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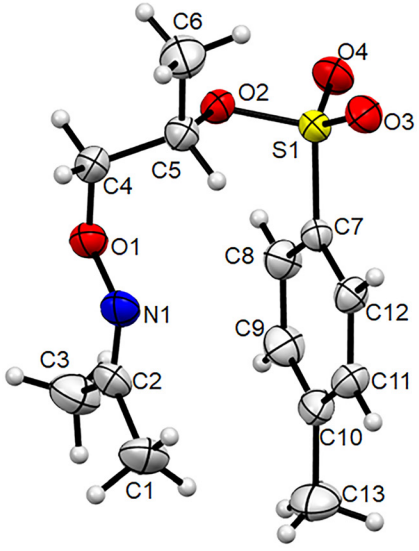
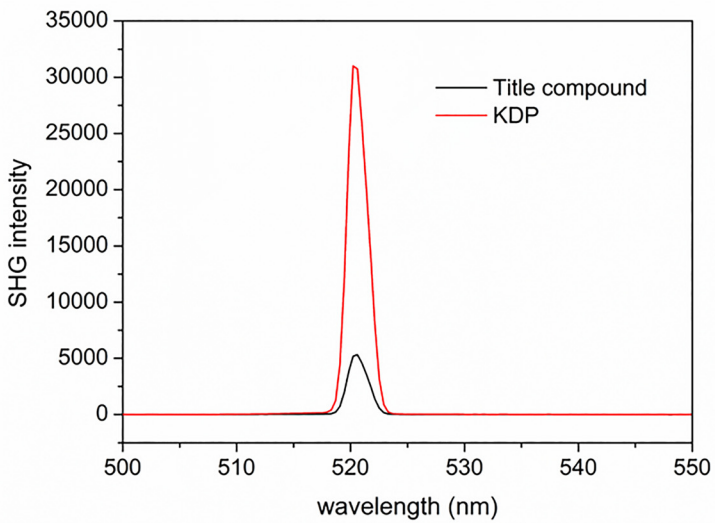
# Synthesis, crystal structure and nonlinear optical property of 1-((propan-2-ylideneamino)oxy) propan-2-yl-4-methylbenzenesulfonate, $C_{13}H_{19}O_4NS$

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**Abstract**

$C_{13}H_{19}O_4NS$, monoclinic, *Cc* (no. 9), $a$ = 11.4661(6) Å, $b$ = 11.7180(7) Å, $c$ = 12.1509(7) Å, $\beta$ = 115.395(2)°, $V$ = 1474.84(15) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0253, $wR_{ref}(F^2)$ = 0.0643, $T$ = 200(2) K. The title compound crystallizes in a non-centrosymmetric space group.

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**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colorless block |
| Size: | 0.18 × 0.12 × 0.11 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| $\mu$: | 0.23 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II, $\varphi$ and $\omega$ |
| $\theta_{max}$, completeness: | 27.5°, 99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 11578, 3094, 0.025 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2981 |
| $N(param)_{refined}$: | 176 |
| Programs: | Bruker,[1] SHELX[2] |

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of materials

The single crystal suitable for X-ray diffraction was obtained via slowly evaporating the dichloromethane/hexane solution of the title compound.

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.1658 (3) | 0.4056 (3) | 0.3497 (3) | 0.0575 (7) |
| H1A | 0.1562 | 0.4429 | 0.4175 | 0.086* |
| H1B | 0.1945 | 0.3267 | 0.3720 | 0.086* |
| H1C | 0.0826 | 0.4059 | 0.2776 | 0.086* |
| C2 | 0.2641 (2) | 0.4689 (2) | 0.3219 (2) | 0.0407 (5) |
| C3 | 0.3000 (3) | 0.4244 (3) | 0.2261 (3) | 0.0585 (7) |
| H3A | 0.2753 | 0.4800 | 0.1596 | 0.088* |
| H3B | 0.2550 | 0.3522 | 0.1946 | 0.088* |
| H3C | 0.3935 | 0.4118 | 0.2610 | 0.088* |
| C4 | 0.4367 (2) | 0.71699 (19) | 0.4175 (2) | 0.0422 (5) |
| H4A | 0.3574 | 0.7602 | 0.4036 | 0.051* |
| H4B | 0.4870 | 0.7631 | 0.3847 | 0.051* |
| C5 | 0.5152 (2) | 0.70220 (17) | 0.55234 (19) | 0.0346 (4) |
| H5 | 0.4703 | 0.6486 | 0.5855 | 0.042* |
| C6 | 0.5404 (3) | 0.8149 (2) | 0.6198 (3) | 0.0550 (7) |
| H6A | 0.6004 | 0.8029 | 0.7054 | 0.082* |
| H6B | 0.4589 | 0.8458 | 0.6149 | 0.082* |
| H6C | 0.5783 | 0.8689 | 0.5827 | 0.082* |
| C7 | 0.62054 (19) | 0.43482 (16) | 0.60765 (18) | 0.0283 (4) |
| C8 | 0.6405 (2) | 0.38220 (19) | 0.5148 (2) | 0.0392 (5) |
| H8 | 0.6988 | 0.4139 | 0.4863 | 0.047* |
| C9 | 0.5741 (3) | 0.2830 (2) | 0.4646 (2) | 0.0446 (6) |
| H9 | 0.5887 | 0.2456 | 0.4023 | 0.053* |
| C10 | 0.4867 (2) | 0.23663 (17) | 0.5029 (2) | 0.0394 (5) |
| C11 | 0.4685 (2) | 0.29085 (18) | 0.5964 (2) | 0.0370 (5) |
| H11 | 0.4092 | 0.2597 | 0.6239 | 0.044* |
| C12 | 0.5354 (2) | 0.38931 (17) | 0.64963 (19) | 0.0325 (4) |
| H12 | 0.5233 | 0.4252 | 0.7140 | 0.039* |
| C13 | 0.4122 (3) | 0.1291 (2) | 0.4451 (3) | 0.0607 (7) |
| H13A | 0.4379 | 0.0677 | 0.5057 | 0.091* |
| H13B | 0.4311 | 0.1063 | 0.3768 | 0.091* |
| H13C | 0.3195 | 0.1436 | 0.4153 | 0.091* |
| N1 | 0.30897 (18) | 0.55844 (17) | 0.38457 (18) | 0.0399 (4) |
| O1 | 0.40103 (15) | 0.61259 (14) | 0.35198 (14) | 0.0412 (4) |
| O2 | 0.64038 (14) | 0.65337 (12) | 0.56860 (13) | 0.0345 (3) |
| O3 | 0.68501 (17) | 0.58971 (14) | 0.77536 (14) | 0.0424 (4) |
| O4 | 0.83360 (16) | 0.55218 (15) | 0.68119 (16) | 0.0467 (4) |
| S1 | 0.70501 (4) | 0.56085 (4) | 0.67094 (4) | 0.03183 (13) |

## 2 Experimental details

Single-crystal X-ray data for the title compound were collected on a Bruker D8 Venture diffractometer using Bruker APEX2 program[1] at 200 K. The structure of the title compound was solved using Direct Methods and refined with the SHELXTL 2014 program[2] All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were added theoretically.

## 3 Comment

Nonlinear optical (NLO) materials have received sustained research attention due to their irreplaceable roles in the field of photonics.[3–8] In particular, organic compounds exhibiting NLO properties possess certain unique advantages, including superior second and third order NLO responses, ultrafast response times, variable structures for adjusting transparency in a wide spectral region, and ease of synthesis and crystal growth.[9–13] Generally, organic NLO compounds feature π-conjugation systems asymmetrized by electron donor or acceptor groups (such as amino-, azo-, halo-, cyano-, hydroxy, sulfo-), which is conducive to their polarization.[9] What's more, crystallization in a non-centrosymmetric (NCS) space group is the key to the production of NLO responses. Herein, a benzene sulfonate derivative, 1-((propan-2-ylideneamino)oxy)propan-2-yl-4-methylbenzenesulfonate, crystallized in an NCS space group was obtained, and its synthesis, crystal structure, and NLO property are presented.

The title compound has a molecular formula of $C_{13}H_{19}O_4NS$ and crystallizes in a monoclinic non-centrosymmetric space group *Cc*. In the title compound, the acetone oxime fragment and the methylbenzene group are connected by the sulfonic acid ester unit. Generally, if there are two different substituent groups attached to the carbon atom of the C–O ester bond, the larger group may be on the same side as the methylbenzene group or on the opposite side.[14–16] As for the title compound, the acetone oxime fragment and the methylbenzene group are on the same side, and thus the molecular structure of the title compound exhibits an 'n' shape. The plane of the acetone oxime is almost parallel to the plane of the toluene with a small dihedral angle of 1.18° and a distance of 3.62 Å.

Because the title compound has the features of organic NLO materials and crystallized in an NCS space group, its NLO property was carefully checked. The second harmonic generation (SHG) of the title compound was measured based on the Kurtz–Perry method using a Q-switched Nd:YAG laser (1064 nm) and $KH_2PO_4$ (KDP) was used as the reference. Indeed, the title compound shows obvious SHG response at around 520 nm, which is about 0.2 times of that for KDP.[17] This result indicates that the title compound is a potential organic NLO material.

The method for synthesizing the title compound was according to its analogues, which contains two steps.[18] All chemicals used were received commercially. Firstly, the reaction of acetone oxime (4.32 g, 59.2 mmol) with propylene oxide (3.65 g, 62.8 mmol) in a basic environment (2 % NaOH solution) at room temperature produces the intermediate product propan-2-one O-(2-hydroxypropyl) oxime, which was separated from the above reaction mixture via extraction using dichloromethane. $^1$H NMR (600 MHz, $CDCl_3$) d:4.16–4.08 (m, 1H), 4.02 (dd, *J* = 11.7, 2.5 Hz, 1H), 3.87 (dd, *J* = 11.7, 7.8 Hz, 1H), 3.05 (s, 1H), 1.92–1.88 (m, 6H), 1.19 (dd, *J* = 12.6, 6.5 Hz, 3H).

The target compound 1-((propan-2-ylideneamino)oxy) propan-2-yl 4-methylbenzenesulfonate was prepared as follows: Tosyl chloride (2.62 g, 20 mmol) in 10 mL of dichloromethane was added dropwise to a mixture of propan-2-one O-(2-hydroxypropyl) oxime (2.62 g, 20 mmol) and triethylamine (2.32 g, 23 mmol) while stirring. After adding the catalyst 4-dimethylaminopyridine (0.18 g, 1.5 mmol), the reaction mixture was stirred at room temperature for 24 h. After that, the reaction mixture was poured into 10 mL of water and the organic layer was separated. The crude product was obtained by evaporating the organic solvent, which was purified via silica gel chromatography using hexane/dichloromethane as the eluent, affording the pure product as a white crystal powder with a yield of 81.3 %. $^1$H NMR (600 MHz, $CDCl_3$) d 7.82 (d, $J$ = 8.3 Hz, 2H), 7.33 (s, 2H), 4.88 (dd, $J$ = 10.6, 6.8 Hz, 1H), 4.04–3.99 (m, 1H), 3.94 (dd, $J$ = 12.2, 3.8 Hz, 1H), 2.46 (s, 3H), 1.75 (d, $J$ = 48.2 Hz, 6H), 1.33 (d, $J$ = 6.5 Hz, 3H).

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