



## A New Type of Organic Ferroelectric N-Dehydroabietyl-4-bromobenzamide

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A new organic low-molecular-mass compound N-dehydroabietyl-4-bromobenzamide (**1**) was synthesized using natural biomass dehydroabietylamine and 4-bromobenzoic acid. Single crystal structure analysis revealed that compound **1** crystallized in a chiral and polar space group  $P2_1$  and adjacent molecules were held together by almost straight line N-H...O hydrogen bond chain. Compound **1** exhibits good second-order nonlinear optical and ferroelectric properties. The results indicated a new type organic ferroelectric material derived from natural biomass dehydroabietylamine.

**Keywords:** N-Dehydroabietyl-4-bromobenzamide, Ferroelectric, Nonlinear optical, Dielectric.

### INTRODUCTION

Ferroelectricity is one of the major subjects in the field of materials science due to its wide applications in ferroelectric random-access memories (FeRAM), switchable nonlinear optical devices, electro-optical devices and light modulators<sup>1-5</sup>. For the past few decades, great efforts have been devoted to synthesize various inorganic or inorganic-organic hybrid ferroelectric compounds<sup>6-12</sup>, but the pure organic ferroelectrics, especially low-molecular-mass organic ferroelectrics still remain sparse<sup>13-16</sup>. Organic ferroelectrics should be important functional materials in the future due to their advantage in the fabrication of flexible, lightweight, large-area, low-cost organic devices<sup>17,18</sup>.

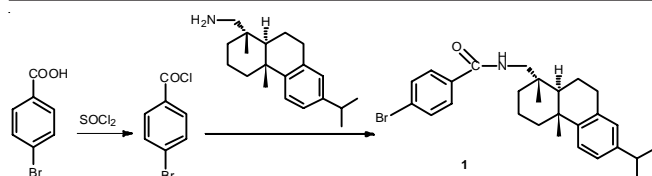
Dehydroabietylamine, a low-cost natural biomass with enantiomeric pure diterpenic structure, can be easily separated from natural rosin<sup>19-21</sup>. The chirality in dehydroabietylamine is useful to construct noncentrosymmetric structure. As an extension of our interest in molecule-based ferroelectrics<sup>22,23</sup>, a new organic low-molecular-mass compound N-dehydroabietyl-4-bromobenzamide was prepared by the reaction of dehydroabietylamine and 4-bromobenzoic acid (**Scheme-I**). Its ferroelectric, dielectric and second-order nonlinear optical properties were reported here.

### EXPERIMENTAL

Elemental analyses for C, H and N were performed on a CHN-O-Rapid analyzer and an elemental vario MICRO analyzer. The IR spectrum was performed on a Bruker Vector

22 FT-IR spectrometer with KBr discs in the 4000-400  $\text{cm}^{-1}$  range. The CD spectra were recorded on a JASCO J-810 Spectropolarimeter. The electric hysteresis loops were recorded on a ferroelectric tester multiferroic made by Radiant Technologies, Inc. complex dielectric permittivity was performed using automatic impedance TongHui 2828 Analyzer. The measuring AC voltage was 1 V. For second harmonic generation (SHG) experiments, an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used. The instrument model is FLS 920, Edinburgh Instruments. The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP reference.

**Synthesis of N-dehydroabietyl-4-bromobenzamide:** A mixture of 4-bromobenzoic acid (2.01 g, 10 mmol) and thionyl chloride (10 mL) was refluxed for 3 h and then residual thionyl chloride was removed to obtain 4-bromobenzoyl chloride in a solid state. The fresh 4-bromobenzoyl chloride was dissolved in anhydrous dichloromethane (20 mL) and added dropwise into the solution of dehydroabietylamine (10 mmol, 2.85 g) in anhydrous dichloromethane (20 mL). After the addition of triethylamine (1.6 mL), the mixed solution was kept stirring overnight at room temperature. The reaction mixture was treated by small amount of water and the organic layer was dried and evaporated to obtain crude product in a solid state. This product was dissolved in ethanol solution and left to stand undisturbed. Upon slow evaporation at room temperature for several days, single crystals of compound **1** suitable for X-ray



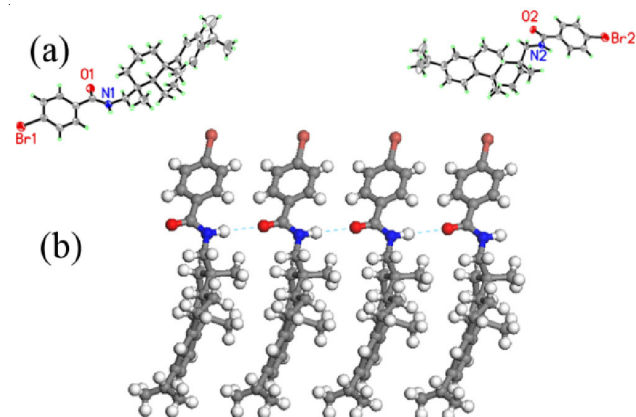
**Scheme-I:** Synthesis of N-dehydroabietyl-4-bromobenzamide

analysis were collected. FT-IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3355(s), 3062(w), 2958(w), 1640(s), 1520(s), 1340(s), 1055(m). Anal. Calcd. for  $\text{C}_{27}\text{H}_{34}\text{BrNO}$ : C, 69.22, H, 7.32, N, 2.99; found: C, 29.12, H, 7.31, N, 2.90 %.

**Single crystal X-ray crystallography:** Diffraction intensity for **1** was collected at 293(2) K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption corrections were applied using SADABS. The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXTL-97 programs, respectively. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The H atoms were positioned geometrically and treated as riding on their parent atoms, with C-H distances of 0.97  $\text{\AA}$  (methylene) and 0.96  $\text{\AA}$  (methyl).

## RESULTS AND DISCUSSION

**Crystal structure:** Compound **1** crystallizes in monoclinic space group  $P2_1$ . As shown in Fig. 1a, the asymmetric unit consists of two independent N-dehydroabietyl-4-bromobenzamide molecules divided by a  $C_2$  symmetry axis. There are four crystallographically distinct six-membered rings in each N-dehydroabietyl-4-bromobenzamide. The two phenyl rings are planar and the dihedral angle between them is  $71.4^\circ$ . The two cyclohexyl groups adopt half-chair and chair conformation, respectively. There exists weak N-H...O hydrogen bond interactions, which are arranged in almost straight line with a hydrogen-bond angle of  $167.4^\circ$  to hold adjacent molecules into one dimensional extended chain (Fig. 1b). Although the N-H...O hydrogen-bond is a little weak, the uniform orientation may play a crucial role in producing spontaneous polarization by the order-disorder motion of hydrogen atom between N and O atom, just like the parallel bistable N-H...N hydrogen bonds in ferroelectric compound DabcoHReO<sub>4</sub><sup>24</sup>. The parallel and nearly ideal linear hydrogen bonds aggregates are unique

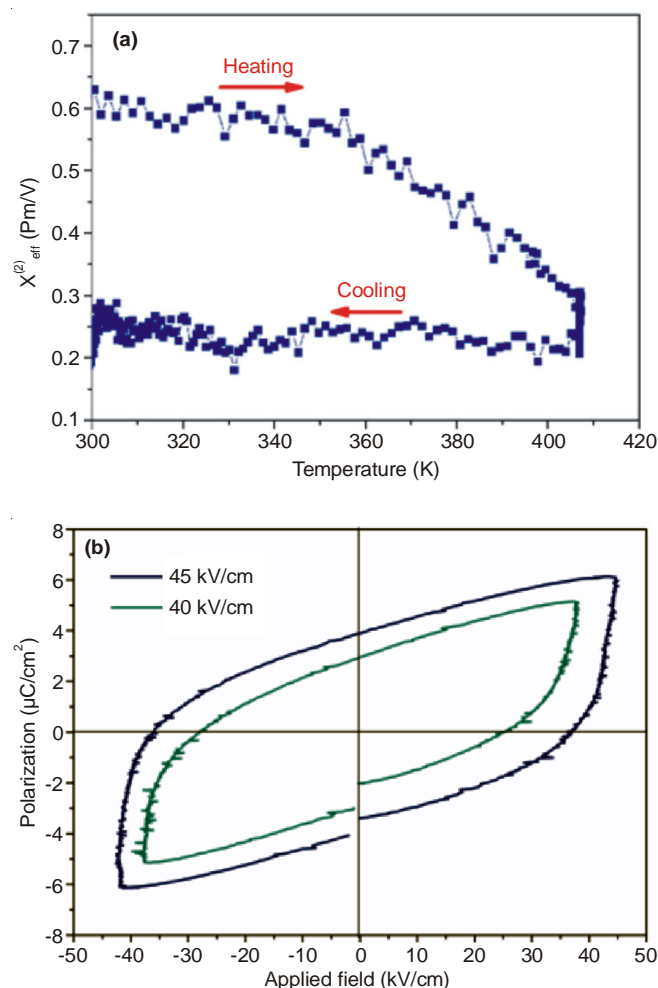


**Fig. 1.** (a) Crystal structure of compound **1** (30 % probability thermal ellipsoids); (b) Hydrogen bond chain in compound **1**

crystal in general. In dabcoHClO<sub>4</sub><sup>25</sup> and dabcoHBF<sub>4</sub><sup>26</sup> the consecutive chains of N-H...N hydrogen-bonded dabcoH<sup>+</sup> cations are arranged antiparallel and the cations in piperazinium tetrafluoroborate ( $[\text{NH}_2(\text{CH}_2)_4\text{NH}][\text{BF}_4]$ )<sup>27</sup> and lithium hydrazinium sulfate ( $\text{LiN}_2\text{H}_5\text{SO}_4$ )<sup>28</sup> are linked into zigzag chains.

**Circular dichroism spectra:** To confirm the optical activity of compound **1**, the solid circular dichroism spectrum was measured in KBr pellet. Compound **1** exhibits negative cotton effects at about  $\lambda_{\max} = 242 \text{ nm}$ , which should be related to the  $\pi$ - $\pi^*$  transition.

**Ferroelectric and nonlinear optical properties:** As compound **1** crystallized in a chiral space group ( $P2_1$ ), belonging to the polar point ( $C_2$ ), its second-order nonlinear optical and ferroelectric properties were investigated. The temperature dependence of second-order nonlinear optical effect for powdered samples was given in Fig. 2a. The result indicated that compound **1** was second-harmonic-generation-active, but when heating up to 360 K, the SHG effect was gradually decreased. The reason should be related to the gradual decomposition of compound **1** because dehydroabietylamine was not thermally stable higher than 373 K<sup>29</sup>.



**Fig. 2.** (a) Temperature dependence of second-order nonlinear optical coefficient; (b) Electric hysteresis loops at r.t. for single crystal samples at different electric field

The ferroelectric property of **1** was investigated using single-crystal and powder samples, respectively. The single-

crystal sample of compound **1** indeed displays an obvious ferroelectric behaviour with a remnant polarization ( $P_r$ ) of ca. 2.92–3.90  $\mu\text{C cm}^{-2}$  and  $E_c$  of ca. 25.57–36.85  $\text{kV cm}^{-1}$  (Fig. 2b). The almost ideal hysteresis loops of single-crystal sample indicated the reality of ferroelectricity for compound **1**. The ferroelectric properties of powdered samples were also investigated, but no ideal loops can be obtained due to the irregular arrangement of dipole direction, which only reflects the average polarization behaviour. The observed hysteresis loops and the low leakage currents (less than  $10^{-7}$   $\text{A cm}^{-2}$  at electric field of even higher than 100  $\text{kV/cm}$ ) indicated that compound **1** indeed display obvious ferroelectric behaviour and the observed hysteresis loops were clearly due to ferroelectricity.

**Dielectric properties:** The temperature dependence of dielectric constant for compound **1** was shown in Fig. 3. It remains almost unchanged below 360 K and shows a wide peak at about 400 K on the heating process. On the following cooling process, no obvious peak was found. The irreversible wide peak should be resulted from the gradual decomposition of compound **1**. The ferroelectric-paraelectric phase transition can not be observed because  $T_c$  is higher than the decomposition temperature.

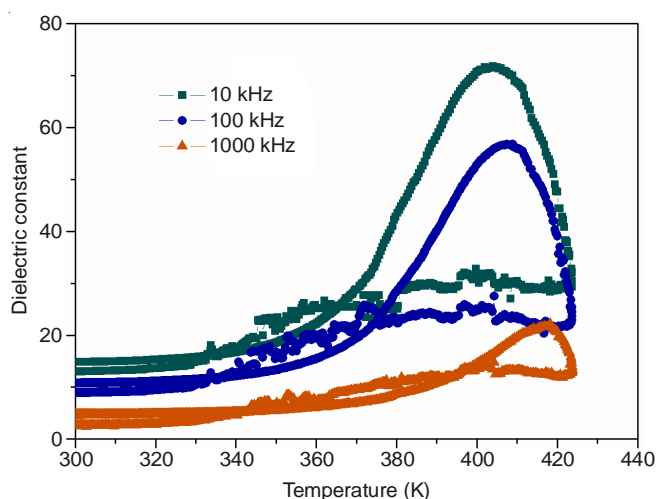


Fig. 3. Temperature dependence of dielectric constants at different frequencies

## Conclusion

In summary, we found a new organic low-molecular-mass compound N-dehydroabietyl-4-bromobenzamide with good second-order nonlinear optical and ferroelectric properties. The results indicated a new type organic ferroelectric material derived from natural biomass dehydroabietylamine.

## Supplementary data

CCDC No. 1005430 contains the supplementary crystallographic data for this paper. It can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## ACKNOWLEDGEMENTS

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