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X-ray Structure Analysis Online

Synthesis, Characterization and Crystal Structure of 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate

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The title compound, $C_{19}H_{18}NO_2^+ \cdot C_6H_4ClSO_3^-$, was synthesized and characterized by UV-Vis, FT-IR, NMR and single crystal X-ray diffraction. The compound crystallizes in the monoclinic *Pc* space group; $a = 7.8386(1)$, $b = 6.7731(1)$, $c = 21.7096(3)$Å, $\beta = 108.476(1)^\circ$, $V = 1093.19(3)$Å^3, $Z = 2$ and D_x 1.470 g cm^{-3}. In the crystal packing, the cations and anions are linked by weak C–H···O interactions into individual chains along the *b*-axis. The anionic and the cationic chains are alternately arranged and interconnected to form a three-dimensional network. The second-harmonic generation (SHG) efficiency of the compound is about 0.5-times that of urea.

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Organic molecules that exhibit second-order nonlinear optical (NLO) properties usually consist of a frame with a delocalized π system, and end-capped with either a donor or an acceptor substituent or both. The most important requirement for these materials to exhibit second-order NLO properties is for the molecules to be oriented in a non-centrosymmetric environment.[1] Benzenesulfonate is frequently used to co-crystallize with cations to form compounds which are expected to have NLO properties.[2] Our continuing research on non-linear optical materials[3,4] has led us to synthesize the title compound

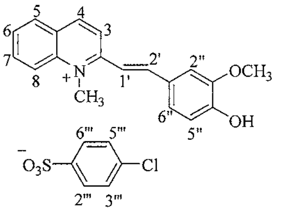

Fig. 1 Chemical scheme of I.

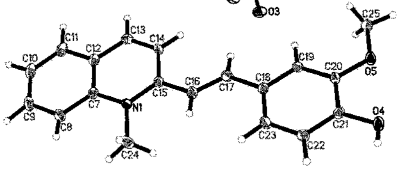

Fig. 2 ORTEP view of I with the atomic-numbering scheme. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 1 Crystal and experimental data

Chemical Formula: $C_{19}H_{18}NO_2^- + C_6H_4ClO_3S^-$
Formula weight = 483.96
Crystal system: monoclinic
Space group: *Pc* $Z = 2$
$a = 7.8386(1)$Å
$b = 6.7731(1)$Å
$c = 21.7096\ (3)$Å
$\beta = 108.476(1)^\circ$
$V = 1093.19(3)$Å^3
$D_x = 1.470$ g cm^{-3}
$\mu(\text{Mo } K_\alpha) = 0.310$ mm^{-1}
$T = 100.0(1)$K
$F(0\ 0\ 0) = 504$
Crystal size = 0.22 × 0.15 × 0.06 nm
θ range for data collection 2.74 to 30.00°
$R = 0.0371$
$R_w = 0.0792$
No. of unique data measured = 6151
No. of observed data with $[I > 2\sigma(I)] = 5510$
No. of parameters = 325
Goodness-of-fit = 1.033
$(\Delta\rho)_{max} = 0.298$ e.Å^{-3}
$(\Delta\rho)_{min} = -0.353$ e.Å^{-3}
Measurements; Bruker APEX2 CCD diffractometer
Program system: Apex2
Structure determination; direct method (SHELXTL)
Refinement: full-matrix least-squares

CCDC 620712 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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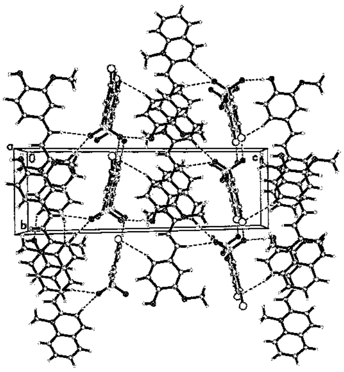

Fig. 3 Crystal packing of I, viewed down the *a*-axis. Hydrogen bonds are shown as dashed lines.

Table 2 Hydrogen-bonding geometry(Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
O4-H1O4...O1^{i}	0.77(2)	1.90(2)	2.6576(19)	169(3)
C2-H2...O3	0.97	2.5543	2.921(3)	103
C3-H3...O1^{ii}	0.97	2.3409	3.189(3)	146
C5-H5...O3^{iii}	0.95	2.2348	3.177(3)	175
C9-H9...O4^{iv}	0.97	2.5288	3.367(3)	144
C10-H10...O5^{iv}	0.96	2.3979	3.310(3)	159
C14-H14...O2	0.94	2.3539	3.296(2)	175
C17-H17...O2	0.93	2.4275	3.332(2)	163

i = *x*, 1–*y*, –1/2+*z*; ii = *x*, 1+*y*, *z*; iii = 1+*x*, *y*, *z*; iv = –1+*x*, –2+*y*, *z*.

(I). We report here on the synthesis and the crystal structure of I, which crystallizes in the non-centrosymmetric monoclinic space group, *Pc*, and has a second-order nonlinear efficiency of 0.5 times that of urea.[5]

2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (compound A) was prepared by the condensation of (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (2.98 g, 10.05 mmol), vanillin (1.60 g, 10.05 mmol) and piperidine (1.00 ml, 10.00 mmol) in methanol (35 ml). The solid formed was filtered and re-crystallized from methanol to give dark-red crystals of A (3.00 g, 68%), mp. 248 – 250°C.

Silver(I) 4-chlorobenzenesulfonate (compound B) was synthesized according to our previous method.[4] Compound I was synthesized by mixing a solution (1:1 molar ratio) of A (0.30 g, 0.72 mmol) in hot methanol (150 ml) and B (0.21 g, 0.72 mmol) in hot methanol (30 ml). The mixture turned dark-red and cloudy immediately. After stirring for 30 min, the precipitate of silver iodide was filtered, and the resulting solution was evaporated to yield an orange solid of I (re-crystallized from methanol): Yield 87%; Mp 262 – 264°C; ^{1}H-NMR (300 MHz, $CDCl_3$ + DMSO-d_6) (δ ppm): 3.98 (3H, s, OCH_3), 4.59 (3H, s, CH_3), 8.42 (1H, d, *J* = 9 Hz, H-3), 8.84 (1H, d, *J* = 9 Hz, H-4), 8.25 (1H, dd, *J* = 1.5, 7.8 Hz, H-5), 7.89 (1H, t, *J* = 7.8 Hz, H-6), 8.14 (1H, dt, *J* = 1.5, 7.8 Hz, H-7), 8.40 (1H, d, *J* = 7.8 Hz, H-8), 7.66 (1H, d, *J* = 15.6 Hz, H-1′), 8.05 (1H, d, *J* = 15.6 Hz, H-2′), 7.48 (1H, d, *J* = 1.8 Hz, H-2″), 6.97 (1H, d, *J* = 8.1 Hz, H-5″), 7.37 (1H, dd, *J* = 1.8, 8.1 Hz, H-6″), 7.76 (2H, d, *J* = 8.4 Hz, H-2‴ and H-6‴), 7.27 (2H, d, *J* = 8.4 Hz, H-3‴ and H-5‴); IR (KBr, cm^{-1}) 3432, 3077, 1584, 1521, 1374, 1189, 1031; UV (λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1}), CH_3OH) 220.5 (2.1), 252.9 (0.8), 310.6 (0.6), 440.1 (1.8), 574.8 (0.9).

The crystallographic and experimental parameters used for data collection and determining of the structure are given in Table 1. All of non-hydrogen atoms were refined anisotropically, The hydroxyl H atom was located in the difference map and isotropically refined. The remaining H atoms were placed at the calculated positions with the C–H distances in the range of 0.93 – 0.97 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atoms for hydroxyl and methyl H atoms, and $1.2U_{eq}$(C) for the remaining H atoms. The final refinement converged well. The largest peak and hole in the final difference map were 0.298 Å^{-3} at 0.88 Å from atom C1 and –0.353 Å^{-3} at 0.51 Å from atom S1, respectively.

The bond lengths and angles are normal.[6] An ORTEP plot of the molecule at 50% probability is shown in Fig. 2. The asymmetric unit of I consists of $C_{19}H_{18}NO_2^+$ and $C_6H_4ClSO_3^-$ (Fig. 2). The cation is almost planar, as indicated by the dihedral angle between the quinolinium (N1/C7–C15) and the benzene (C18–C23) rings, being 4.21(8)° [2.59(9)°,[3] and 2.8(1)°,[4]]. The H atoms attached to C16 and C17 are trans to each other; thus, the cation exists in an E configuration and the torsion angle C15–C16–C1–C18 is –177.82(18)°. In the asymmetric unit, the benzene ring in the 4-chlorobenzenesulfonate anion makes dihedral angles of 87.12(7)° and 83.02(9)°, respectively, with the quinolinium and the benzene rings of the cation. The corresponding values are 59.17(9)° and 60.59° in ref. 3 and 48.97(6)° and 51.63(7)° in ref. 4. The structure shows intramolecular weak C–H···O interactions, namely C14–H14···O2 and C17–H17···O2 (Table 2). The packing of the molecule down the *a*-axis is as shown in Fig. 3; the cations and anions are linked by weak C–H···O interactions into individual chains along the *b*-axis. The anionic and cationic chains are alternately arranged and interconnected to from a three-dimensional network.

Acknowledgements

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