separate determination of the ground state molecular dipole moment μ^{exp}_g can considerably diminish errors encountered in estimation of molecular excited state dipole moment μ_e from set of equations of the type (1). The ground state dipole moment can be determined employing the Guggenheimprocedure [9] and consists of measurements of low-frequency dielectric constant and the refractive indices of differing in concentration solutions of polar solutes in nonpolar solvents. Neglecting the dependence of n on concentration (which is usually small) one can utilise the formula:

$$\mu^2_g = \frac{\varepsilon_0 3kT}{N_A} \cdot \frac{9}{(\varepsilon^0+2)\cdot(n_0^2+2)} \cdot \frac{M}{\rho_0} \cdot \left(\frac{\partial\varepsilon}{\partial w}\right)_0 \tag{7}$$

where M is the molar mass of the dissolved substance, w is the weight fraction, ε^0, n_0, ρ_0 denote the low-frequency dielectric constant, the refractive index and the density of the pure solvent, respectively. The slope of the dependence of ε on w at small concentrations is used for determination of μ^{exp}_g.

EXPERIMENT

DCNP has been synthesised in this laboratory according to procedure described by Allen et al.[1] and purified by chromatography. Single crystals were grown from saturated solutions of DCNP in acetonitrile. The absorption spectra were taken on Shimadzu uv-vis scanning spectrophotometer UV-2101PS at room temperature. Several solvents of different polarity have been used: hexane, dioxane, carbon tetrachloride, toluene, chloroform, tetrahydrofurane (THF), ethyl acetate, acetone, methanol, acetonitrile and dimethylsulfoxide (DMSO). Due to specific interaction between solvent molecules and the dissolved DCNP molecule one has to check which combination of solvents may lead to reasonable results, i.e. giving close (± 5 nm) values of the transition frequency in vapor ω_{eg}. In order to choose the proper set of solvents to get at least three equations of type (1) we plotted ω^{s}_{eg} in function of the first and the second terms of the right hand side of Eq. (1). The results are shown in Fig. 1. An analysis of these plots allows one to choose a set of three solvents: hexane, THF and DMSO which behave linearly with respect to both parts of Equation (1). Any other set of solvents, as follows from our analysis, will give less consistent results within the model of solvatochromism employed. In Fig. 2 we present the absorption spectra of DCNP taken in three chosen solvents with clearly seen red-shift of ω^{s}_{eg} with increasing solvent polarity.

In Table 1 we listed all the data necessary to solve the set of Equations (1) in order to obtain three unknown values ω_{eg}, μ_g and μ_e.

TABLE I Data for calculation of molecular parameters of DCNP by solvatochromic method.

Solvent	ω^{s}_{eg} [10^{15} Hz]	λ_{eg} [nm]	a [A]	ε^0	n
Hexane	4.233	445	5.995	1.81	1.3753
THF	4.086	461	5.693	7.58	1.4071
DMSO	3.974	474	5.622	46.7	1.4790

However, having in mind the discussion put forward by Bosshard et al.[8] on possible errors in determination of μ_g, we additionally measured the ground state dipole moment of DCNP molecule dissolved in benzene employing the Equation (7) and using the Meratronik capacitance bridge operating at 1 kHz and specially designed capacitor. The results of three independent measurements allowed us to estimate the value of μ_g being equal to 4.54 D ± 0.6 D. Then we solved the set of equations with the data from Table 1 obtaining for DCNP the following results: the angular frequency for S_0 - S_1 transition in diluted vapours ω_{eg} = 4.361 10^{15} Hz (λ_{eg} = 431.9 nm), the ground state dipole moment μ_g = 4.54 D and the excited state dipole moment μ_e = 10.67 D.

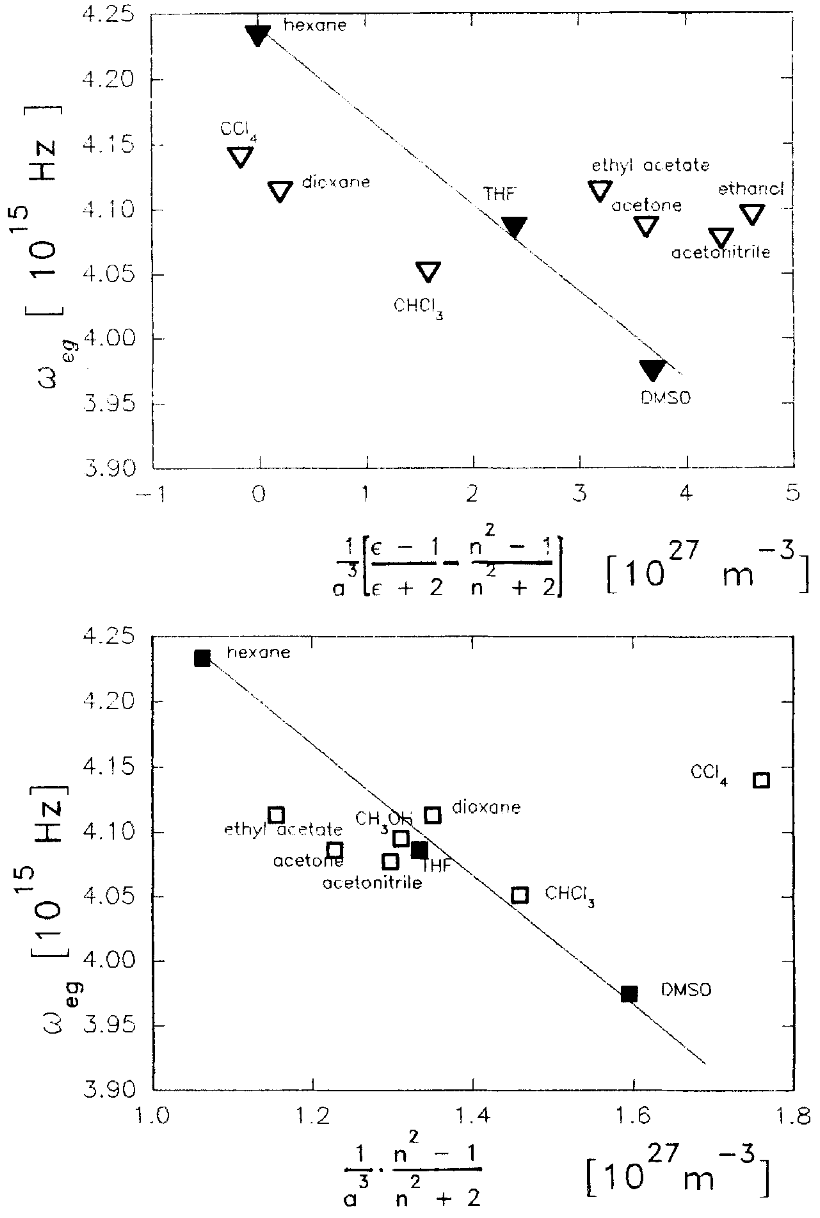

FIGURE 1 Plot of transition frequency ω^s_{eg} versus first (a) and second (b) terms of Equation 1 for DCNP dissolved in various solvents.

The remaining, for determination of dipersion properties of β_{CT}, parameter the transition dipole moment μ_{eg} we calculated from Eq. (5) for hexane solution of DCNP. In order to avoid any contribution from higher energy transitions for integration of the band (cf. Eq. (5)) we used only the low-energy half of the band and added the symmetrical part: such a procedure yielded a value $\mu_{eg} = 5.79$ D.

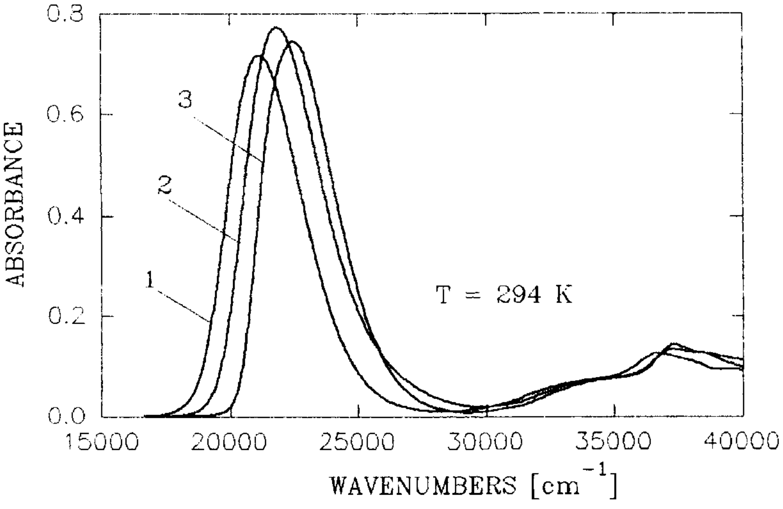

FIGURE 2 Absorption spectra of DCNP dissolved in hexane -1, THF -2 and DMSO -3.

Determination of molecular dipole moments from solvatochromic shifts can be charged with important errors then we decided to perform the quantum-mechanical calculations for DCNP molecule and to compare the obtained results with our estimations from the experiment.

QUANTUM-MECHANICAL CALCULATIONS

For calculations of the electronic spectrum of DCNP molecule we used a semi-empirical method GRINDOL [10]. The energies of fundamental singlet and triplet transitions as well as the dipole moments of ground and all excited states were determined. In Fig. 3 we present schematically the positions of singlet electronic states represented by bars of heights proportional to their respective oscillator strengths. The calculated spectrum (cf. Fig. 3) represents the molecule with optimised molecular coordinates using the AM1 hamiltonian with constraints for planarity (the molecule of DCNP in crystalline form is essentially planar [1]). There is a close resemblance between the spectrum calculated and that measured in the hexane solution. The blue shift amounting ca. 2500 cm^{-1} is partially due to solvent effect not taken into account in calculations. We must stress that the existence of a single, very strong CT transition S_0 - S_1 justifies the two-state approach for calculation of the dispersion of molecular second-order hyperpolarizability β_{CT}. Knowing the distribution of charges at atomic positions one can state that the main charge redistribution upon excitation occurs from the sp^2 nitrogen atom in a five-membered pyrazoline ring (which becomes positively charged) to the neighbouring nitrogen which becomes negatively charged. The charge distribution observed by us is similar to the charge redistribution calculated by Morley [11] for other 1,3-substituted pyrazoline derivatives. Calculations of absolute values of molecular dipole

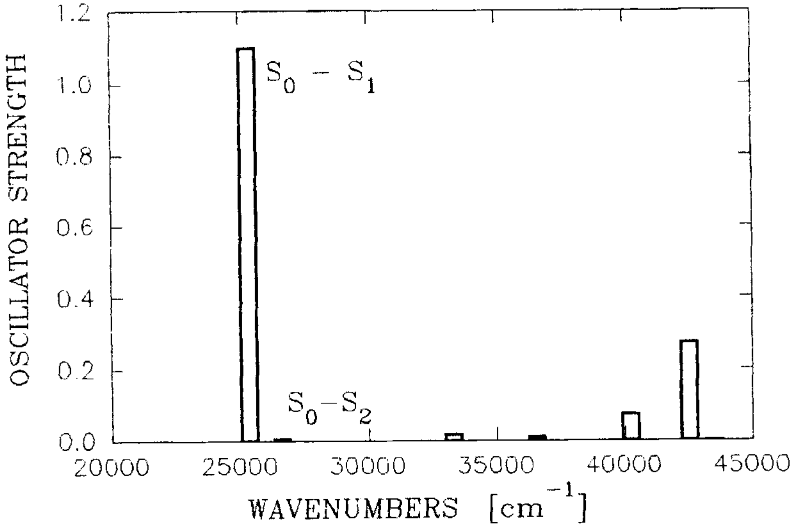

FIGURE 3 Singlet excitations transitions calculated for planar DCNP molecule using quantum-mechanical GRINDOL method.

moments in the ground S_0 and first excited S_1 states are the following: μ_g = 4.44 D and μ_e = 10.01 D. The two vectors are parallel to each other. One should notice that the value of μ_g obtained by us is about 2.5 D lower than the one quoted in by Allen et al. [1]. The value obtained by us agrees well with the experimentally obtained value 4.54 D, however, we found that the calculations of ground state dipole moment of DCNP by standard packet of programs called MOPAC (version 6.00) give higher value of $\mu_g \sim 6.9$ D, but the molecule is nonplanar.

Using the calculated value of the oscillator strength f for the lowest S_0 - S_1 transition and using the following formula [12]:

$$f = \frac{2m\omega^{s}_{eg}}{e^{2}\hbar} \cdot \mu^{2}_{eg} \tag{8}$$

where m is the electron mass and ω^{s}_{eg} is the transition frequency (in hexane in this case), we evaluated μ^{theor}_{eg} = 5.88 D. The obtained value is very close to the experimentally obtained one μ^{exp}_{eg} = 5.79 D.

DISPERSION OF MOLECULAR HYPERPOLRIZABILITY

In Fig. 4 we present the results of calculations of the dispersion function $\beta(-2\omega;\omega,\omega)$ from the theoretical formula (Eq. 4) derived within the quantum-mechanical two-level system (which is justified for DCNP molecule) and employing two sets of parameters.

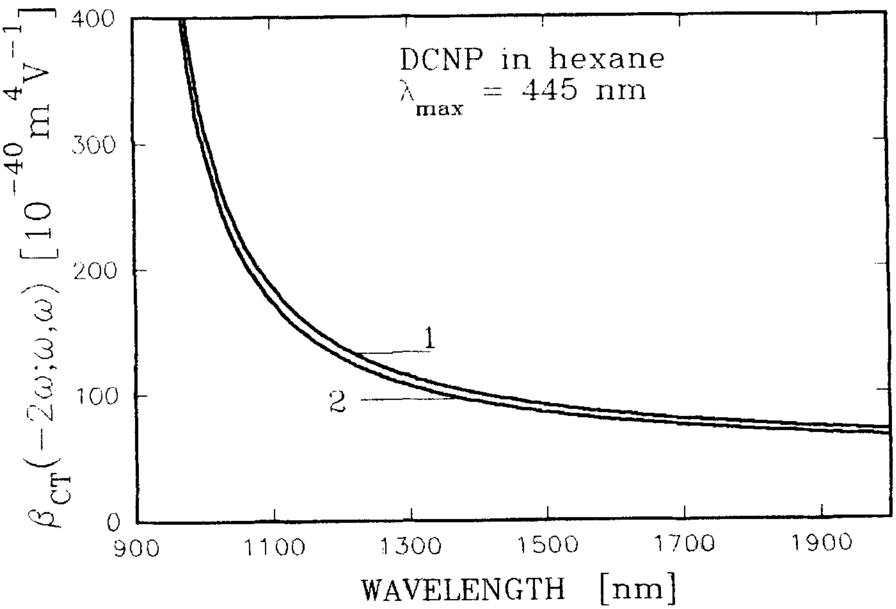

FIGURE 4 Dispersion of the second order molecular hyperpolarizability β_{CT} for DCNP in hexane. The curve labelled 1 is calculated basing on parameters obtained from the solvatochromic method supplemented with separately determined ground state dipole moment and the curve 2 bases on parameters obtained from quantum-mechanical GRINDOL method.

One can notice that the curve representing the solvatochromic method supplemented with experimentally obtained dipole moment and that obtained from GRINDOL calculations are very close to each other (less than 7% difference for $\beta(-2\omega;\omega,\omega)$ at 2000 nm), $\beta^{solvatochromic}(2000\ nm) = 70.2\ 10^{-40}\ m^4\ V^{-1}$, $\beta^{GRINDOL}(2000\ nm) = 65.7\ 10^{-40}\ m^4\ V^{-1}$. This result confirms the agreement between solvatochromic and quantum-mechanical determination of molecular parameters. However, the real value of β_{CT} strongly depends on the radius of a spherical cavity a used in calculations hence our results can be charged with some error whose importance should be verified by an independent measurement e.g. by electric field induced second harmonic generation of light (EFISH) experiment [13] for DCNP in hexane. Usually the difference for short molecules are within a half of an order of experimental values.

PHOTOCONDUCTIVE AND PYROELECTRIC PROPERTIES OF DCNP

In order to examine the DCNP single crystal for presence of photorefractive properties we studied its photoconductive properties. Illuminating the sample, biased by a dc voltage, along the b-axis by a light coming from HeNe laser (λ = 632.8 nm) we noticed an appearance of photocurrent. As is known from polarised absorption spectrum of single crystal of DCNP[1], the absorption for this wavelength occurs mostly along the z-axis

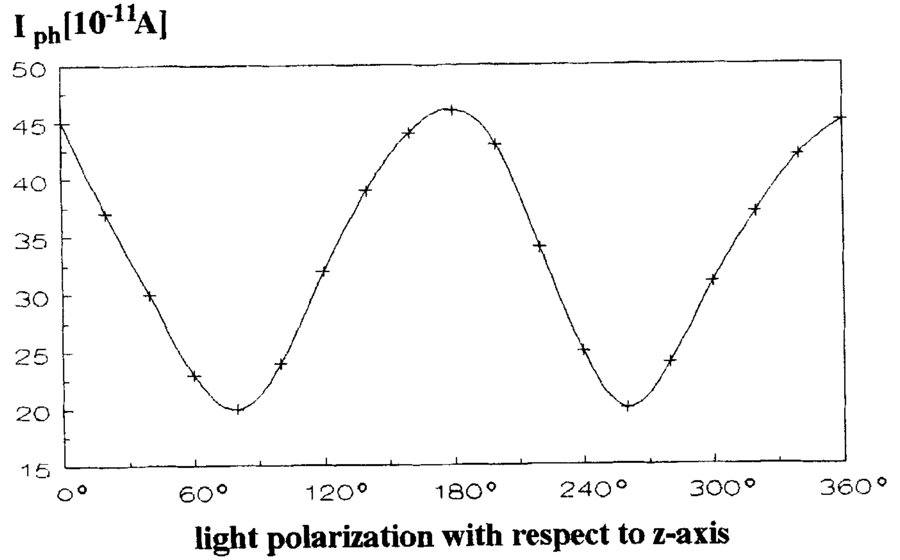

FIGURE 5 Angular dependence of photocurrent (I_{ph}.) on light polarisation with respect to the z-axis in DCNP single crystal, (λ = 632.8 nm, 10 mW, distance between electrodes applied perpendicular to the z-axis was equal to 2mm and applied voltage amounted to 1 kV)).

which is parallel to the long molecular axis and is inclined by about 26° to the c-axis within the ac- plane. This anisotropy of absorption at that wavelength is understood as connected with an interstack CT transition. It is probable that such an absorption can produce a CT excitons and finally can lead to photogeneration of charge carriers [14]. The anisotropy of photocurrent have been measured for different polarisations of light with respect to the z-axis (cf. Fig. 5). Occurrence of photoconductivity combined with a large electrooptic coefficient at that wavelength should allow one to observe photorefractive properties. We cannot observe this effect until now due to insufficient optical quality of crystals.

Using the well known Chynoweth method we established the pyroelectric properties of the DCNP crystal along the z-axis. Presence of pyroelectricity can also be useful in formation of pyro-electrooptic transient gratings [15].

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