

Synthesis, Characterization and DFT Studies of Two New π -conjugated Pyridine-based Tetrathiafulvalene Derivatives

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Abstract

Two new π -conjugated pyridine-based tetrathiafulvalene derivatives, 2-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-6-phenyl-[1,3]dithiolo[4,5-b][1,4]dithiin-5-yl)pyridine (**2a**) and 3-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-6-(pyridin-2-yl)-[1,3]dithiolo[4,5-b][1,4]dithiin-5-yl)quinoline (**2b**), have been synthesized and characterized by ¹H NMR, elemental analysis and mass spectroscopies. The compound **2a** has also been studied by X-ray crystallography and theoretical calculations using density functional theory (DFT) framework with B3LYP/6-311+G(d,p) level of theory. Its crystal structure is triclinic system, space group *P* $\bar{1}$. The unit cell dimensions are: $a = 8.813(3)$ Å, $b = 11.082(3)$ Å, $c = 12.620(4)$ Å, $\alpha = 88.805(5)^\circ$, $\beta = 80.440(5)^\circ$, $\gamma = 75.680(5)^\circ$, $V = 1177.3(6)$ Å³, $Z = 2$. The molecule exhibits one classical C–H \cdots N intermolecular hydrogen bonds, two kinds of short intermolecular S \cdots S interactions and two types of C–H \cdots π supramolecular interactions.

Keywords: Tetrathiafulvalenes; Pyridine; Synthesis; Crystal Structure; DFT calculations

1. Introduction

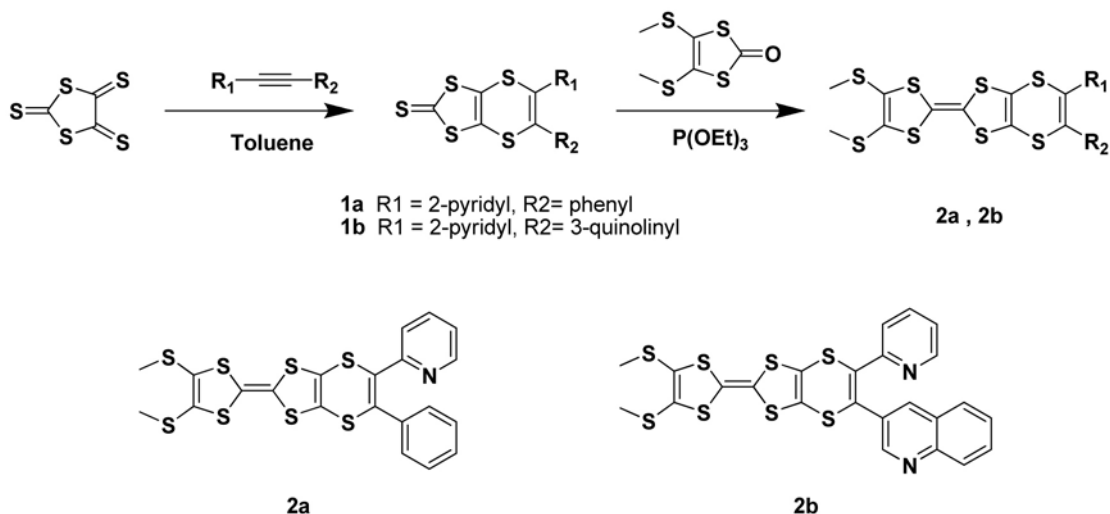
Tetrathiafulvalene (TTF) and its derivatives have attracted chemists' considerable interests during the past two decades, because of their unique π -electron donor properties and serving as useful building blocks for new advanced materials.^{1–2} One of the research trends in new TTF derivatives for functional materials is to search for molecules with more π -extended systems exhibiting unusual geometric and electronic properties.^{3–5} In general, π -extended tetrathiafulvalene framework (exTTF) can enhance the dimensionality in materials by increasing intermolecular $\pi\cdots\pi$ and/or S \cdots S interactions.⁶ Moreover, these short intermolecular distances within a column, corresponding to an overlap of the π /p orbitals, allow the delocalisation of electrons and thus conduction along the stacking direction.⁷ Therefore, a large synthetic effort has also been devoted to the preparation of exTTF derivatives.^{8–10}

In our previous paper, we have reported several classes of π -conjugated pyridine-based TTF derivatives,^{11–12} which are beneficial to intramolecular electron transfer and communications. Our longer term goal is develop a new class of exTTF derivatives. In the current report, two new π -conjugated pyridine-based TTF derivatives (**2a–2b**) have been synthesized and characterized. Optimized conformation and molecular orbital diagram of **2a** has been calculated with density functional theory (DFT).

2. Experimental

2.1. Materials and Instrumentations

The starting materials 1,3-dithiole-2,4,5-trithione,¹³ 2-(phenylethynyl)pyridine¹⁴ and 4-(pyridin-2-ylethynyl) isoquinoline¹⁴ were synthesized as described



Scheme 1. Synthetic route of compounds 2a–2b.

in the literature. All commercial chemicals were used without further purification unless otherwise stated. Solvents were dried and degassed following standard procedures. ^1H NMR spectra were recorded on a Bruker AM 500 MHz instrument. Chemical shifts were reported in ppm relative to Me_4Si as internal standard. Elemental Analyses for C, H, and N were performed on a Perkin-Elmer 240 C analyzer. ESIMS spectra were recorded on a LCQ Fleet instrument.

2. 2. Synthesis of 5-phenyl-6-(pyridine-2-yl)-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (1a)

A suspension of 2-(phenylethynyl)pyridine (273 mg, 1.53 mmol) and 1,3-dithiolo-2,4,5-trithione (200 mg, 1.02 mmol) in toluene (15 mL) were stirred at reflux under a nitrogen atmosphere for 20 h. The mixture was cooled to room temperature, filtered and washed with chloroform. The filtrate was evaporated and the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (30:1) to give compound **1a** (125 mg, 32.7%) as a pale yellow solid. ^1H NMR (500 MHz, CDCl_3): δ 8.65 (d, $J = 4.0$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.32–7.35 (m, 1H), 7.27–7.30 (m, 4H), 7.24 (t, $J = 6.0$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H). Analysis calculated for $\text{C}_{16}\text{H}_9\text{NS}_5$: C, 51.17; N, 3.73; S, 42.69%; found: C, 51.09; N, 3.77; S, 42.70%. EI-MS (m/z): 375.8 $[\text{M} + 1]^+$.

2. 3. Synthesis of 5-(pyridin-2-yl)-6-(quinolin-3-yl)-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (1b)

The procedure of compound **1b** (pale yellow solid, 136 mg, 28.2%) used 3-(pyridin-2-ylethynyl)quinoline as starting material was similar to that of compound **1a**. ^1H

NMR (500 MHz, CDCl_3): δ 8.59–8.64 (m, 2H), 8.36 (s, 1H), 8.22 (d, $J = 6.0$ Hz, 1H), 7.84 (t, $J = 8.0$ Hz, 2H), 7.66 (t, $J = 7.0$ Hz, 1H), 7.42 (t, $J = 7.0$ Hz, 1H), 7.16–7.18 (t, $J = 6.0$ Hz, 1H), 76.85 (d, $J = 6.0$ Hz, 1H). Analysis calculated for $\text{C}_{19}\text{H}_{10}\text{N}_2\text{S}_5$: C, 53.49; N, 6.57; S, 37.58%; found: C, 53.54; N, 6.51; S, 37.56%. EI-MS (m/z): 426.9 $[\text{M} + 1]^+$.

2. 4. Synthesis of 2-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-6-phenyl-[1,3]dithiolo[4,5-b][1,4]dithiine-5-yl)pyridine (2a)

A mixture of compound **1a** (69 mg, 0.16 mmol) and 4,5-bis(methylthio)-1,3-dithiol-2-one (45 mg, 0.21 mmol) was stirred together in freshly distilled triethylphosphite (3 mL) at 110 °C under a nitrogen atmosphere. After 3 h, the reaction was concentrated and purified by chromatography over silica eluting with chloroform/methanol (50:1) to afford **2a** (21 mg, 21.3%) as a bright orange solid. ^1H NMR (500 MHz, CDCl_3): δ 8.54–8.56 (m, 2H), 7.64–7.68 (m, 2H), 7.41 (s, 1H), 7.21–7.28 (m, 4H), 2.39 (s, 3H), 2.38 (s, 3H). Analysis calculated for $\text{C}_{21}\text{H}_{15}\text{NS}_8$: C, 46.89; N, 2.60; S, 47.69%; found: C, 46.74; N, 2.56; S, 47.72%. EI-MS (m/z): 538.0 $[\text{M} + 1]^+$.

2. 5. Synthesis of 3-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-6-(pyridin-2-yl)-[1,3]dithiolo[4,5-b][1,4]dithiine-5-yl)quinoline (2b)

The procedure of **2b** (bright orange solid, 29 mg, yield: 27.2%) was similar to that of **2a**. ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, $J = 4.5$ Hz, 1H), 7.44–7.47 (m, 1H), 7.28–7.35 (m, 4H), 7.23–7.25 (m, 2H), 7.08–7.11 (m, 1H), 6.67 (d, $J = 9.0$ Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H). Analysis calculated for $\text{C}_{21}\text{H}_{15}\text{NS}_8$: C, 46.89; N,

2.60; S, 47.69%; found: C, 46.74; N, 2.56; S, 47.72%. EI-MS (*m/z*): 587.8 [*M* + 1]⁺.

2. 6. Crystallographic Studies

X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo *K*α ($\lambda = 0.71073 \text{ \AA}$) radiation at 293 K. Absorption corrections were applied using SADABS program.¹⁵ The structure was solved and refined using full-matrix least-squares based on F^2 with program SHELXS97 and SHELXL97¹⁶ within Olex2.¹⁷ All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Particularly, the anisotropic displacement parameters of these atoms on the pyridine ring (C10, C11, C12, C13, C14 and N1) and the terminal group (C1, C1', C4, S7 and S7') were restrained using DFIX, SIMU and ISOR commands. Crystallographic details, selected interatomic distances and angles are provided in supporting information.

2. 7. Computational Method

The geometry of compound **2a** was optimized starting from the X-ray data by the DFT (density functional theory) method with B3LYP (Becke three-parameter Lee-Yang-Parr) hybrid density functional theory and the 6-311+G(d,p) basis set. All calculations were carried out with Gaussian 09 software package.¹⁸

3. Results and Discussion

3. 1. Description of Crystal Structure of 2a

Compound **2a** crystallizes in the triclinic space group $P\bar{1}$ and an ORTEP plot of the molecule with atomic num-

bering scheme is shown in Fig. 1. The crystallographic data are listed in Table S1; selected bond lengths and bond angles are collected in Table S2. In the structure, the TTF moiety adopts a boat-like conformation with the average deviation from a least-squares plane of 0.3295 \AA ¹⁹ and bond lengths and angles are in the range expected for neutral TTF derivatives.²⁰ While the pyridine ring (C10-N1-C11-C12-C13-C14) and the phenyl ring (C16-C17-C18-C19-C20-C21) are twisted against the six-membered ring (C7-S2-C9-C15-S1-C8), with the dihedral angle being 65.53° and 35.60° , respectively. The distances of C=C double bond [C(3)=C(4), C(5)=C(6), C(7)=C(8) and C(9)=C(15)] are in the range of $1.328(3)$ – $1.347(3) \text{ \AA}$ (Table S2), as well as in good agreement with those found in related structures.²¹ Besides, the terminal methyl group of the compound **2a** is disordered over two sites (C1 and S7 with 0.526 occupancy, C1' and S7' with 0.474 occupancy).

Perspective view of the crystal packing in the unit cell is presented in Figs. 2–3 and the details of the hydrogen bonds are summarized in Table 1. In the crystal structure, there are one classical C-H...N intermolecular hydrogen bonds, two kinds of short intermolecular S...S interactions and two types of C-H... π supramolecular interactions. The primary interactions are C1-H1C...N1 hydrogen bonds with distance H1C...N1 = 2.51 \AA and angle C1-H1C...N1 = 130.3° , resulting in dimerization of the molecules within the lattice. These dimers are further connected by another S...S interaction (S1...S6ⁱ = 3.843 \AA , S6...S1ⁱ = 3.843 \AA , S4...S4ⁱⁱ = 3.859 \AA and S4ⁱ...S4ⁱⁱⁱ = 3.859 \AA ; symmetry codes in Fig. 2), completing the two-dimensional array. It is noteworthy that the strengths of the S...S distances are slightly longer than those in previously reported examples, which may be attributed to the boat-like conformation of the TTF unit.^{22–24} Molecules are also linked in a head-to-tail fashion into chains running along *c* (Fig. 3), involving weak C-H... π contacts (C2-H2B...Cg5ⁱ and C1'-H1'C...Cg5ⁱⁱ,

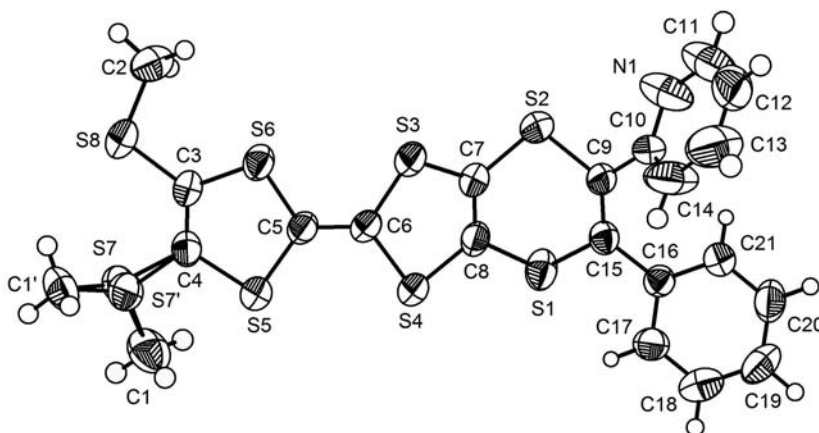


Fig. 1. Molecular structure of compound **2a**. Selected bond length and angles: S(1)–C(8), 1.742(2); S(2)–C(9), 1.782(3); S(3)–C(6), 1.752(3); S(4)–C(8), 1.759(3); S(5)–C(5), 1.739(3); S(6)–C(3), 1.763(3); S(7)–C(1), 1.693(8); S(8)–C(3), 1.737(3); C(3)–C(4), 1.342(5); C(5)–C(6), 1.337(4); C(7)–C(8), 1.329(5); C(9)–C(15), 1.343(4); N(1)–C(11), 1.367(7); C(17)–C(18), 1.359(5); C(8)–S(1)–C(15), $100.83(11)$; C(7)–S(3)–C(6), $93.55(16)$; C(5)–S(5)–C(4), $93.95(15)$; C(10)–N(1)–C(11), $116.3(5)$; C(17)–C(16)–C(21), $118.9(3)$.

symmetry codes in Table 1) between hydrogen atoms of two terminal methyl groups and the plane of the phenyl group (C16–C17–C18–C19–C20–C21). Analyses of the data in Table 1 give C⋯centroid distances of 3.483 Å and 3.689 Å, with corresponding C–H⋯centroid angles of 142° and 152°, respectively. In the crystal lattice, all abo-

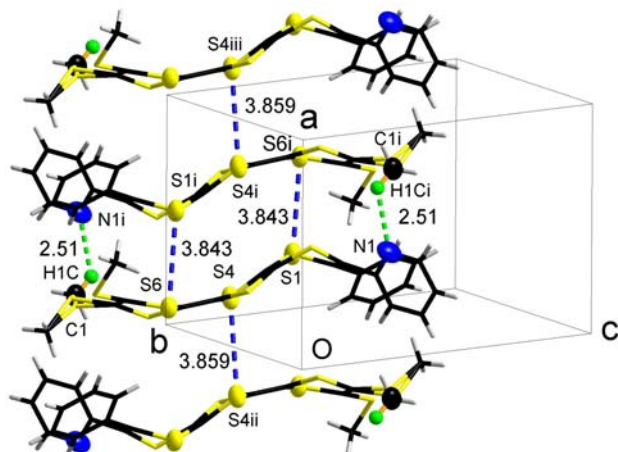


Fig. 2. Representation of part of the lattice contents of compound **2a**, the dotted line representing the S⋯S nonbonded contacts (blue) and the hydrogen bonds (green). [symmetry code: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z$; (iii) $x+1, y, z$]

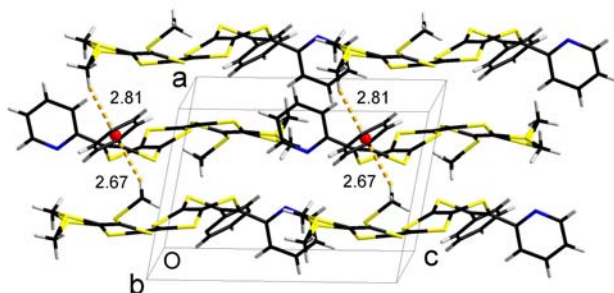


Fig. 3. Views of the three-dimensional network which makes up the structure of compound **2a**. C–H⋯ π contacts are shown as dotted lines. Red sphere represents the centroid of the C16–C21 benzene ring.

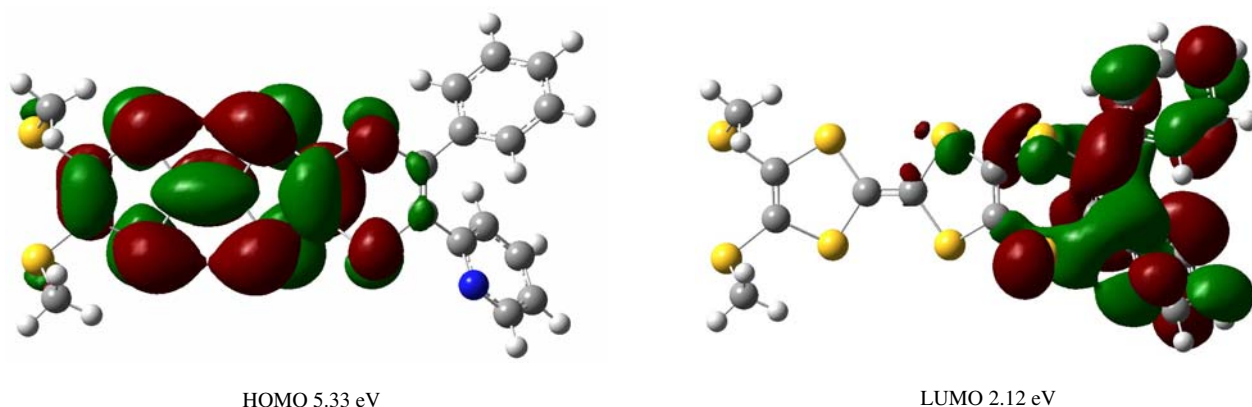


Fig. 4. Molecular orbital diagram of the HOMO and LUMO of compound **2a**.

Table 1 Hydrogen bond lengths (Å) and bond angles (°) for compound **2a**

D–H⋯A	$d(\text{D–H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{DHA}$
C1–H1C⋯N1 ⁱ	0.96	2.51	3.211	130.3
C2–H2B⋯Cg5 ⁱ	0.96	2.67	3.483	142
C1'–H1'C⋯Cg5 ⁱⁱ	0.96	2.81	3.689	152

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x, -y+1, -z$. Cg5 is the centroid of the C16–C21 benzene ring.

ve hydrogen bonds and intermolecular interactions play a significant role in stabilizing the crystal structure. No obvious $\pi\cdots\pi$ interactions are found in the structure.

3. 2. Theoretical Calculations

A DFT calculation was carried out to predict the geometry of the molecule **2a**. The actual and optimized bond lengths and angles, which were obtained by X-ray crystallographic study as well as by geometry optimization at B3LYP/6-311+G level of theory, are reported in Table S2. Considering the sulfur as the focal point, some main structural parameters differ slightly between the X-ray and the theoretical structure. It is seen from Table S2, most of the optimized S–C bond lengths are longer than experimental ones agreeing within 0.2138 Å. And the deviations of C–S–C bond angles between optimized and measured structures are within 1.852°. In addition, the C–C distance in phenyl group and the pyridine C–C distance are calculated as of 1.3949–1.4072 and 1.3945–1.4023 Å ranges, respectively.²⁵ It should be noticed that slight differences in bond parameters are attributed to the fact that the experimental results belong to solid phase while theoretical calculations belong to gaseous phase.²⁶

The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, and the energy gap for mentioned molecule in above have calculated. The calculated HOMO–LUMO gap of molecule is 3.21 eV. The molecu-

lar HOMO/LUMO orbital pictures are depicted in Fig. 4. In analogy to other TTF(donor)-Acceptor compounds,^{27–29} the HOMO is mainly located on the TTF moiety, whereas the LUMO is mostly located on electron acceptor fragment.

4. Conclusions

In this paper, two new π -conjugated pyridine-based tetrathiafulvalene derivatives (**2a–2b**) have been successfully prepared and characterized. The crystal structure of **2a** has been determined by single-crystal X-ray diffraction. The DFT geometry optimization has been carried out using B3LYP/6-311+G(d,p) basis sets and the calculated geometrical parameters are consistent with X-ray diffraction data. In the crystal packing, few weak C–H \cdots N and C–H \cdots π interactions and short intermolecular S \cdots S contacts have been observed, which result in the forming of 3D structure.

5. Acknowledgements

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6. Supplementary Material

Crystallographic data for the structural analyses have been deposited in the Cambridge Crystallographic Data Centre, CCDC reference number 955915. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

7. References

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Povzetek

Sintetizirali in karakterizirali (^1H NMR, elementna analiza in masna spektroskopija) smo dva nova π -konjugirana piri-dinska tetratiafulvalenska derivata, 2-(2-(4,5-bis(metiltio)-1,3-ditio-2-iliden)-6-fenil-[1,3]ditiolo[4,5-*b*][1,4]ditiin-5-il)piridin (**2a**) in 3-(2-(4,5-bis(metiltio)-1,3-ditio-2-iliden)-6-(piridin-2-il) -[1,3]ditiolo[4,5-*b*][1,4]ditiin-5-il)kinolin (**2b**). Spojino **2a** smo raziskali tudi z rentgensko kristalografijo in teoretičnimi izračuni z uporabo teorije gostotnih funkcionalov (DFT) na nivoju B3LYP/6-311+G(d,p). Kristalna struktura je v triklinskem sistemu prostorske skupine *P*. Velikost osnovne celice je: $a = 8.813(3) \text{ \AA}$, $b = 11.082(3) \text{ \AA}$, $c = 12.620(4) \text{ \AA}$, $\alpha = 88.805(5)^\circ$, $\beta = 80.440(5)^\circ$, $\gamma = 75.680(5)^\circ$, $V = 1177.3(6) \text{ \AA}^3$, $Z = 2$. Molekule kažejo eno klasično C–H \cdots N intermolekularno vodikovo vez, dve vrsti kratkih intermolekularnih S \cdots S interakcij in dve vrsti C–H \cdots π supramolekularnih interakcij.