비선형 광학적 소재로서 2-methyl-4-nitroaniline, MNA(T) , $C_7H_8N_2O_2$ 의 결정성장 및 그 구조

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Crystal Growth and Structure of 2-Methyl-4-nitroaniline, MNA(T), $C_7H_8N_2O_2$ As A Non-linear Optical Material

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Introduction

Several organic materials have been investigated because of their exceptional non-linear optical (NLO) properties. They consist of a frame of conjugated double bonds, and electron-donating and electron-attracting substituents. Usually organic compounds exist in only one equilibrium phase in the solid state, but sometimes polymorphs are observed, with different crystal packing, and subtly different physical properties.

Of particular promise are the organic materials known for their efficient second harmonic generation. The crystal and molecular structure of 2-methyl-4-nitroaniline(MNA, Fig.1), was determined previously[1]: MNA is monoclinic, and belongs to the space group Ia (no. 9): we will call this the MNA(M) structure. The optical nonlinearities of MNA(M) have been studied[2]. The second order nonlinearlity is important in determining threshold of nonlinear optical device such as harmonic generators. By experimental and theoretical studies it was shown[3] that benzene molecular units, substituted, as in MNA, with electron donors such as $-NH_2$ of MNA and acceptors like $-NO_2$, posses extremely large second-order nonlinear optical susceptibilities. For example, MNA(M) has two very large second-order nonlinear coefficient, $\chi_{133}^{(2)} = 2d_{12} = 75$ and $\chi_{111}^{(2)} = 2d_{11} = 500$ pm/V[4]. However, the practical use of MNA(M) has been impeded by the limited size of MNA(M) crystals, and by the bad phase matching, I.e. the unfavorable relative orientation of the normal to the largest crystal faces versus the directions of the two largest tensor components $\chi_{133}^{(2)}$ and $\chi_{111}^{(2)}$.

In this work, the evidence for a new triclinic polymorph of MNA(T), compare it to the known monoclinic polymorph MNA(M), and provide the 4 x 4 cell transformation matrix between the two polymorphs. The crystal structure and packing of MNA(T) will be shown to be almost equivalent to that of MNA(M).

Experimental

MNA was obtained commercially (Aldrich), and purified by vapor transport in an oxygen atmosphere. DPA (2,4-dinitrophenyl-L-alanine) was synthesized, using Sanger's method, as described in the literature[5]. Two sets of crystals were grown upon slow evaporation of a 50-50 volume% ethyl acetate: hexane solution of an equimolar mixture of MNA and DPA. The first set consists of light yellow crystals, up to 2 mm x 1 mm x 1 mm in size: these are MNA(T), and are discussed below. A second set of orange-yellow crystals are the 1:1 DPA:MNA complex.

The X-ray diffraction data were collected for one of these white single crystals by an ENRAF-Nonius CAD-4F automated four-circle X-ray diffractometer using Mo(Kα) radiation. For the compound 2-methyl-4-nitroaniline, MNA(T), the crystal data are: molecular formula $C_7H_8N_2O_2$, molar mass Mr = 152.15 g/mol, crystal system triclinic, space group P1 (no. 1), unit cell constants **a** = 7.621(2), **b** = 7.952(5), **c** = 8.200(2)Å, α = 118.84(20°, β = 93.76(2)°, γ = 116.84(3)°, unit cell volume V = 362 Å^3, Z = 1 asymmetric units/cell = 2 molecule/cell, computed density D_x = 1.40 g/cm^3, λ(Mo Kα) = 0.71069 Å, μ = 0.65 cm^{-1}, F(000) = 160, temperature T = 295(3) K. The final weighted R values obtained were R = 0.059 and R_W = 0.055 (715 observations, 196 parameters).

Results and Discussion

Crystallographic parameters for the known monoclinic MNA(M) polymorph is: $\mathbf{a_m}$ = 7.621(2), $\mathbf{b_m}$ = 7.952(5), $\mathbf{c_m}$ = 8.200(2)Å, β = 94.08(2)°. The new triclinic MNA(T) polymorph solved by direct methods is: $\mathbf{a_t}$ = 8.225(1), $\mathbf{b_t}$ = 11.620(1), $\mathbf{c_t}$ = 7.585(2)Å, α = 118.84(2), β = 93.76(2), γ = 116.84(3)°. A 4 x 4 transformation matrix for the monoclinic to triclinic unit cell was obtained, as shown in the matrix equation

$$(a_m\ b_m\ c_m\ O_m) = (a_t\ b_t\ c_t\ O_t)\begin{bmatrix} 0 & -1 & -1 & -0.5024 \\ 0 & -2 & 0 & 0.2455 \\ -1 & -1 & 0 & 0.5197 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

The calculated monoclinic cell for MNA(T), and the deviations, Δ, from the monoclinic cell given are a'_m = 8.20Å (Δ = -0.025 Å), b'_m = 11.610Å (Δ = 0.010 Å), a'_m = 8.20Å (Δ = 0.036 Å), α = 90.48° (Δ = 0.48°), β = 93.76° (Δ = -0.32°), γ = 89.86° (Δ = 0.14°). The geometrical relationship between triclinic and monoclinic direct cells is shown in Fig. 2.

A stereoscopic illustration of the packing in the cell for MNA(T) and MNA(M) with hydrogen bonds drawn as dotted lines, is given in Fig. 3.

In MNA(T) the two crystallographically distinct MNA molecules (MNA1 and MNA2) stack approximately along a, with the least-squares benzene plane forming a dihedral angle of 4.5° with each other; these planes are slanted 25.17° and 26.08°, respectively, with respect to a. The MNA···MNA2 overlap is staggered; the center of the benzene ring of MNA1 lies below the benzene ring carbon atom of MNA2 that is bonded to the methyl carbon. The vector connecting the two nitrogen atoms in MNA1 forms an angle of about 60o with the corresponding nitrogen-nitrogen vector of MNA2 (so that the two molecular dipoles are in approximate addition). There are some significant non-bonded intermolecular contacts: O10···N7′ = 3.122 Å, O10′···N7 = 3.134 Å, C8···O10′ = 3.267 Å, N7···O11 = 3.269 Å, C8′···O10 = 3.285 Å, O11···N7′ = 3.341 Å, N7···O11′ = 3.384 Å, C8···O11′ = 3.451 Å.

The crystal structure shows alternating perpendicular π overlap between C1 of MNA1 and C6′ of MNA2, C4 of MNA1 and C4′ of MNA2, at typical van der Waals distances (the MNA1-MNA2 overlap is staggered). Since the dipole moments of the molecules are almost aligned with each other[1] the structure highly acentric. The packing seems to be dominated by π-π interactions between the MNA1 and MNA2 molecules, with some contribution from the localized hydrogen bond, due to a weak charge-transfer interaction between MNA1 and MNA2. The MNA moment is slanted from (001). There are four inter-

molecular hydrogen bonds: two shorter ones (O10···H72′ = 2.233Å and O10′···H72 = 2.294Å) between MNA1 and MNA2, and four longer ones: O11···H71 = 2.565Å between MNA1 and MNA1′ along **b**, O11′···H71′ = 2.586Å between MNA2 and MNA2′ along the cell diagonal, O11···H72′ = 2.587Å between MNA1 and MNA2, and O11′···H72 = 2.676Å between MNA2 and MNA1′ along [101].

To compare critically the MNA(T) and MNA(M) crystal structures, the observed structure factor amplitudes reported here and those given previously were used, after suitable transformations, to refine both data sets in the two space groups P1 and Ia. The final unweighted R-indicies were, for the MNA(T) data in both space groups P1 (R = 5.87%: 715 data, 196 parameters) and Ia (R = 8.51%: 715 data, 100 parameters), and the MNA(M) data in space groups P1 (R = 3.59%, 750 data, 196 parameters) and Ia (R = 4.89%, 750 data, 100 parameters: this refinement yielded R = 4.8%[1].

The optical absorption spectrum, Fig. 4, is recorded in the range 450-2000 nm. A typical spectrum of the triclinic MNA(T) crystal plate shows a broad absorption band from 480-650 nm[6]. The Raman spectrum, Fig. 5[6], of triclinic MNA(T), is almost identical, except for a few bands, to that of the spectra of monoclinic MNA(M) in the form of powders, vapor-grown crystalline plates, and crystals obtained by slow evaporation of ethyl acetate/hexanes solution containing MNA.

It remains to be seen whether any differences in nonlinear susceptibility tensor components could the ambiguity, or whether both polymorphs can be grown from the same solution[4].

Conclusion

Evidence has been presented for a new polymorph of a known molecule, 2-methyl-4-nitroaniline (MNA). By refinements of the MNA(T) and MNA(M) data in both space groups, P1 and Ia, very similar structures are obtained. In the MNA(T) structure, the two crystallographically distinct MNA(T) molecules, MNA1 and MNA2, are stacked MNA1 and atop MNA2, inclined to the stack approximately along a by 25.17° (MNA1) and 26.08° (MNA2); six hydrogen bonds contribute to the crystal binding. A 4 x 4 transformation matrix for the monoclinic MNA(M) to triclinic MNA(T) unit cell was obtained.

References

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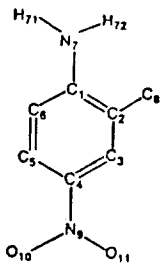

Fig. 1. Chemical structure of MNA.

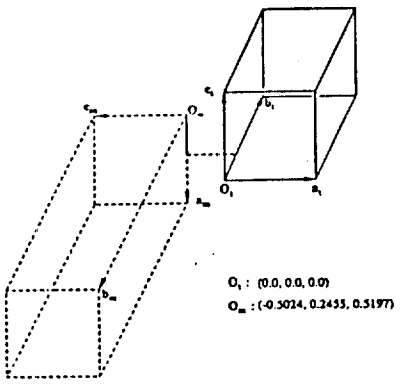

Fig. 2. Triclinic (—) and monoclinic (----) direct cells for MNA molecules.

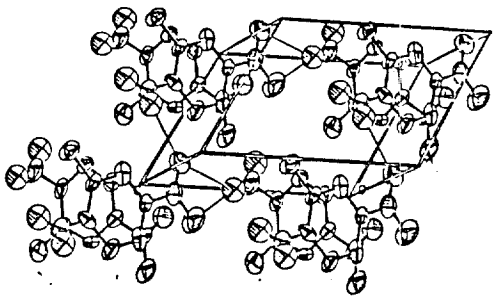

Fig. 3. Stereoscopic ORTEP drawing of the packing of the triclinic MNA(T) molecules in the unitcell.

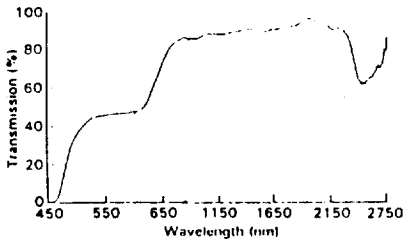

Fig. 4. Optical absorption spectrum of MNA(T) in the range 450-2600 nm.

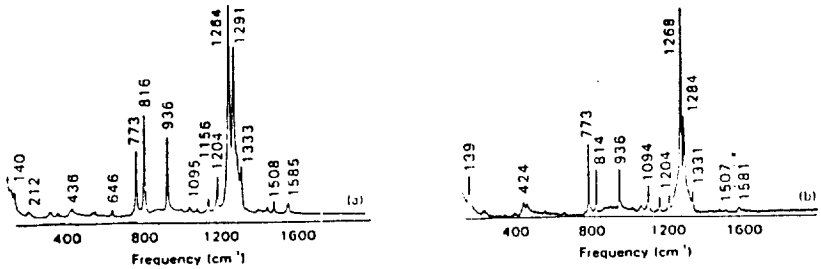

Fig. 5. Raman spectrum of (a) MNA(T) and (b) MNA(M).