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The Structure and Nonlinear Optical Properties of Octupolar Compound: 2, 4, 6-Tristyryl-*s*-triazine

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Abstract: The crystal of 2, 4, 6-tristyryl-*s*-triazine (TSTA) has been prepared and its crystal structure been determined to be in the polar non-centrosymmetric space group $Cmc2_1$. The molecular structure of TSTA is characterized by the slightly curved planar configuration and the octupolar C_{3v} molecular symmetry. As expected, TSTA crystal shows a quite novel nonlinear optical (NLO) property with its powder second harmonic generating (SHG) intensity of 1.8 times as that of urea. It also shows excellent transparency (with the peak position of 322 nm in absorption spectrum) and good thermal stability (with the melting point of 225-229°C).

Keywords: TSTA, crystal structure, SHG..

Organic second order nonlinear optical (NLO) materials have attracted considerable research attention for their potential applications in many fields, such as information storage, optical communications and optical chemistry. Most works of second order NLO compounds are concentrated on the traditional D-π-A molecules[1-4]. In the last decades, Zyss *et al.* introduced octupolar model for second-order nonlinear optics[5]. Without permanent dipole moments and therefore no dipolar interaction which is the main origin of centrosymmetric molecular packing style, this kind of compounds show a much higher probability of crystallizing in noncentrosymmetric space groups. Besides, unlike the mono-directional charge-transferred dipolar D-π-A molecules which frequently subject to a red-shift in the absortion spectra, the octupolar molecules can be more transparent and the efficiency-transparency trade-off can be remarkably improved[6]. Because of these advantages, quite a number of octupolar compounds, which were proved to have excellent NLO properties, have been investigated[7,8]. In this letter, we mainly report the crystallographic and optical properties of the octupolar compound: 2, 4, 6-tristyryl-*s*-triazine (**TSTA**, $C_{27}H_{21}N_3$).

Crystallographic Property of TSTA

TSTA was synthesized referring the literature method[9]. The transparent and pale yellow crystals of **TSTA,** of which a 0.38×0.14×0.1 mm single crystal was chosen for

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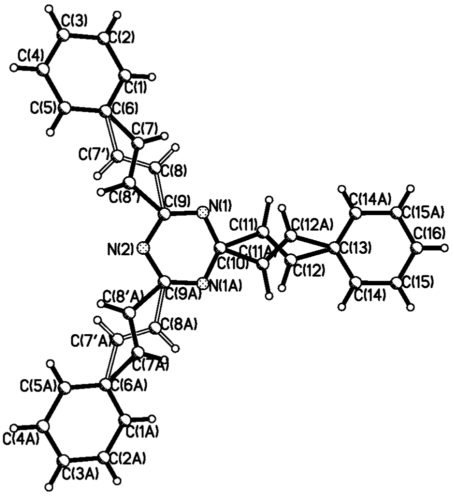
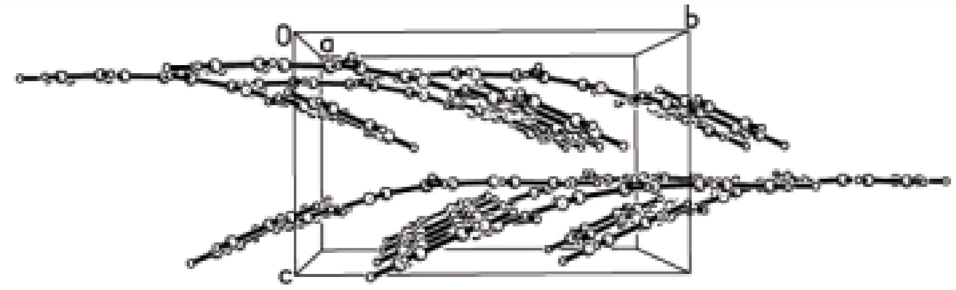
X -ray structure determination, were grown from benzene solution by solvent evaporation at room temperature. The X-ray diffraction data of **TSTA** were collected by Bruker P4 four-circle diffractometer with the Mo K_α radiation (λ = 0.71073 Å) and resolved by SHELXL-97 programs. The results indicate that **TSTA** crystal is in orthorhombic system, $Cmc2_1$ (No.36) space group. The cell parameters: a = 22.689(3) Å, b = 12.4638(14) Å, c = 7.4086(11) Å, V = 2095.1(5) $Å^3$, D_c= 1.228 mg/m^3. The final R indices are R_1 = 0.0527, wR_2 = 0.1047 for the collection of data with $I > 2\sigma(I)$. The molecular structure is shown in **Figure 1** and the molecular packing in the cell is shown in **Figure 2**.

Figure 1 The molecular structure of TSTA



TSTA is a multi-branched compound with three styryls attaching to the central triazine, forming a molecular configuration of something like slightly curved planar triangular kite (See **Figure 1** and **2**). Besides the three benzene rings, the six-menbered triazine ring is also strictly planar. The vinyls in the three branches of the molecule are all disordered, which endow the molecule with an additional crystallographic mirror symmetry in addtion to its molecular three-fold rotation symmetry. As shown in **Figure 1**, A symmetric mirror, passing through N2, C10, C13 and C16, cuts the molecule into two enantiomorphous parts. Nearly all the bond lengths are between that of typical single C—C（1.54 Å）and that of double C=C（1.34 Å）, or between that of C—N (1.47 Å) and that of C=N(1.30 Å), and all the bond angles except those involved in the disordered vinyl are close to 120°. These aromatic characterized bond parameters show that all of the non-hydrogen atoms of TSTA form a large π-conjugated system.

Figure 2 The molecular packing in the unit cell (view along a-direction)



There are four molecules in an unit cell. As shown in **figure 2**, all the planar TSTA molecules are roughly parallel to the (001) plane, and the benzene ring containing C13~C16 and C14A, C15A is strictly parallel to the (001) plane. So the charge distribution shows a octupolar symmetry in (001) plane. We believe that this octupolar non-centresymmetry is the main origin of optical nonlinearity. The secondary origin of optical nonlinearity is the dipolar non-centresymmetry because the molecular plane is slightly curved forming a small dipole moment along the normal line of the triazine plane. Interestingly, all of the small dipole moments are basically along the *c*-direction as all the planar triangular kite are curved in the same direction. This kind of full molecular cooperation is just the pursued goal of phase-matching in crystal engineering for NLO materials. By the way, the polar non-centrosymmetric *mm*2 point group, which the TSTA crystal belongs to, is the best group in the orthorhombic system in the view of NLO.

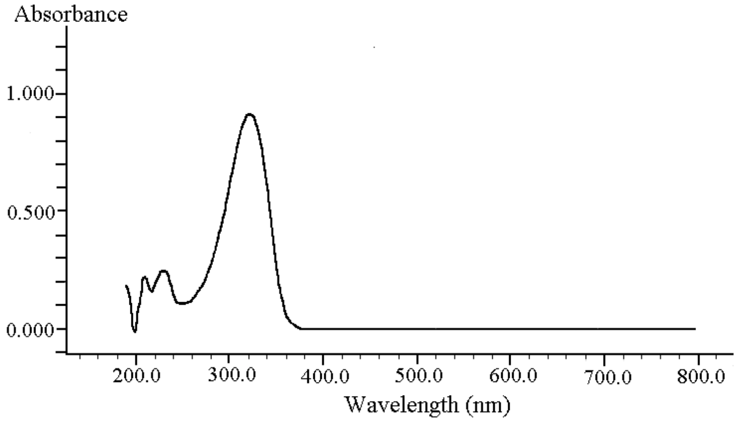
The Nonlinearity of TSTA

The SHG intensity of TSTA was measured by the powder technique of Kurtz and Perry[10]. The powder sample was located in between two transparent glass plates and sample thickness were kept constant in all subsequent experiments. The fundamental wave (1064 nm) of a passive mode-locked Nd:YAG laser was surved as incident beam, and the SHG signal from the sample was detected by a photomultiplier. The results indicate that the powder SHG efficiency of TSTA is 1.8 times as large as that of urea.

Transparency and Physicochemical Stability of TSTA

Transparency is a very important issue for a SHG material. The absorption spectrum of **TSTA** in acetonitrile is shown in **Figure 3**. Its absorption peak is at 322 nm and it has no absorption above 370 nm. This spectrum shows that TSTA is transparent enough to be an efficient doubler for the 1064nm YAG:Nd^{3+}. Its melting point is 225-229°C which is high enough for most applications of TSTA as SHG material.

Figure 3 The absorption spectrum of TSTA in acetonitrile（1×10^{-5}mol/L）



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