

## SYNTHESIS AND STRUCTURAL STUDY OF STYRYL QUINOLINIUM DYE

Mina Todorova<sup>1</sup>, Rumyana Bakalska<sup>1</sup>, Stoyanka Atanasova<sup>1</sup>,  
Rüdiger W. Seidel<sup>2</sup>, Tsonko Kolev<sup>3</sup>, Emiliya Cherneva<sup>4,5</sup>✉

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### Abstract

A new styryl quinolinium dye (*E*)-4-(2-(2-hydroxynaphthalene-1-yl)ethenyl-1-octyl quinolinium iodide (**3**) was obtained by Knoevenagel condensation. Single crystal X-ray diffraction, spectral methods IR, <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy and TGA-DTA analysis were used to characterize the compound. The title compound crystallized in the triclinic space group P-1 and exhibited thermal stability up to 212 °C. The vibrational spectra were completely determined through the quantum chemical calculations.

**Key words:** styryl quinolinium dye, X-ray, IR, TGA-DTA

**Introduction.** The design of nonlinear optical (NLO) materials has been the focus of modern research due to the possible numerous applications in various high-tech fields, such as telecommunications, information technology, and optical data storage [1]. Nonlinear optics considers the interaction of an applied electromagnetic field with different materials, generating a new electromagnetic field that differs in frequency, phase, polarization, or direction from the initial field [2,3].

Molecular compounds with high initial hyperpolarizability ( $\beta$ ) typically have a conjugated  $\pi$ -system with donor and acceptor moieties (D- $\pi$ -A) linked [4]. The linear optical properties of these dipolar molecules are characterized by low-energy

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charge transfer transitions [5]. The optimization of non-linear optical response at the molecular level has received a lot of attention. In the design of chromophores with high nonlinear second-order optical values, the following criteria need to be considered: polarizability of the material; symmetric charge distribution using suitable strong donor and acceptor groups; length of the  $\pi$ -conjugated bridge; asymmetric arrangement in the crystal packing to observe high even-order nonlinear susceptibilities [6–9]. The reason for the large nonlinear optical susceptibility of these materials is due to the possibility of strong polarizability of the  $\pi$ -electron cloud in these systems. The large charge displacement when small electric fields are applied leads to a non-linear response of the medium and therefore to a modulation of its refractive index. The polarization caused in this way has a purely electronic nature, which is a prerequisite for the occurrence of extremely fast nonlinear optical processes. Particularly effective in the design of D- $\pi$ -A-chromophores is the introduction of electron-rich and electron-deficient heterocycles, which act as electron donors and electron acceptors at both ends of a bridge molecular skeleton [10, 11]. Although most nonlinear optical materials are neutral, salts are particularly promising due to their high stability and ease of preparation, and are therefore particularly attractive for application in various devices [12–14].

**Experimental section. Synthesis of compound (1).** To a solution of 2.15 g (15 mmol) of 4-methylquinoline in dry toluene (20 mL) was added dropwise 3.60 g (15 mmol) of n-octyl iodide. The quaternary salt (4-methyl-1-octylquinolin-1-ium iodide) was obtained after boiling for 13 h at 110 °C. The reaction mixture was subjected to vacuum distillation to remove the solvent toluene. A dark green oil was obtained with yield 80 %.

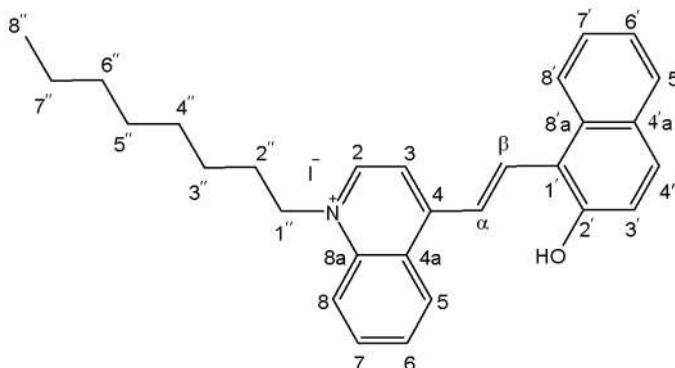
The progress of the reaction mixture was monitored by thin layer chromatography (TLC) under the following conditions: Stationary phase: Silica gel 60 plates (Merck); Mobile phase: benzene:methanol (8:2). Developer: Cerium sulphate reagent. 4-methyl-1-octylquinolin-1-ium iodide was purified by column chromatography under the following conditions: Stationary phase: Silica gel 60, 70–230 mesh (Merck); Eluent: 1 to 3 % (v/v) methanol in diethyl ether.

The composition of the fractions was monitored by thin layer chromatography (TLC) under the following conditions: Stationary phase: Silica gel 60 plates (Merck); Mobile phase: C<sub>6</sub>H<sub>6</sub>:CH<sub>3</sub>OH (9:1) and C<sub>6</sub>H<sub>6</sub>:CH<sub>3</sub>OH (7.5:2.5). Developer: cerium sulphate reagent.

**IR** [KBr]:  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3066, 3019 ( $\nu_{\text{C-H}}$  (Ar-H)), 2955 ( $\nu^{\text{as}}$  (CH<sub>3</sub>)), 2927 ( $\nu^{\text{as}}$  (CH<sub>2</sub>)), 2855 ( $\nu^{\text{as}}$  (CH<sub>2</sub>)), 2728, 1617, 1603, 1587, 1531  $\nu$ (C=C), 1495, 1466 ( $\delta^{\text{as}}$ (CH<sub>3</sub>)), 1369 ( $\delta^{\text{s}}$ (CH<sub>3</sub>)), 1166, 732 cm<sup>-1</sup> ( $\rho$ (CH<sub>2</sub>)).

**Synthesis of compound (3).** A 100 mL round flask was filled with 4-methyl-1-octylquinolin-1-ium iodide (0.73 g; 1.91 mmol) and 0.33 g (1.91 mmol) of 2-hydroxynaphthaldehyde in 20 mL of dry benzene. Additionally, 0.016 g (0.19 mmol) of piperidine and (0.02 g; 0.39 mmol) of glacial acetic acid were added to the mixture. Reflux condenser with a calcium chloride drying tube on top of the

condenser were used to boil the reaction mixture for 21 h. The dark-red crystals were filtered off, washed with benzene, and allowed to dry at room temperature. The progress of the reaction was monitored by TLC. The TLC was performed on plates of silica gel 60 (Merck) with mobile phase: 1-propanol:formic acid (8:2, v/v) was used to elute the product, and UV light or J<sub>2</sub>-vapour was used to visualize it. Yield: 74.34 %. Compound (**3**) was purified by recrystallization from methanol solvent.



Chemical structure of compound **3**

**<sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)**  $\delta$  9.4 (d,  $J_{2,3} = 6.5$  Hz, 1H, H2), 8.7 (d,  $J_{2,3} = 6.5$  Hz, 1H, H3), 8.7 (dd,  $J_{5,6} = 8.6$  Hz,  $J_{5,8} = 0.9$  Hz, 1H, H5), 8.6 (s, 2H, vinyl H <sub>$\alpha$</sub> , H <sub>$\beta$</sub> ), 8.6 (d,  $J_{7,8} = 8.9$  Hz, 1H, H8), 8.4 (d,  $J_{7',8'} = 8.6$  Hz, 1H, H8'), 8.2 (ddd,  $J_{6,7} = 6.9$ ;  $J_{5,7} = 1.6$  Hz, 1H, H7), 8.0 (ddd,  $J_{5,6} = 8.6$ ;  $J_{6,8} = 1.1$  Hz, 1H, H6), 7.9 (d,  $J_{3',4'} = 8.9$  Hz, 1H, H4'), 7.9 (dd,  $J_{5',6'} = 8.4$  Hz,  $J_{5',8'} = 0.7$  Hz, 1H, H5'), 7.6 (ddd,  $J_{7',8'} = 8.4$ ;  $J_{6',7'} = 6.8$ ;  $J_{5',7'} = 1.3$  Hz, 1H, H7'), 7.4 (m, 1H, H6'), 7.3 (d,  $J_{3',4'} = 8.9$  Hz, 1H, H3'), Octyl: 4.98 (t,  $J = 7.5$  Hz, 2H, N<sup>+</sup>CH<sub>2</sub>, 1''), 1.95 (p, 2H, CH<sub>2</sub>, 2''), 1.40 (p, 2H, CH<sub>2</sub>, 3''), 1.31 (p, 2H, CH<sub>2</sub>, 4''), 1.29–1.19 (m, 6H, CH<sub>2</sub>, 5''; CH<sub>2</sub>, 6''; CH<sub>2</sub>, 7''), 0.85 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>, H8'').

**<sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>)**  $\delta$  157.7 (C2'), 154.2 (C4), 147.6 (C2), 138.2 (C8a), 137.2 (C <sub>$\beta$</sub> ), 135.4 (C7), 133.4 (C8'a), 133.1 (C4'), 129.8 (C6), 129.3 (C5'), 128.6 (C4a), 128.0 (C4'a), 127.0 (C7'), 126.5 (C5), 123.9 (C6'), 123.9 (C <sub>$\alpha$</sub> ), 123.4 (C8'), 119.8 (C8), 119.2 (C3'), 116.8 (C3), 114.7 (C1'); Octyl: 56.9 (C1''), 31.6 (C6''), 29.9 (C5''), 29.0 (C4''), 29.0 (C3''), 26.3 (C2''), 22.5 (C7''), 14.44 (C8'').

**Thermal analysis.** The thermal analyses were realized at 25–300 °C on a DTA/TG Setaram with the sample in the 1.5–2.5 mg mass range placed in alumina crucibles. The experiments were carried out with scanning rate of 10 K min<sup>−1</sup> under argon atmosphere.

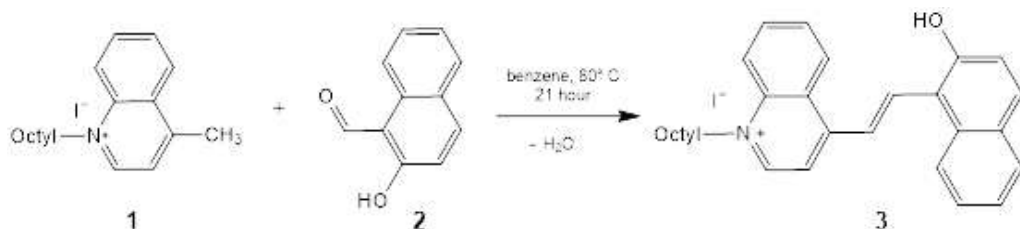
**Computational details.** All theoretical calculations were performed using the Gaussian 03 package of programs [15]. Optimization of the structure of com-

pound **3** was carried out by DFT calculations, employing the B3LYP (Becke's three-parameter non-local exchange) [16] functional correlation, 6-311++G(d,p) basis set.

**Single crystal X-ray diffraction.** X-ray diffraction intensities were measured on a Siemens P4 diffractometer equipped with Mo K $\alpha$  radiation ( $\lambda = 0.71077 \text{ \AA}$ ). Data reduction was performed with program packages *R3m/V User's Guide* and *XDISK*. The structures were solved with *SHELXS97* program [17].

$^1\text{H}$  and  $^{13}\text{C}$  NMR measurements, referenced to TMS, were made with Bruker BioSpin GmbH (600 MHz) spectrometer. The dye was dissolved in  $\text{CD}_3\text{OD}$ . The chemical shifts were referenced internally in  $\delta$ -units.  $J_{\text{HH}}$  coupling constants were measured in Hz.

**Results and discussion.** Knoevenagel condensation of 2-hydroxynaphthaldehyde and 4-methyl-1-octyl quinolinium iodide was used to synthesize styryl quinolinium dye (**3**) in solvent benzene by using a catalyst combination of piperidine and acetic acid (Scheme 1).



Scheme 1. Preparation of (*E*)-4-(2-(2-hydroxynaphthalene-1-yl)ethenyl)-1-octyl quinolinium iodide (**3**)

The synthesized compound was obtained with a high chemical yield (74.34 %) and purity. Its structure was confirmed by spectral methods such as IR, Raman, NMR, and X-ray. Fine crystals appropriate for single crystal X-ray diffraction were afforded during the crystallization of (**3**) from methanol. Analyses of single crystals reveal that compound (**3**) crystallized in the triclinic space group P-1 (Fig. 1a). The unit cell contains four molecules of the dye chromophores and two iodide anions. The head-to-tail principle determines the parallel arrangement of molecules in the crystal. The fragments of quinoline and naphthalene were twisted to 45.36° and 25.23°, respectively, to the plane of the double bond (Fig. 1b).

The deviation from planarity could be attributed to the second-place hydroxyl group of the naphthalene fragment and its involvement in hydrogen bond formation with the iodide anion ( $\text{OH}\cdots\text{I}^-$ , 3.440 Å).

The conjugated system's  $\pi$ -bridge bond length values in dye **3** are C10–C11 (1.465 Å), the double bond C11–C12 (1.325 Å), and C12–C13 (1.456 Å). The target compound has a longer single bond and a shorter double bond in comparison to dyes that are similar to it. Moreover, the  $\pi$ -bridge of **3** has a double bond length



and that for H-8 at 8.55 (d,  $J_{7,8} = 8.9$  Hz, 1H), similar to other charge-transfer dyes [18].

The protons from the methyl or methylene groups immediately associated with the electron-deficient N atom from the quinolinium nucleus also undergo a shift to a lower field, appearing in the  $\delta$  4.98–4.57 range.

Proton-proton (COSY) correlation helped to group the fourteen protons appearing as signals in the 9.4–7.3 ppm interval of the two aromatic nuclei and the bridging double bond (Fig. 3b).

In compound **3**, the signals for the two vinyl protons  $H_\alpha$  and  $H_\beta$  appear as a singlet at 8.63 (s, 2H), similar to the treatment described by GROMOV et al. [18]. This fact could be explained by the significant deviation of the quinolinium and naphthalene nuclei from the double bond plane leading to a disorder of confinement, resulting in the two vinyl protons behaving as equivalent ones in an isolated double bond. X-ray structural analysis of compound **3** confirms the absence of planarity in the chromophore (crystal structure).

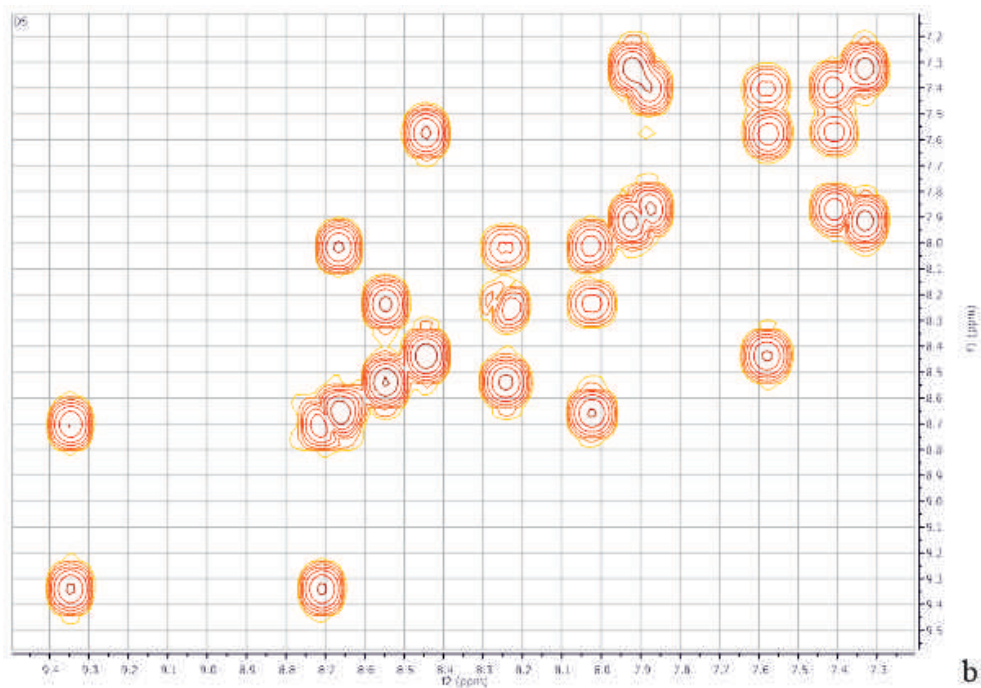
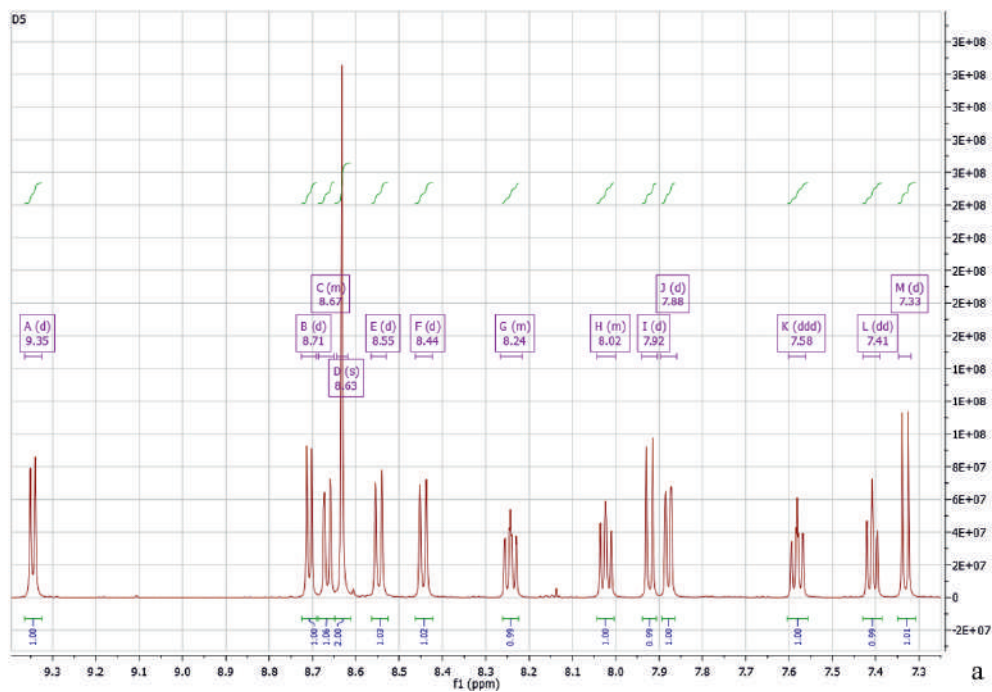
The reasons influencing the offset proton signals described above are the same as those determining the appearance of the carbon atom signals in a weaker or stronger field in the  $^{13}\text{C}$  NMR spectrum (Fig. 3c).

Using heteronuclear carbon-proton correlation through a single bond (HSQC), the bonding between a carbon atom and the corresponding proton was established (Fig. 3d).

Compound **3** exhibits thermal stability up to 212 °C, according to TGA-DTA analysis (Fig. 4). There are destruction processes and a 44 % weight reduction at temperatures higher than this one. The high melting point can be attributed in part to the intermolecular interactions that stabilized crystal structure.

Quantum chemistry simulations showed that most of the bands in the spectra are the result of mixed oscillations. The most likely reason for this is that the degree of charge transfer influences the sensitivity of molecular vibrations [19]. A broadened band at  $3435\text{ cm}^{-1}$  is observed, which is attributed to the hydroxyl group's  $\nu(\text{OH})$  valence vibration at the o-position in the naphthalene core. Calculations predict the band at  $3674\text{ cm}^{-1}$  for the same vibration. The shift by about  $200\text{ cm}^{-1}$  is due to the participation of the phenolic hydroxyl group in the formation of hydrogen bonds with the iodide anion ( $\text{OH} \cdots \text{I}^-$ ,  $3.440\text{ \AA}$ ), which is confirmed by the crystal structure of the dye. The band at  $1600\text{ cm}^{-1}$  is a mixed vibration involving  $\beta(\text{C-H})\text{QF} + \nu(\text{C=C})\text{QF} + \beta(\text{C-H})(\text{C=C})$ , and that at  $1590\text{ cm}^{-1}$  refers to the mixed vibration involving the in-plane C–H vibration of the double bond and the quinolinium fragment and  $\nu(\text{C=C})\text{QF}$ . The band at  $1590\text{ cm}^{-1}$  in the IR and Raman spectra belongs to a mixed vibration, including the in-plane C–H vibrations of the double bond and the quinolinium fragment, as well as the stretching vibration of the quinolinium fragment  $\nu(\text{C=C})\text{QF}$ .

**Conclusions.** A new styryl quinolinium salt was synthesized by Knoevenagel condensation. The structure of the target compound (**3**) was established



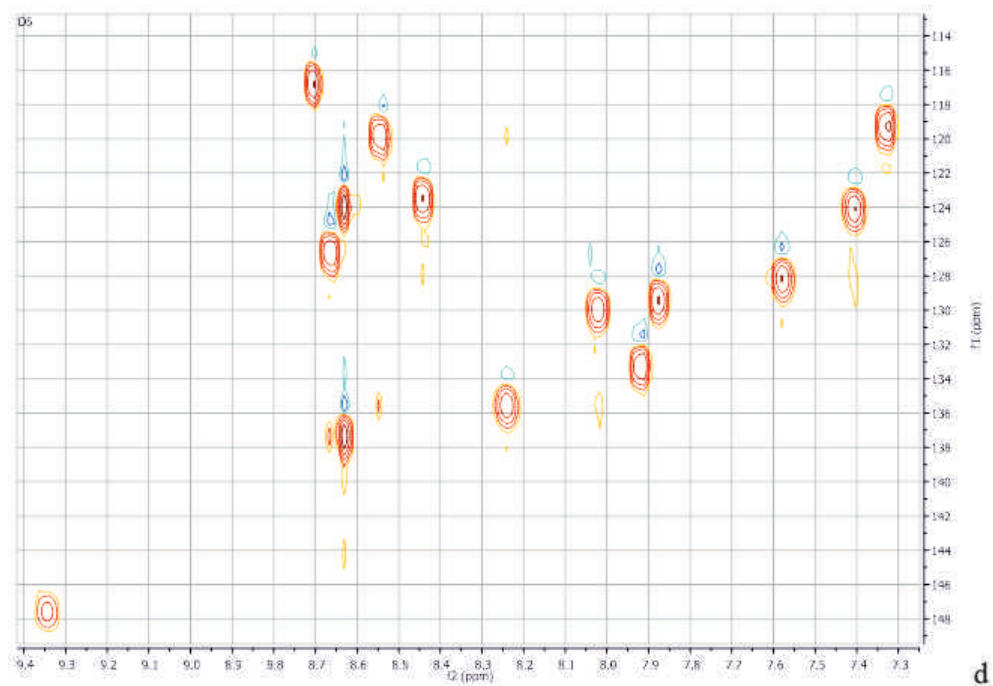
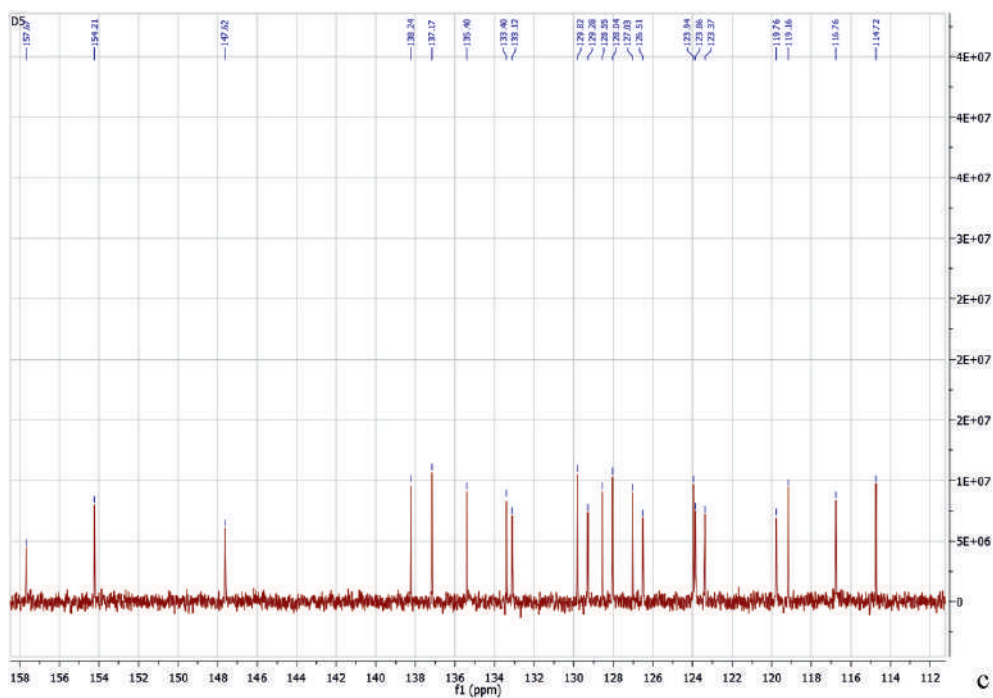


Fig. 3. NMR spectra of compound **3** in the range  $\delta$  9.4–7.3:  
a)  $^1\text{H}$ -NMR; b) COSY; c)  $^{13}\text{C}$  NMR; d) HSQC

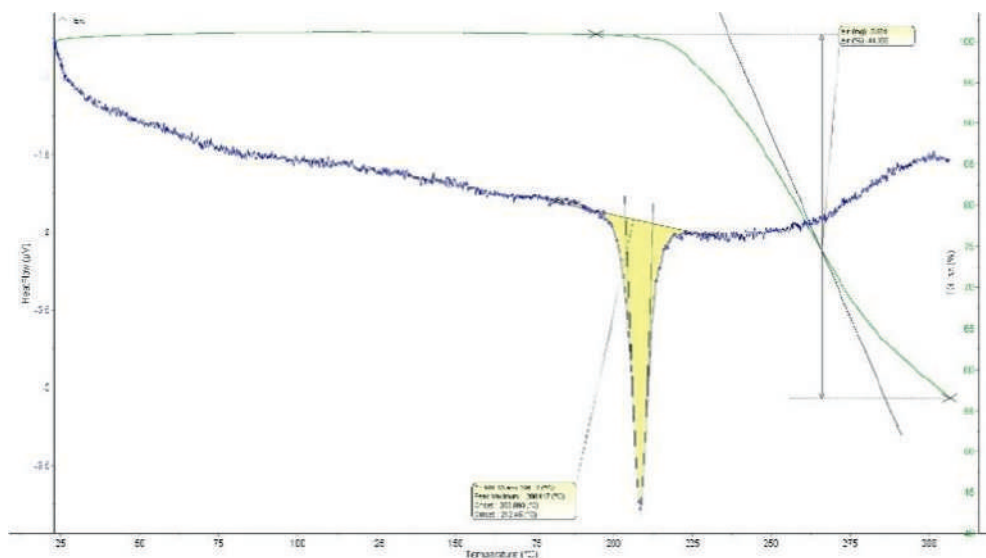


Fig. 4. TGA-DTA analysis of compound **3**

through the utilisation of IR, 1D and 2D NMR, XRD and TGA-DTA techniques. Compound (**3**) was observed to crystallize in the triclinic space group P-1 and exhibited thermal stability up to 212 °C.

## REFERENCES

- [1] GARMIRE E. (2013) Nonlinear optics in daily life, *Optics Express*, **21**(25), 30532–30544.
- [2] NIE W. (1993) Optical nonlinearity: phenomena, applications, and materials, *Adv. Mater.*, **5**, 520–545.
- [3] TREBINO R. (2000) FROG Beam Geometries. In: *Frequency-Resolved Optical Gating: The Measurement of Ultrashort Laser Pulses*, Springer, Boston, MA, 117–139, [https://doi.org/10.1007/978-1-4615-1181-6\\_6](https://doi.org/10.1007/978-1-4615-1181-6_6).
- [4] NALWA H. S., T. WATANABE, S. MIYATA (1997) Organic Materials for Second-Order Nonlinear Optics. In: *Nonlinear Optics of Organic Molecules and Polymers* (eds H. S. Nalwa, S. Miyata), CRC Press, Boca Raton, FL, 89–351, (Ch. 4).
- [5] KENIS P. J. A., O. F. J. NOORDMAN, S. HOUBRECHTS et al. (1998) Second-order nonlinear optical properties of the four tetranitrotetrapropoxycalix[4]arene conformers, *J. Am. Chem. Soc.*, **120**, 7875–7883.
- [6] SAJAN D., I. H. JOE, J. ZALESKI, V. S. JAYAKUMAR (2005) Intramolecular charge delocalization and nonlinear optical properties of Methyl 3-(4-methoxy phenyl) prop-2-enoate from vibrational spectra, *Laser Phys. Lett.*, **2**, 343.
- [7] DAUL C., I. CIOFINI, V. WEBER (2003) Investigation of NLO properties of substituted (M)-tetrathia-[7]-helicenes by semiempirical and DFT methods, *Int. J. Quantum Chem.*, **91**, 297–302.
- [8] MA H., B. CHEN, T. SASSA et al. (2001) Highly efficient and thermally stable nonlinear optical dendrimer for electrooptics, *J. Am. Chem. Soc.*, **123**(5), 986–987.

- [9] DETERT H., M. LEHMANN, H. MEIER (2010) Star-shaped conjugated systems, *Materials*, **3**(5), 3218–3330.
- [10] KIM P. J., J. H. JEONG, M. JAZBINSEK et al. (2011) Acentric nonlinear optical *N*-benzyl stilbazolium crystals with high environmental stability and enhanced molecular nonlinearity in solid state, *Cryst. Eng. Comm.*, **13**(2), 444–451.
- [11] JEONG J.-H., J.-S. KIM, J. CAMPO et al. (2015) *N*-Methylquinolinium derivatives for photonic applications: Enhancement of electron-withdrawing character beyond that of the widely-used *N*-methylpyridinium, *Dyes Pigm.*, **113**, 8–17.
- [12] YANG Z., M. JAZBINSEK, B. RUIZ et al. (2007) Molecular engineering of stilbazolium derivatives for second-order nonlinear optics, *Chem. Mater.*, **19**(14), 3512–3518.
- [13] JEONG J. H., B. J. KANG, J. S. KIM et al. (2013) High-power broadband organic THz generator, *Sci. Rep.*, **3**(1), 3200.
- [14] JAZBINSEK M., L. MUTTER, P. GUNTER (2008) Photonic applications with the organic nonlinear optical crystal DAST, *IEEE J. Sel. Top. Quantum Electron.*, **14**(5), 1298–1311.
- [15] FRISCH M. J., G. W. TRUCKS, H. B. SCHLEGEL et al. (2004) Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford CT.
- [16] BECKE A. D. (1993) Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **98**(7), 5648–5652.
- [17] SHELDRICK G. M. (1997) SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement, University of Gottingen, Gottingen.
- [18] GROMOV S. P., O. A. FEDOROVA, E. N. ANDRYUKHINA et al. (2003) Novel photo-switchable receptors: synthesis and cation-induced self-assembly into dimeric complexes leading to stereospecific [2 + 2]-photocycloaddition of styryl dyes containing a 15-crown-5 ether unit, *J. Org. Chem.*, **68**(16), 6115–6125.
- [19] TODOROVA M., R. BAKALSKA, T. KOLEV (2013) Synthesis, crystal structure, and spectroscopic properties of new stilbazolium salt with enlarged  $\pi$ -conjugated system, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **108**, 211–222.

<sup>1</sup>*Department of Organic Chemistry, Faculty of Chemistry, University of Plovdiv “Paisii Hilendarski”, 24 Tzar Assen St, 4000 Plovdiv, Bulgaria*  
e-mails: minatodorova@uni-plovdiv.bg, bakalska@uni-plovdiv.bg,  
tanya@uni-plovdiv.bg

<sup>2</sup>*Ruhr-Universität Bochum, Lehrstuhl für Analytische Chemie,*  
*Universitätsstraße 150, 44801, Bochum, Germany*  
e-mail: ruediger.seidel@pharmazie.uni-halle.de

<sup>3</sup>*Institute of Molecular Biology “Acad. Roumen Tsanev”, Bulgarian Academy of Sciences,*  
*Akad. G. Bonchev St, Bl. 21, 1113 Sofia, Bulgaria*  
e-mail: tskolev@bio21.bas.bg

<sup>4</sup>*Department of Chemistry, Faculty of Pharmacy, Medical University of Sofia,*  
*2 Dunav St, 1000 Sofia, Bulgaria*  
e-mail: cherneva@pharmfac.mu-sofia.bg

<sup>5</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 9, 1113 Sofia, Bulgaria*