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Cyclohexylammonium sulfanilate: A simple representative of the chiral materials containing only achiral building units

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Chiral building units must pack into chiral crystal structures. However, chiral structures can also be induced from achiral building units. In this letter, the later well-known phenomenon is illustrated with the simple synthesis of a new chiral compound from commonly used achiral organic molecules. Thus, the new compound cyclohexylammonium sulfanilate was synthesized at room temperature and characterized by single crystal X-ray diffraction, spectroscopy (UV/Visible and FT-IR), and thermal analysis. The compound is chiral and crystallizes in orthorhombic system with space group $P2_12_12_1$. Noncentrosymmetry was confirmed by Second Harmonic Generation (SHG) measurements using solid potassium dihydrogenphosphate (KDP) as reference. The organic ions which form this chiral compound namely cyclohexylammonium (C_6NH_3^+) and sulfanilate ($\text{NH}_2\text{PhSO}_3^-$) are both low-cost achiral building units. A statistical investigation of previously reported structures shows that $\text{NH}_2\text{PhSO}_3^-$ stabilized by noncentrosymmetric cations more likely lead to noncentrosymmetric materials.

1. Introduction

The synthesis of noncentrosymmetric (NCS) compounds is of high importance in optics or chemistry owing to their interesting physical properties such as catalysis, dichroism, piezoelectricity, ferroelectricity, pyroelectricity, or Second Harmonic Generation (SHG) [1–10]. These multiple applications require simple synthetic methods of NCS compounds. A well-known method to produce successfully such solids is to use enantiomerically pure molecules because such units must pack into chiral crystal structures [11]. But this method is commonly expensive as the molecules must be enantioenriched and should survive the growth methods without racemization [12]. Another approach is to use achiral building blocks [1,13–15]. However, in this method, the arrangement of the achiral building blocks in the solid must be NCS. For this reason, understanding the packing of achiral molecules into NCS arrangements is a key for the future design of noncentrosymmetric (NCS) functional materials. Previous works reported SHG active chiral compounds from NCS, achiral building units [16,17]. Herein, we

aim at understanding the packing of two achiral molecules through hydrogen bonding into an SHG active chiral compound.

The NCS achiral sulfanilate anion was previously stabilized into diverse materials with counterions such as ammonium, rubidium, lithium or potassium [18–21]. In this letter, we used the NCS achiral cyclohexylamine and obtained a new chiral compound exhibiting a Second Harmonic Generation (SHG) response. A statistical analysis of the arrangement of the sulfanilate anion with different CS or NCS cations provides new insights in the future design of NCS materials.

2. Materials and methods

Sulfanilic acid (99%) and cyclohexylamine (99%) were purchased from Aldrich and used without further purification. Cyclohexylammonium sulfanilate was prepared by mixing cyclohexylamine (0.04 mol) and sulfanilic acid (0.04 mol) in distilled water at room temperature. The solution was stirred for two hours. Large colourless crystals suitable for X-ray diffraction were obtained after slow evaporation of the water. For spectroscopic measurements, these colourless crystals were firstly ground with KBr and pressed into pellets. FT-IR spectra were obtained with a Bruker Vertex 70 instrument, 100 scans were collected with

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a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} . A background spectrum was subtracted. Diffuse reflectance spectrum of the ground crystals was collected with a Perkin Elmer UV-visible-NIR spectrometer (Lambda 1050) equipped with an integrating sphere. The obtained data were treated by Kubelka-Munk transformation. Single-crystal X-ray diffraction was performed using a Bruker-Nonius Kappa CCD diffractometer (MoK α radiation/crystal to detector distance = 60 mm). Absorption corrections were considered using SADABS [22]. Direct methods were used to determine the crystal structure through the program SIR2004 [23]. The crystal structure was refined with SHELXL-2013 [24]. Additional symmetry elements were checked using PLATON [25]. More information on the crystal structure is available in Table S1–3. Differential Scanning Calorimetry (DSC) measurements were carried out with a Setaram Sensys Evo under Argon flow, from room temperature to $800\text{ }^\circ\text{C}$, with a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. A Ti:Sa laser from Spectra Physics (Hurricane model) delivering pulse of 100 fs at 800 nm (1 kHz) was used to detect SHG signals. SHG was collected at 400 nm with a streak camera C7700 from Hamamatsu coupled with a spectrometer from Princeton instruments.

3. Results and discussion

3.1. Structure description

The compound crystallizes in orthorhombic system (space group $P2_12_12_1$). The asymmetric unit contains the cyclohexylammonium cation and the sulfanilate anion. The crystal packing shows supramolecular self-assembly through the three axes a , b and c , resulting from the interactions sulfanilate-sulfanilate and sulfanilate-cyclohexylammonium. The sulfanilate-sulfanilate interactions through $\text{N-H}\cdots\text{O-S}$ connections generate chains. The cyclohexylammonium connects these chains via hydrogen bonding $\text{N-H}\cdots\text{O-S}$, leading to a 3D network of hydrogen bonds (Fig. 1). Comparing with previously reported sulfanilate compounds with

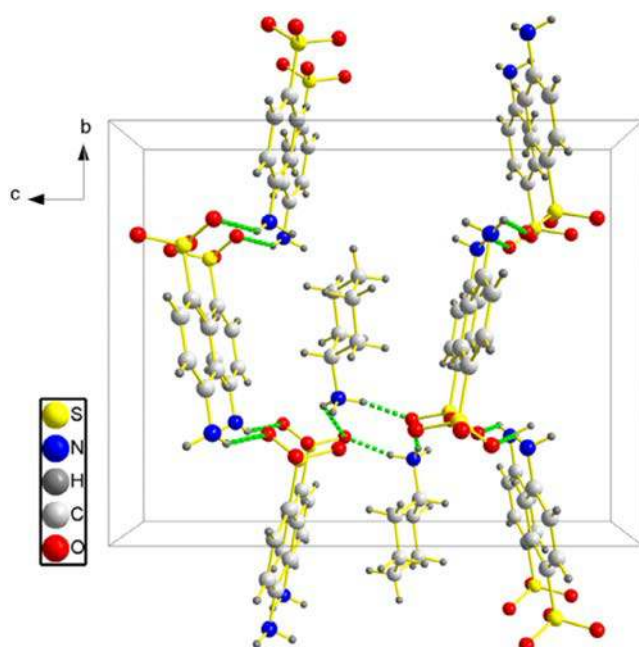


Fig. 1. Crystal structure of cyclohexylammonium sulfanilate (Hydrogen bonds are represented in green dotted lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

counterions such as ammonium, rubidium, lithium or potassium [18–21], this resulting crystal structure is chiral. The main difference between the different crystal structures is the symmetry of the cations: while cations are centrosymmetric in these previously reported compounds, cyclohexylammonium is non-chiral but polar (Fig. 2). Thus, the use of this polar unit might be an important parameter for inducing a NCS material. In our compound, the polar units pack along perpendicular 2_1 axes. For this reason, the net dipole moments of the molecules are cancelled out but chirality is generated from the molecular packing. However, the analysis of crystal habit did not allow to simply distinguish between the opposite chirality senses. To better understand the role of the symmetries of the cations/anions on the final packing, one can perform statistical analysis of the Cambridge Crystallographic Database. Over 88 crystal structures containing the sulfanilate anion, 24 which contain molecular cations were selected for further investigation. Our analysis shows that the ratio of NCS crystal structures is 29% (close to the ratio for all compounds: 22%). Among the CS structures, 41% result from the combination of sulfanilate with NCS cations. On the other hand, among the NCS structures, 86% result from the combination of sulfanilate with NCS cations. The statistical results also show that the packing of sulfanilate with NCS cations through hydrogen bonding network is more likely to lead to NCS structures (54%) than when using CS cations (46%) as if the overall occurrence of NCS structures is much lower (29%). For this reason, one can conclude that combining two NCS molecules might be an interesting strategy to target NCS compound. This could be explained by the fact that each NCS molecule offers an acentric environment for the packing of the other.

3.2. UV/Visible and FT-IR spectra

Diffuse reflectance shows strong absorption below 350 nm for the title compound. This intense UV absorption is mainly due to $\pi\text{-}\pi^*$ transition in the aromatic nucleus, confirming the presence of phenyl (sulfanilate) (Fig. 3). The low absorption around 375 nm can be identified as the substitution effect on the phenyl, namely NH_2 and SO_3 groups. The FT-IR Spectrum is shown in Fig. 4. The full attribution of the main absorption bands is available in Supporting information (Table S4). Absorption bands in the range of $3450\text{--}3200\text{ cm}^{-1}$ are assigned to $\nu_{\text{N-H}}$ vibration modes. $\delta_{\text{N-H}}$ vibration mode is also located from 1650 to 1600 cm^{-1} and $\gamma_{\text{N-H}}$ is in the range of $850\text{--}820\text{ cm}^{-1}$. From 3100 to 2850 cm^{-1} , there are several bands attributed to $\nu_{\text{C-H}}$ of the aromatic nucleus and the $\nu_{\text{C-H}}$ (CH_2) of cyclohexyl. The ones at 600 and 700 cm^{-1} are assigned to $\delta_{\text{C-H}}$ of the aromatic nucleus. $\delta_{\text{C-H}}$ (CH_2) of cyclohexyl also appears from 1466 to 1387 cm^{-1} . According to the literature

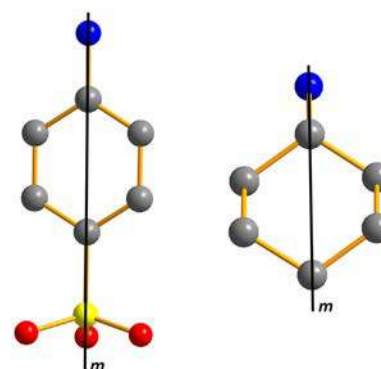


Fig. 2. Symmetry elements of the achiral constituents (anion/left and cation/right) of the title compound (Hydrogen atoms have been removed for clarity).

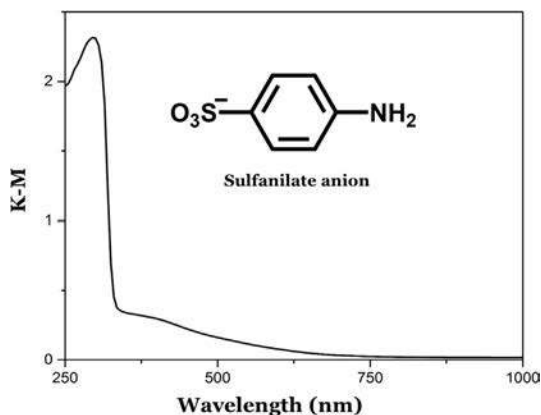


Fig. 3. Kubelka-Munk transformed reflection spectrum of cyclohexylammonium sulfanilate.

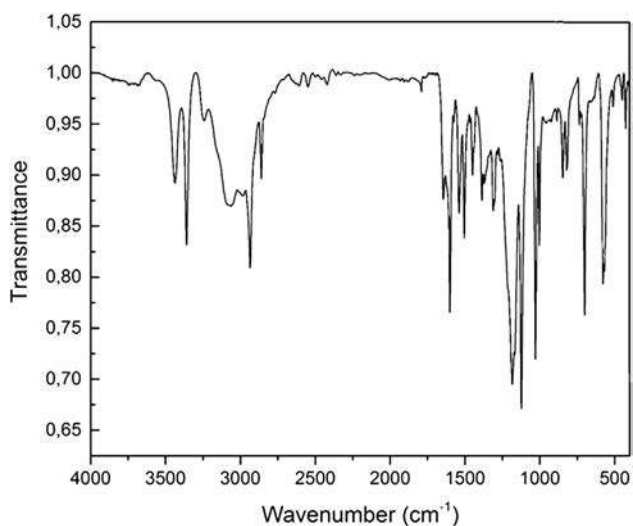


Fig. 4. FT-IR spectrum of cyclohexylammonium sulfanilate compound.

[26,27], the vibration tape at 1214, 1184 and 1169 cm^{-1} are due to ν_{as} of $-\text{SO}_3^-$ group while the ones at 1030 cm^{-1} and 1011 cm^{-1} are assigned to ν_{s} of the same group. $\nu_{\text{C-N}}$ appears at 1000 cm^{-1} .

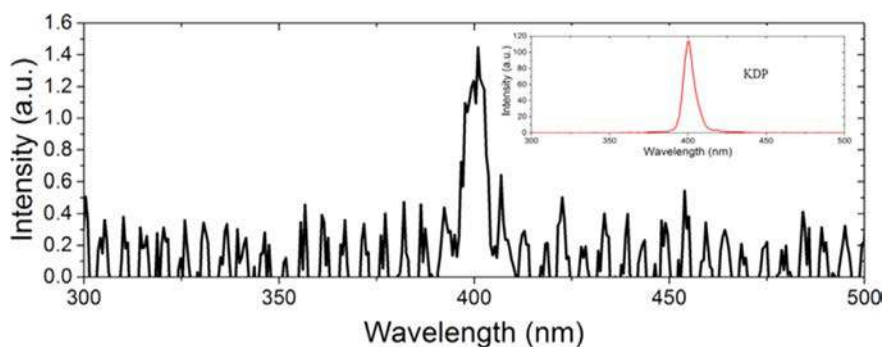


Fig. 5. Second Harmonic Generation response of cyclohexylammonium sulfanilate with incident beam at $\lambda = 800 \text{ nm}$ (Inset: SHG response of the standard KDP).

3.3. Second Harmonic Generation measurements

The differential scanning calorimetry performed on the sulfanilate shows its decomposition at about 250 °C. Thus, Second Harmonic Generation measurement can be carried out without the risk of important degradation due to the excitation power laser (Fig. S1). Every noncentrosymmetric material except the ones in the point-group 432 can be SHG active [7,28]. As our compound crystallizes in the space group $P2_12_12_1$, this material is potentially SHG active. To confirm the noncentrosymmetry of this material, SHG measurement was performed with potassium dihydrogenphosphate (KDP) as reference (Fig. 5). The measurements performed on powder samples at $\lambda = 800 \text{ nm}$ show the same response at 400 nm confirming the simple synthesis of noncentrosymmetric compound from the achiral building units.

4. Conclusion

The new compound cyclohexylammonium sulfanilate was synthesized at room temperature by mixing sulfanilic acid and cyclohexylamine in 1/1 M ratio. The material is chiral and crystallizes in $P2_12_12_1$ space group. The crystal structure consists of a tridimensional network of hydrogen bonds formed by chains of sulfanilate anions interconnected with cyclohexylammonium cations. A statistical analysis showed that the acentric polar sulfanilate is more likely to lead to NCS crystal structures when using NCS cations than CS ones. In this letter, the simple achiral building units (cyclohexylamine and sulfanilic acid) lead, through an easy synthetic approach, to a chiral material exhibiting a SHG response. Thus, we believe this investigation will serve as a simple illustration of the induction of chiral materials which do not require enantioenrichment.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.01.034>.

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