

SYNTHESIS, VIBRATIONAL SPECTRA, AND DFT SIMULATIONS
OF 3-BROMO-2-METHYL-5-(4-NITROPHENYL)THIOPHENEA. A. Balakit,^{a*} Y. Sert,^{b,c*} Ç. Çırak,^d K. Smith,^e
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UDC 535.375.5;543.42

A new thiophene derivative, 3-bromo-2-methyl-5-(4-nitrophenyl)thiophene (**2**), was synthesized through the Suzuki coupling reaction of 4-bromo-5-methylthiophen-2-ylboronic acid (**1**) and 4-iodonitrobenzene, and its structure was confirmed by nuclear magnetic resonance (NMR), low and high resolution mass spectrometry (HRMS), Fourier transform infrared spectroscopy (FT-IR), and X-ray investigations of the crystal structure. The FT-IR spectra (4000–400 cm^{−1}), Raman spectra (4000–100 cm^{−1}), and theoretical vibrational frequencies of this new substance were investigated. Its theoretically established geometric parameters and calculated vibrational frequencies are in good agreement with the reported experimental data. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and other related parameters of the compound were calculated. The ionization potentials given by the B3LYP and HF (Hartree–Fock) methods for this new compound are −0.30456 and −0.30501 eV, respectively.

Keywords: FT-IR spectra, Raman spectra, 3-bromo-2-methyl-5-(4-nitrophenyl)thiophene, vibrational frequencies, frontier molecular orbital.

Introduction. Thiophene derivatives are important compounds that can be used as precursors for the synthesis of materials. They are of great interest due to numerous applications in photoswitching [1, 2], nanotechnologies [3, 4], and biosensorics [5]. Aryl thiophenes are usually synthesized *via* metal catalyzed cross-coupling processes, such as the Suzuki, Negishi, and Stille reactions, in which the organometallic derivatives of thiophene undergo coupling reactions with aryl halides [6, 7]. Also, aryl thiophenes can be synthesized by palladium-catalyzed direct arylation of substituted thiophenes with aryl bromides [8]. 3-Bromo-2-methyl-5-phenylthiophene is one of the most frequently used derivatives. It is usually synthesized via the Suzuki coupling reaction [9, 10].

For our studies of the synthesis and optical properties of various heterocycles [11–16], we synthesized 3-bromo-2-methyl-5-(4-nitrophenyl)thiophene (**2**) and for the first time established its molecular and crystal structures using the methods of Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and quantum chemical calculations for determining the vibrational frequencies.

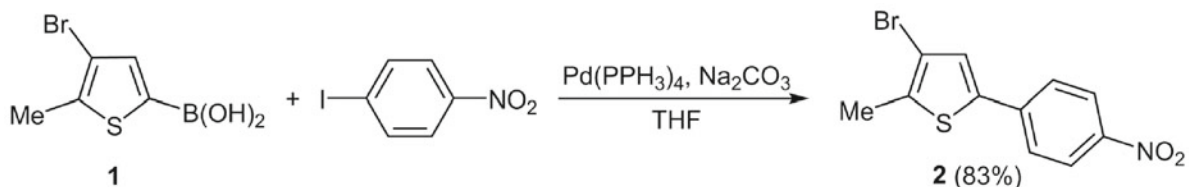
Experimental. *Characterization techniques.* A Gallenkamp melting point apparatus was used to determine the melting point. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ on a Bruker AV400 spectrometer. Chemical shifts δ (ppm) are reported relative to TMS, and coupling constants (*J*) are in Hz. A Waters GCT Premier Spectrometer was used to record the mass spectrum. A Waters LCT Premier XE setup was used to record the accurate mass of the molecular ion peak. A Perkin-Elmer Spectrum Two FT-IR Spectrometer was used to record the IR spectrum (4000–400 cm^{−1}). A Renishaw Invia Raman spectrophotometer was used to record the Raman spectrum (4000–100 cm^{−1}). X-ray crystallographic data were collected at 150 K on a Nonius Kappa CCD diffractometer using graphite monochromated MoK α radiation

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($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$) equipped with an Oxford Cryosystem of cooling. The structures were solved using direct methods and refined with SHELX [17]. It is established that the structure is a two-component inversion twin. There are two molecules in the asymmetric unit, and the thiophene group is disordered in both with occupancies of 0.129(4)/0.871(4) and 0.342(4)/0.658(4). The molecule geometry was reconstructed with the help of the data provided by The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/structures).

Synthesis of 3-bromo-2-methyl-5-(4-nitrophenyl)thiophene (2) (Scheme 1). A mixture of 3-bromo-2-methylthiophen-5-ylboronic acid (**1**) (1.00 g, 4.53 mmol), 4-iodonitrobenzene (1.00 g, 4.02 mmol), anhydrous sodium carbonate (1.28 g, 12.10 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.12 g, 0.11 mmol) in tetrahydrofuran (30 mL, containing 10% water) was refluxed at 90°C for 16 h. The mixture was left to cool to room temperature, after which it was extracted with diethyl ether (3–50 mL). The organic layer was separated, dried (MgSO_4), and evaporated under reduced pressure. The obtained crude product was purified by column chromatography (silica gel; petroleum ether 40–60°C/ethyl acetate 97:3 by volume) to give compound **2** (1.00 g, 3.35 mmol; 83%). Crystallization from diethyl ether gave yellow crystals m.p. 131–132°C. ^1H NMR, δ : 8.15 (d, $J = 8.8$, 2H, H-3/H-5 of Ar), 7.56 (d, $J = 8.8$, 2H, H-2/H-6 of Ar), 7.2 (s, 1H, H-4), and 2.38 (s, 3H, CH_3). ^{13}C NMR, δ : 146.7 (s, C-4 of Ar), 139.5 (s, C-1 of Ar), 138.2 (s, C-5), 137.0 (s, C-2), 128.2 (d, C-4), 125.4 (d, C-2/C-6 of Ar), 124.5 (d, C-3/C-5 of Ar), 111.0 (s, C-3) and 15.1 (q, CH_3). EI-MS (m/z , %): 299 ($[\text{M}^{81}\text{Br}]^+$, 92), 297 ($[\text{M}^{79}\text{Br}]^+$, 94), 269 (100), 267 (93), 188 (20), 171 (70). HRMS (EI): Found, 296.9452. Calculated for $\text{C}_{11}\text{H}_8\text{NO}_2\text{SBr}$ $[\text{M}^{79}\text{Br}]^+$ 296.9459.



Scheme 1. Synthesis of 3-bromo-2-methyl-5-(4-nitrophenyl)thiophene (**2**).

Computational Details. Initial atomic coordinates were determined using the Gauss View software database and experimental XRD data to optimize the input structure to obtain the most stable structure [18]. The DFT/B3LYP and HF methods with the 6-311++G(d,p) basis set were used to calculate the molecular structures (gas phase ground state) of compound **2**. The vibrational frequencies were then found for the calculated optimized structure. The calculated harmonic vibrational frequencies were scaled by 0.9614 (B3LYP) and 0.9051 (HF) for the use with the 6-311++G(d,p) basis set, respectively [18, 19]. The molecular properties, such as optimized geometric parameters and vibrational wave numbers, were calculated using Gauss View molecular visualization [18] and Gaussian 09W [20] software. The calculated vibrational frequencies were assigned via potential energy distribution (PED) analysis of all the fundamental vibration modes by using VEDA 4 software [21, 22]. All the vibrational assignments were based on the B3LYP/6-311++G(d,p) level calculations. Therefore, some assignments might correspond to the value of the previous or next vibrational frequency at the HF/6-311++G(d,p) level.

Results and Discussion. Geometric structure. The X-ray analysis of the crystal structure of compound ($\text{C}_{11}\text{H}_8\text{BrNO}_2\text{S}$) (**2**) showed an orthorhombic system with the $Pca2_1$ space group. It showed the following cell dimensions: $a = 26.1513 \text{ \AA}$, $b = 3.8859 \text{ \AA}$, $c = 21.3942 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, and $V = 2174.11 \text{ \AA}^3$. Since there are two molecules in the asymmetric unit and the thiophene group is disordered in both, the crystal contains four distinct sets of bond lengths and angles, although they are all very similar. Consequently, just one representative set was used in order to compare the experimental and computational values. The bond lengths and bond angles for the selected experimental (X-ray) and optimized theoretical structures are shown in Table 1. The structure of **2** with the atom numbering scheme used for Table 1 is represented in Fig. 1.

The bond length of the C1–C4 bond, at 1.361(11) Å, is similar to the bonds in other thiophene derivatives, which are typically around 1.36–1.38 Å [23–25]. The C2–C3 and C3–Br11 bonds, at 1.283(7) and 1.824(8) Å, respectively, are significantly shorter than similar bonds in other thiophene derivatives (typically 1.35–1.37 Å [23–25] and 1.86–1.90 Å [26–28]). These differences may be due to the nature of the packing in the crystal structure. Both calculation methods also underestimated the length of the C3–C4 bond and consistently overestimated the lengths of the C–H bonds. However, the C2–C7 bond length, experimentally observed as 1.470(9) Å, was similar to the calculated value (1.496 (B3LYP) or 1.501 (HF)) and to the experimental values for similar bonds in related compounds (1.505 [29] and 1.490 Å [30]). So, there was good agreement between the experimental and calculated values of the bonds. The linear regression correlation coefficients (R^2) were reasonable (0.951 for B3LYP and 0.945 for HF).