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Synthesis, Structure, and Biological Activity of (2*Z*)-2-[(2,4-Dinitrophenyl)hydrazinylidene]butanedioic Acid Esters

P. P. Mukovoz[a]*, E. S. Dankovtseva[a], V. P. Mukovoz[a], P. A. Slepukhin[b,c], I. N. Ganebnykh[b,c], A. N. Sizentsov[d], and E. A. Danilova[e]

[a] *All-Russian Research Institute of Phytopathology, ul. Institut 5, Bol'shie Vyazemy, Moscow oblast, 143050 Russia*
**e-mail: mpp27@mail.ru*

[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, ul. S. Kovalevskoi/Akademicheskaya 22/20, Yekaterinburg, 620990 Russia*

[c] *Yeltsin Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia*

[d] *Orenburg State University, pr. Pobedy 13, Orenburg, 460018 Russia*

[e] *Ivanovo State University of Chemistry and Technology, Sheremetevskii pr. 7, Ivanovo, 153000 Russia*

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Abstract—Dialkyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioates have been synthesized by reaction of dialkyl (2*Z*)-2-hydroxybut-2-enedioates with 2,4-dinitrophenylhydrazine, and their structure has been studied by IR and ^{1}H NMR spectroscopy, mass spectrometry, and X-ray analysis.

Keywords: (2*Z*)-2-hydroxybut-2-enedioic acid esters, (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioic acid esters, 1,2,4-tricarbonyl compounds

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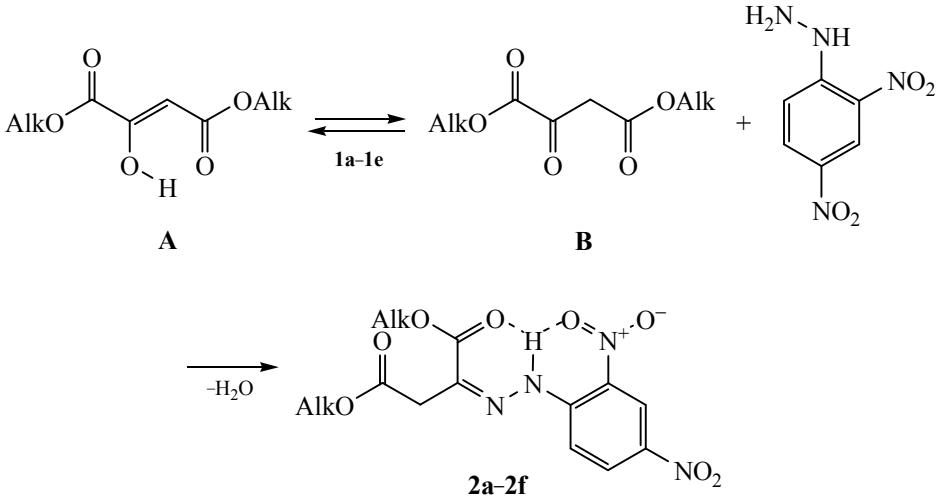
It is known that 1,2,4-tricarbonyl compounds, such as acylpyruvic acids and their esters and amides, react with hydrazines or arylhydrazines to give biologically active compounds [1]. Depending on the conditions and substrate reactivity, the reaction can take different paths to produce either pyrazole-3-carboxylic acid esters or pyrazole-3-carboxylic acids or the corresponding hydrazides. However, in all cases the primary nucleophilic attack of hydrazine on the most reactive C^2=O carbonyl group is followed by heterocyclization involving the C^4=O carbonyl group with the formation of pyrazole derivatives [1, 2]. There are no published data on reactions of arylhydrazines with such 1,2,4-tricarbonyl compounds as 2-oxobutanedioic acid esters [3–5].

Herein, we report the reaction of 2,4-dinitrophenylhydrazine with dialkyl (2*Z*)-2-hydroxybut-2-enedioates **1a**–**1f** which exist as mixtures of major enol tautomer **1A** and minor oxo form (2-oxobutanedioate **1B**) [5]. Instead of expected pyrazole derivatives, we isolated the corresponding dialkyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioates **2a**–**2f** (Scheme 1). Compounds **2a**–**2f** are yellow crystalline solids readily soluble in most organic solvents and insoluble in water. Their structure was determined on the basis of their IR, ^{1}H NMR, and mass spectra and X-ray diffraction data.

The IR spectra of **2a**–**2f** showed a relatively low-frequency NH stretching band at 3281–3228 cm^{-1} due to the secondary amino group, two ester carbonyl bands at 1732–1702 (C^4=O) and 1703–1681 cm^{-1} (C^1=O), absorption bands at 1620–1594, 1593–1576, 1523–1509, and 1457–1436 cm^{-1} belonging to stretching vibrations of aromatic C=C bonds and bands at 1508–1495 and 1345–1326 cm^{-1} due to asymmetric and symmetric vibrations, respectively, of the nitro groups. The asymmetric stretching vibration frequency of the nitro groups is lower than the standard frequency for aromatic nitro compounds (1550–1515 cm^{-1} [6]), which indicates formation of strong intra- or/and intermolecular contacts with participation of the nitro groups. The absorption at 1277–1187 cm^{-1}

Scheme 1.



Alk = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *t*-Bu (**f**).

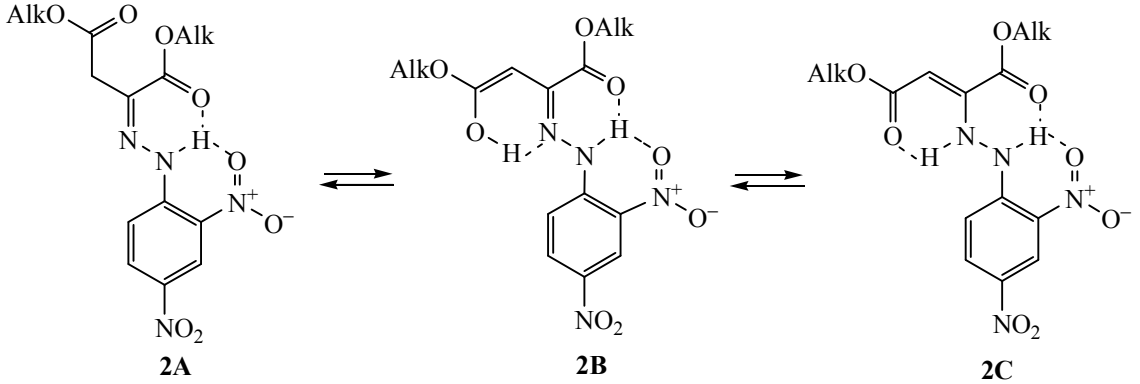
was assigned to vibrations of the ester C–O bonds. The lower C^1=O stretching frequency and relatively low NH stretching frequency suggest participation of these groups in intramolecular hydrogen bonding typical of structure **2A** (Scheme 2).

The IR spectra of **2a**–**2f** contained no broadened low-frequency enol OH bands in the region 3500–2500 cm^{-1}; this means that enol fragments characteristic of tautomer **2B** are absent in the crystalline state. Furthermore, the presence of only one NH band in the spectra of **2a**–**2f** makes it possible to rule out enhydrazine tautomer **2C** in crystal.

However, spectral methods do not allow us to unambiguously determine the structure of hydrazones **2a**–**2f** in the crystalline state. Therefore, we performed X-ray analysis of a single crystal of **2a** (Fig. 1). According to the X-ray diffraction data, molecule **2a** has *Z* configuration of the C=N bond (structure **2A**), so that the C^2=N and C^1=O groups are oriented *cis* with respect to each other.

There is no appreciable equalization of single and double bonds in the above fragments. This indicates both insignificant bond conjugation and the lack of enolization of the $MeOC^1(O)$ fragment. The N^2=C^9 and O^5=C^{10} double bond lengths are 1.288(2) and 1.200(3) Å, respectively, and the N^1–N^2, N^1–C^1, and C^9–C^{10} single bond lengths are 1.348(2), 1.373(2), and 1.499(3) Å, respectively; these values are close to the corresponding reference values (N=C 1.28 Å, C=O 1.21 Å, N–N 1.37 Å, N–C 1.36 Å, C–C 1.54 Å) [7]. The NH group of the hydrazone fragment is involved in bifurcated intramolecular hydrogen bond with the *o*-NO_2 group and C^1=O carbonyl group (Table 1). This hydrogen bond gives rise to two six-membered H-chelate rings

Scheme 2.



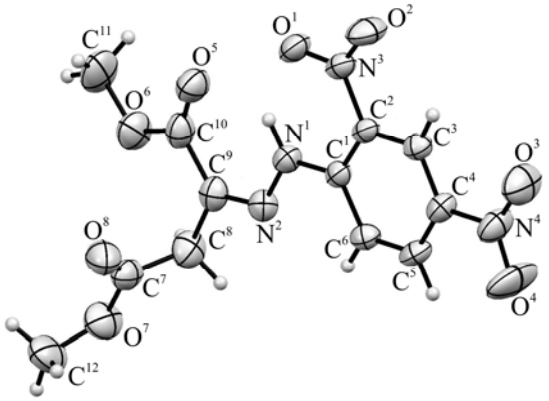


Fig. 1. Structure of the molecule of dimethyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (**2a**) in crystal according to the X-ray diffraction data.

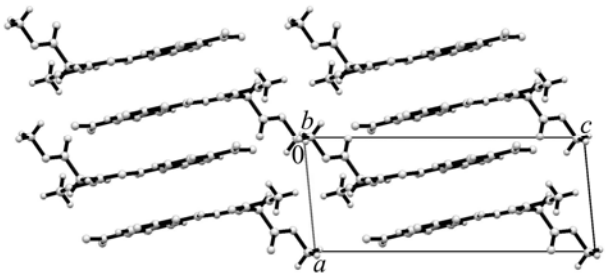


Fig. 2. A fragment of crystal packing of compound **2a**.

and thus fixes planar configuration of the polyene fragment. It should be noted that the other ester fragment (C^4OOMe) deviates from the plane of the hydrazone fragment for steric reasons, and the C^4-ester group plane is almost orthogonal to the plane of the hydrazone fragment (the corresponding dihedral angle is 85°).

Molecules **2a** in crystal are packed in layers (Fig. 2) where the oxygen and nitrogen atoms of the *ortho*-nitro groups of the neighboring molecules form a short π-contact with a $O^1 \cdots N^3$ distance of 3.009 Å [1 – *x*, 1 – *y*, 1 – *z*], which is shorter by 0.06 Å than the sum of the corresponding van der Waals radii. Among other intermolecular contacts, a short T-shaped polar contact between the oxygen atom of the nitro group and sp^2-carbon atom of the ester group not included in the conjugation system {$C^7 \cdots O^4$ 3.043 Å, [–*x*, –*y*, 1 – *z*], 0.177 Å shorter than the sum of the van der Waals radii; Fig. 3} and intermolecular hydrogen bond C^5–$H^5 \cdots O^2$ [*x*, *y* – 1, *z*] between the aromatic proton and oxygen atom of the nitro group should be noted (Table 1). Thus, both nitro groups in molecule **2a** are involved in significant intermolecular contacts which determine the configuration of the nearest molecular environment. Presumably, participation of the nitro groups in intermolecular interactions and spatial proximity of the carbonyl acceptor to the chelated NH proton are responsible for the reduced frequency of asymmetric stretching vibrations of the nitro groups in the IR spectra of **2a**–**2f**.

As in the crystalline state, compounds **2a**–**2f** in nonpolar solutions exist in the hydrazone form (**2A**), which is confirmed by NMR data. The ^{1}H NMR spectra of **2a**–**2f** in $CDCl_3$ contain signals typical of ester alkyl protons, and the signals of the AlkOC^1(O) fragment are located in a weaker field (by 0.03–0.23 ppm) than those of the AlkOC^4(O) protons. This is consistent with the IR and X-ray diffraction data, according to which the C^1=O group is involved in hydrogen bonding. In addition, compounds **2a**–**2f** displayed an indicator two-proton singlet of the C^3H_2 group at δ 3.58–3.89 ppm and NH signal at δ 11.73–14.28 ppm, corresponding to tautomer **2A**. It should be noted that the ^{1}H NMR spectra of structurally related 3-[(2,4-dinitrophenyl)hydrazinylidene]-4,6-dioxoalkanoic and 3-[2-(2,4-dinitrophenyl)hydrazinylidene]-4-oxohexane-1,6-dioic acid esters showed C^2H_2 and NH proton signals in close regions, at 3.90–4.12 and 11.83–11.88 ppm [8] or 3.84–3.87 and 11.86–11.90 ppm, respectively [9, 10]. No signals assignable to CH=C, enolic OH, or enehydrazine NH protons were detected in the ^{1}H NMR spectra, which con-

Table 1. Hydrogen bonds in the crystal structure of compound **2a**

D–H	*d*(D–H), Å	*d*(H···A), Å	∠DHA, deg	*d*(D···A), Å	A
N^1–H^1	0.91(3)	2.01(2)	124(2)	2.624(2)	O^1
N^1–H^1	0.91(3)	1.95(2)	133(2)	2.660(2)	O^5
C^5–H^5	0.93(3)	2.38(2)	171(2)	3.305(2)	O^2 [*x*, *y*–1, *z*]

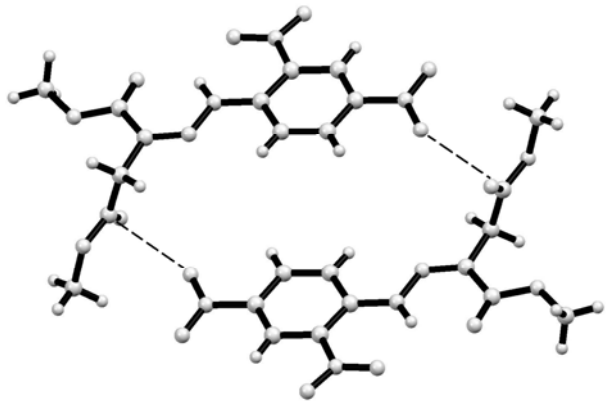


Fig. 3. Short *T*-shaped polar C···O contact in the crystal structure of compound **2a**.

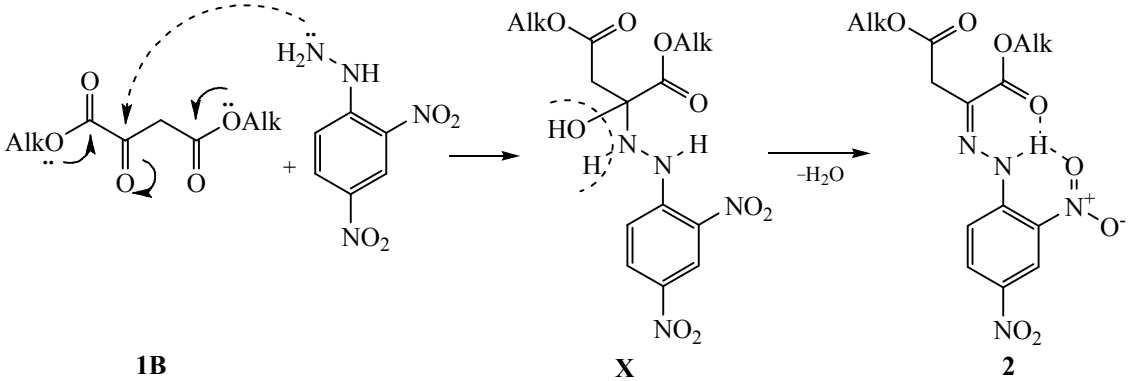
firmed the absence of enol tautomer **2B** or enehydrazine **2C** in solutions of **2a**–**2f** in nonpolar solvents.

The structure of **2a**–**2f** was also confirmed by their high-resolution mass spectra (electropsray ionization from acetonitrile solution) which characteristically contained $[M + H]^+$ ion peaks.

The reaction of diesters **1** with 2,4-dinitrophenylhydrazine is likely to begin with nucleophilic addition of the primary amino group of the latter to the most electrophilic C^2=O carbon atom of oxo tautomer **1B**, and elimination of water molecule from adduct **X** yields compounds **2** (Scheme 3). The effect of unshared electron pairs of the alkoxy oxygen atoms on the C^1 and C^4 electrophilic centers hampers nucleophilic attack on the ester carbonyl groups and prevents compounds **2** from undergoing heterocyclization to pyrazole derivatives, as it occurs in the reactions of other 1,2,4-tricarbonyl compounds (acylpyruvic acids and their esters and amides) with arylhydrazines.

Compounds **2a**–**2f** were tested for antimicrobial activity against gram-positive (*Staphylococcus aureus* P-209, *Bacillus licheniformis* VKPM V 7038) and gram-negative bacteria (*Escherichia coli* M_{17}, *Salmonella typhimurium* 14028S WT), as well as antifungal activity against phytopathogenic fungi *Fusarium sp*., *Alternarium sp*., and *Bipolaris soraciniana* (Table 2). It was found that the activity of compounds **2a**, **2d**, and **2f** against *Staphylococcus aureus* exceeds or is comparable to the activity of nitrofurazone and that compounds **2c** and **2e** exhibit antimicrobial activity exceeding or comparable to the activity of ethacridine lactate. The antimicrobial activity of **2a**, **2e**, and **2f** against *Bacillus licheniformis* was higher than or comparable to the activity of nitrofurazone, and the antimicrobial activity of **2b**, **2c**, and **2d** was comparable to the activity of ethacridine lactate. The activity of **2a**, **2d**, and **2e** against *Salmonella typhimurium* was comparable to that of nitrofurazone but higher than the activity of ethacridine lactate. The antimicrobial activity of **2b** and **2c** was comparable to that of ethacridine lactate. Only compound **2d** turned out to be moderately active against *Escherichia coli*; its activity exceeded the activity of ethacridine lactate. The other compounds tested showed no activity against *E. coli*. Compounds **2a**, **2b**, and **2f** displayed antifungal activity against *Fusarium sp*. at the same level as phytolavin. The antifungal activity of **2a**, **2b**, **2d**, and **2f** against *Bipolaris soraciniana* was moderate, and it did not exceed the activity of phytolavin and previcur. Compounds **2a**–**2f** were inactive toward *Alternarium sp*. The highest antimicrobial activity against gram-positive bacteria was found for compounds **2a** and **2d**–**2f** with methyl or branched alkyl groups in the ester fragments. Compounds **2a**, **2b**, and **2f** were most active against *Fusarium sp*. Fairly high biological activity of the examined compounds is likely to be determined by the presence of nitro groups in the

Scheme 3.



1B **X** **2**

Table 2. Antimicrobial and antifungal activities (MIC, μg/mL) of compounds **2a**–**2f**

Compound	*St. aureus* P-209	*B. licheniformis* B 7038	*S. typhimurium* 14028S WT	*E. coli* M_{17}	*Fusarium* sp.	*Bipolaris soraciniana*
2a	125	250	250	–	31	250
2b	1000	1000	1000	–	16	125
2c	250	1000	1000	–	125	–
2d	63	1000	500	1000	63	500
2e	500	250	–	–	125	–
2f	63	500	250	–	31	500
Ethacridine lactate	500	1000	1000	2000		
Nitrofurazone	125	500	125	500		
Phytolavin					16	63
Previcur					8	31

arylhydrazone fragment; reduction of the nitro groups in pathogen cells could give rise to aromatic amines that are toxic to microorganisms. It should be noted that structurally related 3-[2-(2,4-dinitrophenyl)hydrazinylidene]-4-oxohexane-1,6-dioic acid esters containing a similar dinitrophenylhydrazone fragment also dhowed a high antimicrobial activity against *S. aureus* [11].

In summary, the reaction of dialkyl (2*Z*)-2-hydroxybut-2-enedioates with 2,4-dinitrophenylhydrazine yields the corresponding hydrazones, dialkyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioates, which do not undergo heterocyclization to pyrazole derivatives. The synthesized compounds possess antimicrobial and fungicidal activity at different levels, which is likely to be determined by the presence of nitro groups in their molecules.

EXPERIMENTAL

The IR spectra of crystalline samples were recorded on a Bruker Alpha spectrometer with Fourier transform, equipped with an ATR accessory (ZnSe, incidence angle 45°). The ^{1}H NMR spectra were recorded on a Bruker Avance II spectrometer at 400 MHz using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as internal standard. The mass spectra were obtained on a Bruker Daltonik MaXis Impact HD quadrupole time-of-flight mass spectrometer (electrospray ionization from solutions in acetonitrile, flow rate 240 μL/h; default parameters for infusion analysis of small molecules). The X-ray analysis of compound **2a** was performed using the equipment of the Spectroscopy and Analysis of Organic Compounds joint center of the Institute of Organic Synthesis (Ural Branch, Russian Academy of Sciences). The data were acquired at 295(2) K on an Xcalibur 3 automated four-circle diffractometer with a CCD detector according to standard procedure (monochromatized MoK_α radiation, ω-scanning with a step of 1°). A correction for absorption was applied empirically. The structure was solved by the direct statistical method and was refined against F^2 by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms attached to carbons were placed in giometrically calculated positions and were refined in isotropic approximation, and the positions of OH hydrogens were refined independently. All calculations were performed using OLEX program [12] and SHELX software package [13]. Principal crystallographic parameters of compound **2a**: triclinic crystal system, space group *P*-1; unit cell parameters: a = 6.6752(5), b = 8.0816(5), c = 15.2864(12) Å; α = 82.164(6), β = 81.802(6), γ = 67.286(7)°; μ = 0.129 mm^{-1}. Total of 6588 reflection intensities were measured in the range 2.70° < θ < 30.50°, including 4034 independent reflections (R_{int} = 0.0180), and 2684 reflections with $I > 2\sigma(I)$. Final divergence factors: R_1 = 0.0798, wR_2 = 0.1674 (all independent reflections); R_1 = 0.0506, wR_2 = 0.1409 [reflections with $I > 2\sigma(I)$]. Residual electron density (min/max) $\Delta\rho_e$ = 0.262/–0.213 $\bar{e}$/Å^3. The complete set of X-ray diffraction data for compound **2a** was deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1441915).

The antimicrobial and fungicidal activities of compounds **2a**–**2e** were evaluated by the serial dilution method; each experiment was performed in triplicate.

The antimicrobial activity against *Staphylococcus aureus* P-209, *Bacillus licheniformis* VKPM V 7038, *Escherichia coli* M_{17}, and *Salmonella typhimurium* 14028S WT were determined in meat infusion broth at a bacterial load of 5×10^9 CFU/mL. The minimum inhibitory concentration (MIC) was assumed to be equal to that ensuring inhibition of bacterial growth on the nutrient medium. The inhibitory effect was confirmed by inoculation into solid nutrient media from each test tube. Nitrofurazone and ethacridine lactate were used as reference drugs. The fungicidal activity of **2a**–**2f** against *Fusauium* sp., *Alternarium* sp., and *Bipolaris soraciniana* was evaluated on a Saburo solid nutrient medium. Compounds **2a**–**2f** were dissolved in DMSO, and the stock solutions were diluted with sterile saline to concentrations of 1000 to 8 μg/mL. Solutions of **2a**–**2f** were added to test tubes charged with nutrient medium (preliminarily melted and cooled to 56°C) and were thoroughly mixed with the medium. Fungal cultures were prepared by inoculation of sterile Saburo medium with samples of *Fusauium* sp., *Alternarium* sp., and *Bipolaris soraciniana* from a fungal collection and were cultivated for two weeks 18–22°C, and washouts therefrom were used to inoculate the nutrient medium containing compounds **2a**–**2f**. Nutrient medium without a compound to be tested was used as control. The results were examined after 48 h. The reference drugs were phytolavin and previcur. The data were statistically processed by Student *t*-test using XL 2012 program. The effect was considered to be reliable at $p < 0.001$.

Initial compounds **1a**–**1e** were synthesized according to the procedure described in [5].

General procedure for the synthesis of dialkyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioates 2a–2f. A solution of 20 mmol of compound **1a**–**1f** in 10 mL of acetic acid was added to a solution of 3.96 g (20 mmol) of 2,4-dinitrophenylhydrazine in a mixture of 40 mL of acetic acid and 60 mL of ethanol. The mixture was heated to the boiling point and evaporated, and the residue was dried and recrystallized from ethanol or ethyl acetate.

Dimethyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2a). Yield 2.18 g (32%), mp 177–179°C. IR spectrum, ν, cm^{-1}: 3247 (NH), 3119, 3087 (C–H_{arom}), 2967 ($\nu_{as}CH_3$), 1732 (C^4=O), 1696 (C^1=O), 1603, 1584, 1521 (C=C_{arom}), 1508 ($\nu_{as}NO_2$), 1443 (C=C_{arom}), 1339 (ν_sNO_2), 1277 (ν_{as}(C–O–C), 1213, 1112, 1096, 1052, 1003 (C–C, skeletal), 933, 841 (δC–H_{arom}, out-of-plane), 740 (δC^3H_2, rocking), 701 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 s (3H, C^4OCH_3), 3.86 s (2H, C^3H_2), 3.94 s (3H, C^1OCH_3), 8.17–9.15 m (3H, C_6H_3), 11.73 s (1H, NH). Mass spectrum: *m*/*z*: 341.0729 $[M + H]^+$; calculated for $C_{12}H_{13}N_4O_8$: 341.0728.

Diethyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2b). Yield 3.46 g (47%), mp 147–149°C. IR spectrum, ν, cm^{-1}: 3228 (NH), 3091, 3054 (C–H_{arom}), 2977 ($\nu_{as}CH_3$), 2953 ($\nu_{as}CH_2$), 1718 (C^4=O), 1701 (C^1=O), 1609, 1578, 1516 (C=C_{arom}), 1503 ($\nu_{as}NO_2$), 1465 ($\delta_{as}CH_3$), 1449 (C=C_{arom}), 1332 (ν_sNO_2), 1263 (ν_{as}C–O–C), 1225, 1137, 1110, 1062, 1028, 1013 (C–C, skeletal), 920, 834 (δC–H_{arom}, out-of-plane), 747 (δC^3H_2, rocking), 711 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 t (3H, $C^4OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 1.33 t (3H, $C^1OCH_2C\mathbf{H}_3$, J = 7.5 Hz), 3.65 s (2H, C^3H_2), 4.22 q (2H, C^4OCH_2, J = 7.2 Hz), 4.27 q (2H, C^1OCH_2, J = 7.5 Hz), 8.11–9.15 m (3H, C_6H_3), 14.28 s (1H, NH). Mass spectrum: *m*/*z* 369.1043 $[M + H]^+$; calculated for $C_{14}H_{17}N_4O_8$: 369.1041.

Dipropyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2c). Yield 4.28 g (54%), mp 141–143°C. IR spectrum, ν, cm^{-1}: 3260 (NH), 3096, 3067 (C–H_{arom}), 2973 ($\nu_{as}CH_3$), 2968 ($\nu_{as}CH_2$), 2876 (ν_sCH_3), 1709 (C^4=O), 1689 (C^1=O), 1601, 1582, 1523 (C=C_{arom}), 1506 ($\nu_{as}NO_2$), 1469 ($\delta_{as}CH_3$), 1457 (C=C_{arom}), 1345 (ν_sNO_2), 1209 (ν_{as}C–O–C), 1144, 1169, 1032, 1008 (C–C, skeletal), 927, 901, 848 (δC–H_{arom}, out-of-plane), 756 (δC^3H_2, rocking), 720 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 t (3H, $C^4OCH_2CH_2C\mathbf{H}_3$, J = 7.4 Hz), 1.02 t (3H, $C^1OCH_2CH_2C\mathbf{H}_3$, J = 7.7 Hz), 1.63–1.75 m (4H, $CH_2C\mathbf{H}_2CH_3$), 3.69 s (2H, C^3H_2), 4.02 t (2H, C^4OCH_2, J = 7.4 Hz), 4.17 t (2H, C^1OCH_2, J = 7.7 Hz), 8.05–9.20 m (3H, C_6H_3), 13.82 s (1H, NH). Mass spectrum: *m*/*z*: 397.1355 $[M + H]^+$; calculated for $C_{16}H_{21}N_4O_8$: 397.1354.

Diisopropyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2d). Yield 3.01 g (38%), mp 152–155°C. IR spectrum, ν, cm^{-1}: 3232 (NH), 3103, 3088 (C–H_{arom}), 2970 ($\nu_{as}CH_3$), 2932 (ν_{as}CH), 2869 (ν_sCH_3), 1702 (C^4=O), 1681 (C^1=O), 1610, 1586, 1512 (C=C_{arom}), 1501 ($\nu_{as}NO_2$), 1463 ($\delta_{as}CH_3$), 1441 (C=C_{arom}), 1386, 1364 [$\delta_s(CH_3)_2$CH], 1329 (ν_sNO_2), 1187 (ν_{as}C–O–C), 1166, 1139, 1068 (C–C, skeletal), 909, 864 (δC–H_{arom}), 766 (δC^3H_2, rocking), 707 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t [6H, $C^4OCH(C\mathbf{H}_3)_2$, J = 7.1 Hz], 1.32 t [6H, C^1OCH

($C\mathbf{H}_3)_2$, J = 7.2 Hz], 3.89 s (2H, C^3H_2), 4.30 m (1H, C^4OCH), 4.53 m (1H, C^1OCH), 8.10–9.25 m (3H, C_6H_3), 14.13 s (1H, NH). Mass spectrum: m/z 397.1354 [M + H]$^+$; calculated for $C_{16}H_{21}N_4O_8$: 397.1354.

Dibutyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2d). Yield 2.46 g (29%), mp 122–124°C. IR spectrum, ν, cm^{-1}: 3267 (NH), 3096, 3067 (C–H_{arom}), 2962 ($\nu_{as}CH_3$), 2954 ($\nu_{as}CH_2$), 2868 (ν_sCH_3), 1705 (C^4=O), 1697 (C^1=O), 1594, 1576, 1513 (C=C_{arom}), 1495 ($\nu_{as}NO_2$), 1457 ($\delta_{as}CH_3$), 1438 (C=C_{arom}), 1326 (ν_sNO_2), 1194 (ν_{as}C–O–C), 1181, 1160, 1103, 1061, 1025, 1003 (C–C, skeletal), 914 (δC–H_{arom}, out-of-plane), 777 (δC^3H_2, rocking), 695 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.96 t [3H, $C^4O(CH_2)_3C\mathbf{H}_3$, J = 7.5 Hz], 1.05 t [3H, $C^1O(CH_2)_3C\mathbf{H}_3$, J = 7.5 Hz], 1.35–1.45 m (4H, $C\mathbf{H}_2CH_3$), 1.60–1.70 m (4H, $OCH_2C\mathbf{H}_2$), 3.64 s (2H, C^3H_2), 4.00–4.25 m (4H, OCH_2), 8.00–9.17 m (3H, C_6H_3), 13.95 s (1H, NH). Mass spectrum: m/z: 425.1668 [M + H]$^+$; calculated for $C_{18}H_{25}N_4O_8$: 425.1667).

Di-*tert*-butyl (2*Z*)-2-[(2,4-dinitrophenyl)hydrazinylidene]butanedioate (2e). Yield 1.95 g (23%), mp 172–177°C. IR spectrum, ν, cm^{-1}: 3281 (NH), 3105, 3099 (C–H_{arom}), 2975 ($\nu_{as}CH_3$), 2861 (ν_sCH_3), 1724 (C^4=O), 1703 (C^1=O), 1620, 1593, 1509 (C=C_{arom}), 1497 ($\nu_{as}NO_2$), 1436 (C=C_{arom}), 1327 (ν_sNO_2), 1228 (ν_{as}C–O–C), 1163, 1091, 1053 (C–C, skeletal), 855 (δC–H_{arom}, out-of-plane), 751 (δC^3H_2, rocking), 719 (C–C, skeletal). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s [9H, $C^4OC(CH_3)_3$], 2.22 s [9H, $C^1OC(CH_3)_3$], 3.58 s (2H, C^3H_2), 8.00–9.05 m (3H, C_6H_3), 12.41 s (1H, NH). Mass spectrum: m/z 425.1669 [M + H]$^+$; calculated for $C_{18}H_{25}N_4O_8$: 425.1667.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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