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2-methyl-6-nitroaniline: An organic crystal towards photo induced applications

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ABSTRACT

Single crystals of 2-methyl-6-nitroaniline of reasonable size and excellent quality were grown by the low-temperature solution growth method using methanol as a solvent. Supersaturation was established by lowering the temperature at a rate of 0.2° C/hr. The powder XRD of the samples suggested no significant change in the unit cell dimensions and the presence of any extra phase. The structural analysis and infrared spectroscopy can be useful in the clarification of the role of hydrogen bonds in crystals exhibiting non-linear optical properties. It has found that these crystals have transparency from UV to Far-IR wavelength region. Powder Kurtz-Perry measurements were performed for the investigated material. The efficiency of second order susceptibility was estimated relative to urea: $d_{eff} = 8$ urea. The dependence of the birefringence of the investigated crystal was studied with respect to the applied dc field and the results were discussed.

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Introduction

Organic crystals are usually assembled from discrete units of organic molecules. Research into materials for second-order nonlinear optical processes has taken two distinct approaches, concentrating on the development of large one hyperpolarizability β (i.e., enhancement of molecular properties) and the second concentrating on the development of large $\chi(2)$ materials (i.e., enhancement of macroscopic properties). If the electronic structure of the molecular unit and the geometric crystalline structure of a given organic crystal are known, all of its NLO properties can be calculated. Following the early promising discovery of a number of highly efficient substances, highlighted by the paradigmatic nitroaniline family, intensive efforts had to be further invested in the organization of molecules in stable macroscopic assemblies of sufficient optical quality and long-term stability. Early interest in the paranitroaniline family originated from their attractive structural and electronic properties which are still being extensively investigated for various goals. Delocalization is indeed a well recognized feature of π -conjugated electrons in aromatic systems as reflected by the extension of molecular orbitals over the full six-membered carbon ring. Strategies that use combinations of hydrogen bonds have been particularly effective in the preparation of materials with desirable extended structures [1,2]. The maximisation of intermolecular H-bonding interactions leads to an orthogonal disposition of the molecular planes and a acentric structure [3-8]. Electro-optic modulators are one of the most important devices and used for typical optical communications [9]. In particular, nitroaniline derivatives comprise both electron-donating amine and electronwithdrawing nitro groups and exhibit intriguing threedimensional arrays with extensive hydrogen bonding. A methyl (CH₃) group is also included in the two positions to affect an acentric crystal structure. Molecules of this type are often observed to form infinite polar chains linked by intermolecular hydrogen bonding between amine H and nitro O atoms on neighbouring molecules.

This work elucidate the intermolecular interactions in 2-methyl-6-nitroaniline (2M6NA), by investigation of its molecular structure, IR spectra and the dependence of the birefringence from the optical studies. From this technological point of view, 2M6NA having superior non-linear optical properties has been exploited for variety of optical applications.

Experimental procedure

Solubility and crystal growth

The low-temperature solution growth technique is widely used for the growth of organic and inorganic single crystals to get more transparent single crystals. The commercially available 2-methyl-6-nitroaniline (LOBA Chemie) is purified by repeated recrystallization process. The repeated recrystallized materials have been used for growth as charge material.

2-methyl-6-nitroaniline is insoluble in water but soluble in methanol, ethanol and other organic solvents such as DMF and CCl₄. The solubility in DMF of this compound is very high and made the solution more viscous, so that aqueous solution in DMF was not chosen for the crystal growth experiments. The room temperature solubility of 2M6NA in ethanol was very low. We made an attempt to grow the single crystals of the investigated compound by slow evaporation at constant temperature and temperature reduction method from aqueous solutions. From methanol and ethanol solutions under unconstrained ambient growth conditions, 2M6NA usually exhibits a needle like growth habit. All the faces usually show good optical quality, lateral faces being however of better quality due to more stable growth. The aspect ratio of the crystals increases with supersaturation. The crystal growth process is carried out in a modified Holden crystallizer, particular care being devoted to minimize solvent losses. In order to exploit the stable development of lateral faces together with a reasonable low aspect ratio (prisms rather than needles), the growth along the fast direction is mechanically constrained. The long needle-like seeds were cut from long crystals, obtained by repeated unseeded growth, using an acid wire saw; after cutting, the seeds are carefully polished on an ethanol damped

soft cloth. The seed preparation is critical, because residual damage and extended structural defects can easily develop and act as very active local step sources on the growing surfaces. In this case the surface growth is quite fast and very large growth hillocks, often observable by directly inspection, are formed. These hillocks become easily unstable and give rise to macrosteps, inclusions and parasitic, crystals which spoil optical quality. The saturated solution is filtered to remove undissolved excess matter. The actual saturation temperature of the mother solution is at first measured and then confirmed by careful examination of the growth interface of a test crystal. Before introducing the seeds, the temperature of the solution is raised above its saturation point of about 1°C in order to prevent parasitic nucleation and slightly dissolve the seed surface, so as to remove surface contaminants. The temperature lowering profile employed is shown in Fig.1(a). By this procedure large cross-section crystals (11 x 5 x 5 mm³) of high optical quality have been synthesized in about one month period. Some of the crystals obtained are shown in Fig. 1(b).



Fig. 1(a) Temperature profile employed for slow cooling



Fig. 1(b) Photograph of the 2M6NA crystal grown in methanol

Physical Measurements X-Ray Diffraction Studies

To verify their microstructure and crystal quality the as grown single crystal of 2M6NA was mounted in random orientation on a XRD goniometer head. Diffraction data were gathered on an Enraf Nonius CAD4 diffractometer equipped in the graphite monochromated MoK α radiation (λ =0.71 – 0.73 Å) by using ω scan technique. From the diffraction analysis, it has been found that the investigated compound crystallizes in monoclinic system. The lattice parameters of the 2M6NA obtained in this study are $a(\text{\AA}) = 8.9844$, $b(\text{\AA}) = 11.359$, $c(\text{\AA}) =$ 14.785, $\alpha(^{\circ}) = 90$, $\beta(^{\circ}) = 103.814$ and $\gamma(^{\circ}) = 90$. These values are in good agreement with that ones reported by previous workers [10]. The molecular structure of 2M6NA with intermolecular hydrogen contacts is presented in Fig. 2(a). In the crystal structure of the title compound (C7H8N2O2), the molecules are linked through N-H-O and N-H-N hydrogen bonds, forming an extended supramolecule, which contributes to the stability of the structure in the solid state. There are 8 molecules in a unit cell. The p-substituted NH₂, ortho substituted NO₂ and CH₃ groups are co-planar with the benzene ring. It is

significant that the conjugation of molecule may be raised with donor NO₂ group and acceptor NH₂ at Para position.

The amine protons on one molecule interact with a nitro group of a neighbouring molecule. These interactions link the molecules in a linear polar chain, which lies astride a crystallographic mirror plane.

The hydrogen- bond contacts are of typical lengths for primary amines (N-O 2.941 (Å) and N-H-O 2.334 (Å)). Since alkylation increases the donor character of the amino group, the extent of contribution of quinonoid structures should be greater in the alkylated nitroanilines and result in shorter C-N bond lengths. The packing diagram of 2M6NA viewed along b-axis is shown in Fig.2(b). The crystallographic data of 2M6NA is given in Table. 1.



Fig. 2(a) Molecular structure of 2M6NA with hydrogen contacts



Fig. 2(b) Packing diagram of 2M6NA viewed along b-axis

Table. 1	
Identification code	2M6NA
Empirical formula	$C_7H_8N_2O_2$
Formula weight	152.15
Crystal structure	Monoclinic
Space group	P ₂₁ /c
Cell parameters	
a(Å)	8.9844
b(Å)	11.359
c(Å)	14.785
α(°)	90
β(°)	103.814
γ(°)	90
Volume (Å) ³	1465.1
Z	8
Point group	C^5
symmetry	C_{2h}
Crystal size	11 x 5 x 5
	mm ³
rvstallogranhic d	ata of 2M6N

Recording of FT IR Spectra

The room temperature mid Fourier transform infrared spectrum of 2M6NA shown in Fig.3 was recorded in the spectral range 400-4000cm⁻¹ at a spectral resolution of 4 cm⁻¹ using Perkin Elmer Fourier transform infrared spectrophotomer, model SPECTRUM RX1. The observed wavenumbers, relative

intensities obtained from the recorded spectra and the asssignments proposed for the title nonlinear optical crystal is given in Table. 2.



Fig 3. Experimental FT IR spectrum of 2M6NA Table 2

Wavenumber	Assignments
FTIR	
3415 ms	$v_{as}(NH)$
2934 w	v _s (NH)
2808 w	v(CH)(aromatic)
2723 w	$v(CH), v_{as}CH_3$
2184 w	$v(CH), v_sCH_3$
1594 s	ν(C=C), δ (NH)
1513 ms	vring, $v_{as}(NO_2)$
1434 w	vring
1464 w	δ(NH), vring, CH ₃ umbrella mode
1349 s	ν(CN), δ _{in plane} (CH), v _s (NO ₂), δ _{in-plane}
	(N-HO)
1251 ms	$\delta_{in \ plane}$ (N-HO), $\delta_{in \ plane}$ (CH), ν (CN)
1150 ms	vring, $\delta(NH_2)$, $\nu(CN)$, $\rho(CH_3)$
1064 ms	ν(CCN), δ(NH ₂), ν(CN), τ(CH ₃)
1024 w	v(C-C)
930 w	$\delta_{\text{in plane}} \operatorname{ring}$
811 ms	$v(NH), \beta(ring)$
758 s	$\delta_{out of plane}$ (C-H), v(CN), ϕ (NO ₂)
705 m	$v_{as}(CN)$
638 m	$\tau ring, \delta(CN)$
572 m	$\omega(NH_2)$
511 m	$\delta(CN), \omega(CH_3)$

Observed FT IR wavenumbers (in cm⁻¹) of 2M6NA and its vibrational assignments

Results and Discussions

Vibrational Analysis

There were many important works devoted to the relation between nonlinear and vibrational properties of molecular systems at the molecular and crystalline levels [11-16]. A number of papers devoted to aniline vibrations were already published [17]. FTIR analysis further supports the purity of material. The bands observed in the measured region 400-4000 cm⁻¹ arise from the vibrations of protons in the hydrogen bonds. The importance of hyperconjugative interaction and electron density transfer from lone electron pairs of the Y atom to the X-H anti -bonding orbital in the X-H-Y system have been analyzed. The intermolecular N-H-O hydrogen bonding is formed due to the overlap between n(O) and $\sigma^*(N-H)$ which results causing stabilization of H-bonded systems. The nature and the strength of the intermolecular hydrogen bonding is formed due to the overlap between n(O) and $\sigma^*(N-H)$ which results intermolecular charge transfer using stabilization of hydrogen bonded systems. The bands corresponding to e.g. antisymmetric and symmetric stretching of amino groups disappear in the region 3500-3200 cm⁻¹ due to self-association

with intermolecular interactions through hydrogen bonds. Also the presence of well-defined symmetrical and asymmetrical modes of NH₂ in this envelope evidently prove conjugation of secondary amino grouping NH rather than NH₂ attached to benzene group. Further this asymmetric N-H stretching wavenumber is red shifted in IR around 3415 cm⁻¹. The 2934 cm⁻¹. The strong band symmetric stretching is found at at 1624 cm⁻¹ in IR is attributed to NH asymmetric deformation mode. These are due to the extensive hydrogen bonding of the crystal. The broad band of NH vibrations also reveals that the packing cores in the crystal lattice are large due to dipolar and hydrogen bonding interaction. The dipole interaction between neighboring molecules is expected to be the dominating molecular force in molecular packing of crystal lattices. The C-N stretching vibrations expected to occur as around 1180-1360 cm⁻¹ [19,20] are observed at 1394 and 1251 cm⁻¹ respectively in the present study.

Phenyl Ring Vibrations

In 2M6NA molecule, the aromatic ring is asymmetrically disubstituted. The phenyl ring mode manifests shoulder band in IR 1513 cm⁻¹. The intensity is dependent on the algebraic difference of the electronic polarizabilities of the substituents. The intense IR band at 1594 cm⁻¹ is attributed to the Kekule C-C stretching mode. The ring stretching vibrations are interesting as the double bond is in conjugation with the ring. The doubly degenerate ring stretching modes of benzene are not perturbed upon substitution. It consists of lateral dilation and contraction of the ring produced mainly by stretching and compressing of the bonds. On the removal of degeneracy the vibrations appear separately. It is usually observed while the other component retains the energy of the degenerate vibration in benzene. These vibrations are expected to interact a little with C-H in plane bending, hydrogen and its carbon moving oppositely but the substituents are nearly motionless. For the substituted phenyl ring, the aromatic C-H vibrations usually give rise to bands in the region 3100-3000 cm⁻¹ [20,21]. In disubstituted benzene four of these modes gives rise to C-H stretching wavenumbers which almost retain the wavenumbers of benzene which lie in the region of 3100-3000 cm⁻¹ while the other two modes of substituents depend on the mass and the ionicities of the substituents and decrease considerably. Thus they are found to be at 2808, 2723 and 2184 cm^{-1.} The in-plane and out of plane vibrations are also mixed with C-H deformations at 1349 and 1251 cm⁻¹.

Methyl Vibrations

Methyl groups are generally referred to as electron denoting substituents in the aromatic ring system. The asymmetric and symmetric stretching mode of CH₃ is expected in the spectral range around 2723 and 2184 cm⁻¹. The methyl hydrogen atoms may be subjected to hyperconjugation and induction. The electronic effect, hyperconjugation usually means the interaction of the orbitals of a methyl or methylene group with π orbitals of an adjacent C-C bond. The twisting, scissoring and rocking vibrations are well found in the characteristic regions.

Nitro Vibrations

The NO₂ group is predominantly subject to the attractive interaction by the NH₂ group of the neighboring molecule due to intermolecular hydrogen bonding. Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the nitro group at 1570-1485 cm⁻¹ and 1370 -1320 cm⁻¹. Usually the symmetric vibration is stronger than antisymmetric one in the Raman spectra and the contrary

holds in infrared [22,23]. This could be due to the electron withdrawing substituent adjacent to the nitro group tending to increase the frequency of asymmetric vibration and decrease of the symmetric vibration. Due to the presence heavy nitro group which opposite to the meta position tries to be out of the plane of the ring bulky substituent at 1513 and 1349 cm⁻¹ respectively. NO₂ stretching modes are observed at 1520 and 1348 cm⁻¹.

Thus the shifting of stretching and bending vibrations of various essential functional groups suggests a large charge delocalization on hydrogen mode which in turn strengthens the intermolecular hydrogen bonding. This has great impact in deciding the nonlinear optical behaviour of the title crystal.

Optical Behaviour

The internal transmittance of 2M6NA crystal was recorded using Varian Cary 500 scan double-beam UV–VIS–NIR spectrophotometer in the spectral range 190–2000 nm as shown in Fig. 4(a). A small plate of thickness 0.5 mm was used for recording of the spectra. From the recorded UV spectra it is evident that the 2M6NA displays an excellent transparency window in the entire UV-VIS region. An increase in transmittance exists near 190 nm of the optical transmission spectrum. The analyses of our data showed that the plots of $(\alpha hv)^{1/n}$ versus hv with n=1/2. This indicates that the allowed direct transition is responsible for the inter-band transition in the 2M6NA crystal. Fig. 4(b) shows the plot of $(\alpha hv)^2$ versus photon energy hv for the 2M6NA crystal. The bandgap for the crystal is calculated as 5.89eV. The energy gaps of semiconductors are much smaller than those of the organic crystals.



Fig.4(a) Optical transmission spectrum of 2M6NA



Fig. 4(b) Plot of $(\alpha hv)^2$ versus photon energy hv of 2M6NA Second harmonic generation Measurements

For the powder SHG efficiency of the crystal presented here we have obtained the following value relative to Urea (25 mV): $d_{eff} = 8$ Urea using Nd: YAG laser radiation of wavelength 1064 nm and of the laser input power of 5.7 mJ/pulse. The behaviour of aniline molecule in nonlinear optical processes of second and third order was discussed by Nalwa and Miyata respectively. In the benzene molecule, quadratic polarizability disappears due to symmetry with the center of inversion. For conjugated molecules β arises from the distortion of the π electron distribution caused by substituent group. The aniline molecule consists of a phenyl ring, in which an electron donor amino (NH₂) group is substituted. This substitution removes such a restriction and thus generates β . In the investigated crystal the intermolecular interactions of the amino group with the nitro group of the neighbouring molecule leads to a non centrosymmetric crystal architecture and the inherent properties of the aniline molecule are conserved on the macroscopic scale. In spite of limitations due to the crystal structure the studied crystal provides additional arguments in the discussion of the role of hydrogen bonds in the self-assembly phenomenon giving non-centrosymmetric crystals with potential applications in nonlinear optics.

Dependence of the birefringence

Following the presented structural and non-linear optical data one can expect that these crystals should possess large optically induced changes of refractive indices. For this reason we have performed measurements of birefringence for the He-Ne laser wavelength 633 nm induced by Nd:YAG laser emitting at 1064 nm with polarization under angle 45 degree with respect and y axis and incident angle about 16 degree. to х Interestingly in Fig.5 that at the beginning we observe an increase of the birefringence (at photoinduced power density upto 500 MW/cm²) corresponding to enhancement of the birefringence upto 0.035. With further increase of the photoinduced power density there appears the diminishing of the birefringence which even changes its sign about 1100 MW/cm². Existence of such maximum may indicate on a competition between the photoinduced carrier photodiffusion and its disappearance due to photothermal re-orientation. Substantial role begin to play here difference between the state dipole moments of the particular structural fragments, which following the results of the works [23,24] should favor additional noncentrosymmetry and electron-vibrational anharmonicity.



Fig 5. Dependence of the birefringence Conclusion

This work briefly discusses various vibrational and spectral optical aspects of the significant nitroaniline based nonlinear optical crystal 2-methyl-6-nitroaniline. Growth rate and transparency level are high for the crystals grown by slow cooling method. FT IR spectral analyses confirm the presence of N-H-O hydrogen bonds in the crystal. Optical transparency of the crystal lies in the spectral range 190 nm. The SHG efficiency of this crystal is estimated to be as equal to about 10 pm/V. Thus the high intrinsic optical nonlinearities and low dielectric constants measured for organic crystals have generated significant interest in their use in high-bandwidth electro-optic modulators and switches. Following the presented structural and non-linear optical data one can expect that these crystals should possess large optically induced changes.

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