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Structures and nonlinear optical properties of molecular crystals DMCC and DBCC

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Abstract

Structures and nonlinear optical properties of dimethylcroconate (DMCC) and dibenzoylcroconate (DBCC) are reported. The SHG active DMCC crystal packed in non-centrosymmetric $P_{2_1}2_{1_2}2_{1_2}$ space group. The DBCC crystal has a host–guest structure and crystallized in centrosymmetric P_{2_1}/n space group. In DBCC crystal, the host DBCC molecules build channels along the *b* direction with the guest benzene molecules trapped in the channels. DSC, XRD, SHG and structural studies reveal that these benzene molecules can be removed at 90 °C, accompanying the loss of the centro-symmetry and resulting in the SHG active new crystalline phase. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

In the past three decades, molecular nonlinear optical (NLO) materials have been intensively explored because of their large NLO response, structural diversities and intriguing structure–property relationships [1–5]. Second harmonic generation (SHG) is a basic 2-order NLO process, which is characterized by molecular 2-order polarizability β (known as superpolarizability) and crystalline 2-order susceptability $\chi^{(2)}$. For molecular crystals, their macro SHG intensities are dominated by the β value and the molecular packing style in the crystal.

Among the most significant experimental results in 2-order organic NLO field are, for example, the neutral organic crystals [6] and organic salts [7] with a typical SHG efficiency being about 1000 times that of urea reference and the metal–organic complexes with large β values being the order of 1000×10^{-30} e.s.u. [8,9]. In exploring the structure–property relationships, the most successful theoretical approach may be the double-energy model for D- π -A type of dipolar molecules [10]. This was followed by an interesting idea of the non-polar and non-centrosymmetric octupoles [11]. An octupolar NLO crystal TTB (1,3,5-tricy-ano-2,4,6-tris(*p*-diethylaminostyryl)benzene) was recently reported to have an extraordinarily large SHG efficiency which is double of that of the well known dipolar NLO crystal DAST [12].

The croconate compounds belong to a member of so called oxocarbons $C_nO_n(n = 3 \text{ for deltate}, 4 \text{ for squarate}, 5 \text{ for croconate}, 6 \text{ for rhodizonate})$. All atoms of these oxocarbons are coplanar and their dianians are well delocalized [13]. A theoretical study indicates that the oxocarbons have moderate β values of the order of $10-100 \times 10^{-30}$ e.s.u., which increase with increasing the ring size [14]. For squarate compounds, there is only one

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report about the measured β values but the crystals are virtually SHG inactive because of the unfavorable molecular packing [15]. As for croconate derivatives, to our knowledge, there is no experimental NLO result reported.

In this work, we synthesized and grew two single crystals of the croconate derivatives, dimethlycroconate (DMCC) and dibenzoylcroconate (DBCC). The DBCC forms centrosymmetric crystal in which benzene molecules are incorporated in a ratio of 2 (DBCC):1 (benzene) and its crystal structure is first reported here. The DMCC forms non-centrosymmetric crystal and its structure has been briefly reported by our group [16]. The SHG intensities of DMCC and DBCC were measured and the structure–property investigation has been carried out.

2. Experimental and calculation

The synthesis for the two title compounds is outlined in Scheme 1. A solution of dipotassium croconate (5 g) in water (300 ml) was mixed with another solution of silver nitrate (9 g) in water (50 ml) in the dark. Orange disilver croconate immediately precipitated and the mixture was kept stirring for 20 min. The orange solid was then filtered out and dried at 50–60 °C for several hours, resulting 7.5 g of disilver croconate.

To synthesis DMCC, 7.4 g anhydrous disilver croconate was placed in a Soxhlet extractor, which was fitted on a flask containing methyl iodide (7 ml) and 200 ml anhydrous benzene (freshly distillated with Na). The reactionand-extraction process under reflux lasted for 24 h. The solvent was removed and 2.6 g of yellow DMCC solid was obtained (yield 73%). DBCC was synthesized in the similar way by reacting 7.5 g disilver croconate with 12 ml benzoyl chloride and 4.4 g of pale-yellow tiny needle crystals were obtained (yield 68%). Yellow parallelepiped DMCC crystals were obtained by spontaneously evaporating its benzene solution at room temperature in a waterfree atmosphere. Yellow rod DBCC crystals were obtained by slowly cooling its benzene solution from 70 °C to room temperature.

X-ray refraction data of the DMCC and DBCC single crystals were collected by ω scan method by a Bruker P4 diffractometer with Mo K α radiation at room temperature. DMCC crystal has a formula of C₇O₅H₆ and packed in

P2₁2₁2₁ space group with a = 7.181(5), b = 8.069(5), c = 13.015(5) Å, v = 754.1(8) Å³, Z = 4, $R_1 = 0.040$ and $wR_2 = 0.117$ ($I > 2\sigma(I)$). DBCC crystal has a host-guest structure formulated as C₁₉H₁₀O₇·0.5C₆H₆ and crystallized in P2₁/n space group with a = 11.203(2), b = 5.7765(9), c = 28.073(5) Å, $\beta = 97.525(9)^\circ$, v = 1801.1(5) Å³, Z = 4, $R_1 = 0.060$ and $wR_2 = (I > 2\sigma(I))$.

The molecular ground-state dipole moment μ was calculated by using Gaussian 03 program within the framework of HF/6-31G [17]. The geometry conformations for the calculations are the X-ray molecular structures of DMCC and DBCC in this work. The excited-state dipole moment μ_e , the oscillator strength f and energy differences between various states were calculated by the same program within the framework of RCIS/6-31G [17]. Based on these calculated results, the hyperpolarizability tensor components β_{ijk} were then calculated by the sum-over-states method [18]. A total of 20 states were taken.

The β value listed in Table 2 is the vector component β_{μ} along the direction of the molecular dipole moment μ , defined as [19]

$$\beta_{\mu} = \sum_{i} \mu_{i} \beta_{i} / |\mu|, \quad i = x, y, z \tag{1}$$

where
$$\beta_i = \frac{1}{3} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}), \quad i, j = x, y, z$$
 (2)

For DMCC and DBCC, the molecular dipole moment is along the y direction shown in Fig. 1.

3. Results and discussion

3.1. Crystal structure

DMCC molecules are packed in non-centrosymmetric space group $P2_12_12_1$, while DBCC molecules are packed in centrosymmetric space group $P2_1/n$. As shown in Fig. 1, DMCC molecule has very good planarity, but DBCC molecule is non-planar. The flexibility of the Λ shaped DBCC molecule has been overcome to some extent by some intramolecular connections.

The croconate moieties in the two compounds show C_{2v} symmetry. As listed in Table 1, for DMCC the five C–C



Scheme 1.



Fig. 1. Molecular structures for (a) DMCC and (b) DBCC.

 Table 1

 Bond lengths related to croconate moiety in the title compounds

DMCC	DBCC
O1-C3 1.319(4) C3-C4 1.373(5)	C1-O1 1.196(5) C1-C3 1.521(6)
O2-C4 1.315(4) C3-C7 1.452(5)	C2-O2 1.208(5) C1-C2 1.527(6)
O5-C7 1.222(5) C4-C5 1.454(5)	C3-O3 1.203(5) C2-C4 1.481(6)
O3-C5 1.219(4) C5-C6 1.502(5)	C4-O4 1.364(5) C3-C5 1.472(6)
O4-C6 1.202(4) C6-C7 1.509(5)	C5-O5 1.348(5) C4-C5 1.344(6)

bonds lengths of the five-membered ring are within the range 1.373(5)-1.509(5) Å and the C=O bonds lengths are within 1.202(4)-1.319(4) Å. For DBCC, the five C-C bonds and the five C=O bonds of the croconate moiety are characterized by 1.344(6)-1.527(6) and 1.196(5)-1.364(5) Å, respectively. The difference for the same type bond of the croconate moiety in DBCC is much larger than that in DMCC. This means the electronic delocalization of the croconate moiety in DMCC is relatively larger.

The calculated ground-state dipole moment of the DBCC is almost double that of DMCC (see Table 2). This may be the reason why DBCC crystal has a centrosymmetric structure.

It is noteworthy that DBCC crystal has an host-guest structure with a stoichiometric ratio of 2 (DBCC):1 (benzene) (see Fig. 2). Two DBCC molecules coupled to form a near-square and all these squares form channels, which

Table 2 Experimental absorption wavelength and the calculated electronic structural parameters

	λ_{\max} (nm)	$\lambda_{\text{cut-off}}$ (nm)	$\mu_{g}\left(\mathbf{D}\right)$	$\mu_{\rm e} ({\rm D})^{\rm a}$	$f_{\rm ge}{}^{\rm b}$	β_{μ} (10 ⁻³⁰ e.s.u.) ^c	SHG ^d
DMCC DBCC	301 234	404 313	4.770 8.970	6.910 10.398	0.7885	15.31	0.9 Urea

^a According to the results of the RCIS/6-31G scheme, the charge-transfer excited-state $| e \rangle$ of DMCC mainly consists of the LUMO orbital; while that of DBCC consists of many orbitals.

^b Oscillator strength.

^c The calculated β_{μ} is at the $\lambda = 1064$ nm of fundamental light.

^d The SHG intensities (1080 nm \rightarrow 540 nm) of the powder crystal samples are the relative values with urea powder as the standard.



Fig. 2. Packing diagram of DBCC crystal.

are all along the *b* axis direction to accommodate the guest benzene molecules and have a transverse area about 40 \AA^2 .

3.2. Linear and nonlinear optical properties

The absorption spectra of DMCC and DBCC in acetonitrile are shown in Fig. 3. The cut-off wavelength $\lambda_{cut-off}$ for the two compounds is about 420 and 320 nm, respectively. And their absorption maximum wavelength λ_{max} is



Fig. 3. Absorption spectra for DMCC and DBCC in acetonitrile at concentration of 10^{-5} mol L⁻¹.

301 nm for DMCC and 234 nm for DBCC. The $\lambda_{cut-off}$ of the two compounds are short enough for the SHG of Nd:YAP or Nd:YAG lasers and other green or blue lasers. The bathochromic effect of DMCC relative to DBCC can be interpreted as the stronger donor strength of the methyl group relative to the benzoyl group. Besides, the croconate moiety of DMCC shows better π -conjugation as revealed by the X-ray structural results above. One challenge in molecular NLO field is the so-called trade-off problem between transparency and efficiency. Interestingly, however, DBCC has both larger β value (see Table 2) and better transparency.

SHG intensities of the power DBCC and DMCC crystals were determined by the Kurtz method [20] and urea sample was used as the reference. The input fundamental light has a wavelength of 1080 nm from a Nd:YAP laser. The powder SHG efficiency of DMCC is 0.9 times that of the powder urea standard. However, the "centrosymmetric" DBCC power crystals also exhibited a SHG intensity 0.6 times that of the urea. This result is contrary to the well-established tensor theory about the centrosymmetric forbidden for the 2-order NLO response.

The crystal structure of DBCC shows that there are two guest benzene molecules in the unit cell with weak molecular interaction with the host DBCC molecules. Prompted by the channels along the *b* axis (see Fig. 3), these benzene molecules must be easy to escape. Once the guest molecules get out of the crystal, the crystal perhaps changes to a new phase of structure. The measured SHG efficiency may be the result of the new non-centrosymmetric phase, for the benzene molecules are just located at the inversion centers of the DBCC crystal and the loss of these inversion centers is likely to result in the collapse of the centrosymmetric packing of host DBCC molecules. Because it is difficult to obtain the structure of this new phase, we try to find evidences of the supposed phase transition by thermal analysis and XRD method.

The DSC curves for DBCC crystal were recorded in nitrogen atmosphere at the different heating rate $(10 \,^{\circ}C/min \text{ and } 20 \,^{\circ}C/min, \text{ respectively})$. From Fig. 4, we recognized that the desorption of the benzene took place at



Fig. 4. DSC curves for DBCC crystals.



Fig. 5. XRD spectra for DBCC: (a) slightly grinding sample; (b) long time grinding sample.

90 °C, and its desorption heat is 2.6 kJ/mol. Such low desorption temperature and small desorption heat make the benzene molecules easy to get out of the crystal when it is grinded to powder sample for SHG test.

The DSC curves show partly overlapped double peaks in the melting process, which can be interpreted as the consecutive melting of the no-benzene phase and the original phase. Two curves in different heating rate show different relative height of the double peaks. Slower heating (10 °C/min) activates more benzene molecules to escape, so the first peak should belongs to the melting of the nobenzene phase and the second belongs to the melting of the original phase. Because the melting temperature of the no-benzene phase is close to the benzene desorption point, it is difficult to get the pure no-benzene phase.

To find further evidence of the phase transition, X-ray powder pattern of the crystals were recorded at a scan rate of 10 °C/min on a Rigaku D/Max 2200PC with Cu K α radiation and shown in Fig. 5. The XRD pattern for the slightly grinded sample of DBCC is similar to the simulated pattern from the data of the single crystal structure. When the sample underwent long time grinding, however, its XRD pattern is obviously different from the previous one. Especially, the three strong peak positions are different and the pattern is more complicated.

Although DBCC has larger β value (see Table 2), its crystalline SHG intensity is relatively weak. It is because of the difficulty to isolate the pure non-centrosymmetric phase. One may think the NLO effect of the DBCC molecule may come from the benzene moiety, but DMCC also exhibits considerable NLO effect both at the molecular level and the crystalline level. Thus we conclude that the croconate moiety can independently serve as NLO generator or chromophore.

4. Conclusion

Organic croconate compounds DMCC and DBCC were synthesized and their crystal structures were determined by X-ray diffraction. They are quite transparent and exhibit moderate micro hyperpolarizability and macro SHG efficiency, indicating that the croconate can independently serve as a NLO center. To solve the conflict between the SHG effect and the centrosymmetric structure of DBCC, we found that the SHG turned out to be the result of a new phase of DBCC. The turn-and-off of the SHG signal is accompanied by the out-and-in of the guest benzene molecules. This interesting phenomena of DBCC crystal may find some application as a kind of chemosensor to probe poisonous benzene in air. Noticeably, this kind of application does not demand tremendous SHG intensity, which is once the goal of the organic NLO materials field. SHG here had rather be a tool than be a goal.

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper in the form of CIF file have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-614943 for DBCC and number CCDC-282597 for DMCC. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.01.041.

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