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Molecular Complex 3-Methyl-2,4-dinitrothiophene 1,1-Dioxide–Pyridine in Reactions with Amines

I. E. Efremova, L. V. Lapshina, G. A. Berkova, and V. M. Berestovitskaya

Hertzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: chemis@herzen.spb.ru

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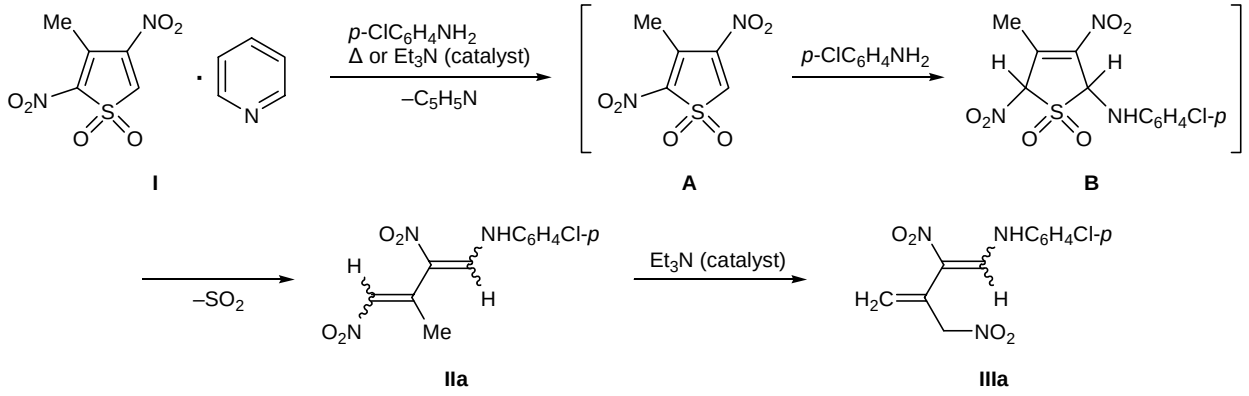
Abstract—Molecular complex 3-methyl-2,4-dinitrothiophene 1,1-dioxide–pyridine gives rise to highly reactive 3-methyl-2,4-dinitrothiophene 1,1-dioxide which is capable of taking up amines at the diene system with subsequent desulfonylation to afford aminodinitrobutadienes. It can also undergo rearrangement into the isomer containing an exocyclic double bond, which is then converted into 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid ammonium salt.

Organic molecular charge-transfer complexes attract interest as primary noncovalent entities which are capable of undergoing further more profound chemical transformations [1]; in addition, some molecular adducts are used as specific synthetic reagents [2].

Molecular adducts formed by reaction of 3-methyl-2,2,4-trinitro-2,5-dihydrothiophene 1,1-dioxide with pyridine and its analogs [3, 4] can be regarded as stable derivatives of a previously unknown polynitroheterocyclene, 3-methyl-2,4-dinitrothiophene 1,1-dioxide. Attempts to isolate the latter from its complexes were unsuccessful, presumably because of its high reactivity. On the other hand, we showed in [5] that heating of such molecular complexes with styrene or phenylacetylene promotes liberation of 3-methyl-2,4-dinitrothiophene 1,1-dioxide which reacts in solution with the initial dienophile according to the reversed Diels–Alder pattern; as a result, mono- and bis-cycloaddition products were obtained.

We have found that under condition of thermal dissociation (55–60°C) molecular complex **I** reacts with primary aromatic amines, in particular with *p*-chloroaniline. The reaction follows the nucleophilic 1,4-addition pattern at the diene system of dinitrothiophene 1,1-dioxide **A** to give intermediate **B**. The subsequent desulfonylation gives known 1-(*p*-chlorophenylamino)-3-methyl-2,4-dinitro-1,3-butadiene (**IIa**) [6] (Scheme 1). In the presence of a catalytic amount of triethylamine, the reaction with *p*-chloroaniline occurs under milder conditions (at 18–20°C) and yields a mixture of isomeric aminodinitrodienes **IIa** and **IIIa** at a molar ratio of 1:4 (according to the ^{1}H NMR spectra). The formation of 1-(*p*-chlorophenylamino)-2-nitro-3-nitromethyl-1,3-butadiene (**IIIa**) is the result of

Scheme 1.



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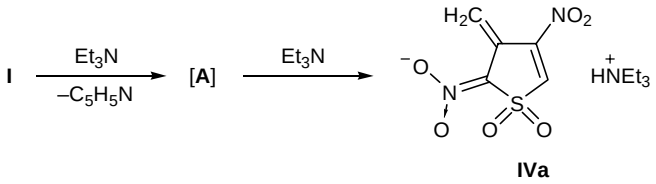
isomerization of initially formed diene **IIa** by the action of base [7].

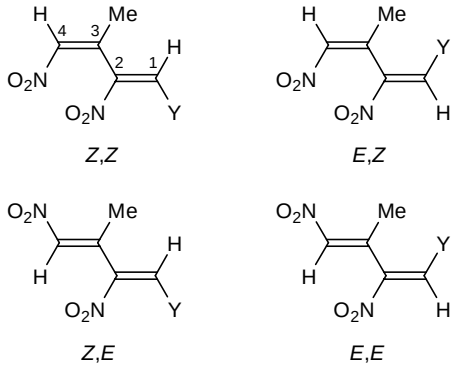
The reaction with triethylamine in the absence of aromatic amine takes a different pathway: dissociation of complex **I** is accompanied by isomerization of dinitrothiophene dioxide **A** to give a structure containing an exocyclic double bond: the product is 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid triethylammonium salt (**IVa**) (Scheme 2). It should be noted that analogous rearrangements of alkyl-substituted thiophene 1,1-dioxides to isomeric structures with an exocyclic double bond were reported in [8–10]; however, these processes occurred in the presence of bases on heating. Milder conditions of the isomerization of dinitrothiophene dioxide **A** may be interpreted in terms of electron-acceptor effect of the nitro groups, which favors prototropic rearrangements [11].

Scheme 2.



The reactions of complex **I** with highly basic proton-containing nitrogen bases, such as piperidine, morpholine, piperazine, and *N*-methylpiperazine take both the above pathways, and the products are 3-methyl-2,4-dinitro-1-piperidino-1,3-butadiene (**IIb**), 2-nitro-3-nitromethyl-1-piperidino-1,3-butadiene (**IIIb**), and 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid piperidinium salt **IVb**, as well as analogous structures containing morpholine (**IIc**–**IVc**), piperazine (**IIId**, **IVd**), or *N*-methylpiperazine residue (**IIIe**, **IVe**). The absence of 1-piperazinyl- and 1-(*N*-methyl-1-piperazinyl)-3-methyl-2,4-dinitro-1,3-butadienes among the products may be explained by their complete isomerization into structures **IIId** and **IIIe** (Scheme 3).

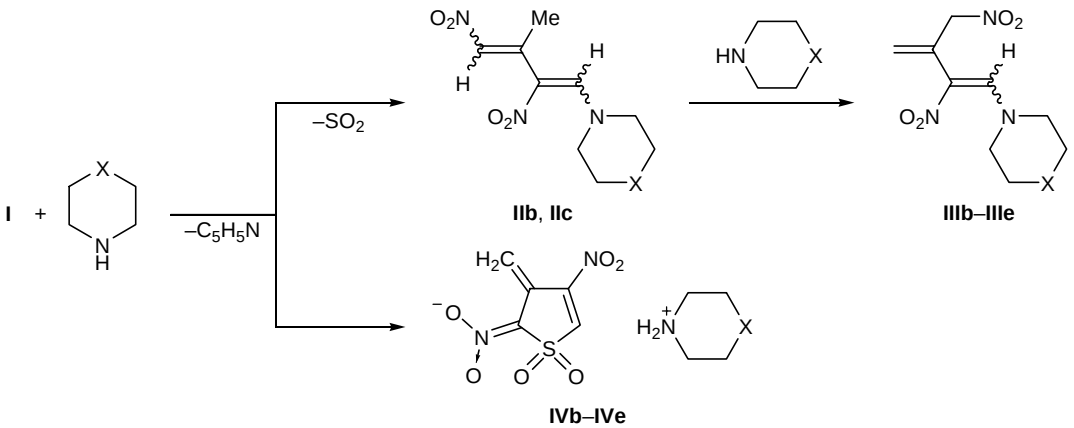
Compounds **IIa**, **IIIb**–**IIIe**, and **IVa**–**IVe** were isolated as individual substances, while dienes **IIb**, **IIc**, and **IIIa** were identified by ^{1}H NMR spectroscopy in mixtures with compounds **IIIb**, **IIIc**, and **IIa**, respectively. Like compound **IIa** [6], dinitrobutadienes **IIb** and **IIc** in solution exist as mixtures of four stereoisomers, *Z*,*Z*, *E*,*Z*, *Z*,*E*, and *E*,*E*.



II, Y = NHC_6H_4Cl-*p* (**a**), piperidino (**b**), morpholino (**c**).

The structure of the $O_2NCH{=}CMe$ fragment was determined from the position of signal from the methyl protons: more downfield signals (δ 2.37–2.62 ppm) correspond to isomers with *cis* arrangement of the methyl and nitro groups (*E* configuration). Likewise, by comparing the chemical shifts of the proton on C^1,

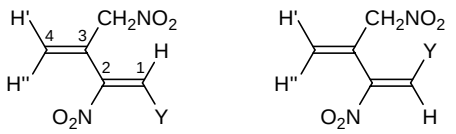
Scheme 3.



II–**IV**, X = CH_2 (**b**), O (**c**), NH (**d**), NMe (**e**).

we determined the configuration of the nitroenamine fragment.

According to the ^{1}H NMR data, butadienes **IIIa**–**IIIe** exist as two geometric isomers, *Z* and *E*, which differ by the position of the substituents at the C^1=C^2 bond. The *E* isomers in which the olefinic proton on C^1 appears spatially close to the nitro group (*cis* orientation) are characterized by downfield location of the 1-H signal (δ 8.07–8.30 ppm). Butadienes **IIId** and **IIIe** possessing an additional amino group in the heterocyclic fragment exhibit enhanced CH acidity of the nitromethyl fragment; therefore, they were isolated as the corresponding ammonium nitronates. Protons in the ionized nitromethyl groups CH=NO_2^- give singlets at δ 7.60 and 7.35 ppm [12]. The IR and UV spectra of compounds **IIIb**–**IIIe** indicate an effective conjugation in the nitroenamine fragment (see Experimental).



The ^{1}H NMR spectra of ammonium salts **IVa**–**IVe** contain singlets in the region δ 4.90–5.35 ppm, which are typical of olefinic protons at the exocyclic double bond [8]. In keeping with published data, signal from the olefinic proton in the thiophene dioxide ring in **IVa**–**IVe** appears in a weak field, δ 7.83–8.20 ppm, and its intensity is ~50–60% of the theoretical value due to fairly fast H–D exchange [8]. The cationic fragment (protonated base) is characterized by a downfield position of signals from the methylene protons neighboring to the ammonium nitrogen atom (δ 3.29, 3.92 ppm for morpholinium salts). We failed to detect NH^+ signal in DMSO. In the IR spectra of **IVa**–**IVe** we observed strong absorption bands belonging to vibrations of the ionized nitro group and C=C and C=N^+ bonds, which are typical of *aci*-nitro thiophene derivatives [13–15].

Thus the molecular adduct 3-methyl-2,4-dinitrothiophene 1,1-dioxide–pyridine is a convenient precursor of a new highly reactive heterocyclic polynitro compound, 3-methyl-2,4-dinitrothiophene 1,1-dioxide, which can readily be generated *in situ* by the action of bases or on heating. Its reactivity is well illustrated by reactions of complex **I** with amines. Depending on the amine basicity, the transformation of 3-methyl-2,4-dinitrothiophene 1,1-dioxide takes two competing pathways: nucleophilic addition at the dinitrodiene system, which is accompanied by desulfonylation and leads to aminodinitrobutadienes, and allyl–vinyl isomerization resulting in formation of 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid ammonium salts. Weakly basic aromatic amines react selectively according to the first pathway, while the reaction of **I** with triethylamine follows the second pathway. Reactions with strongly basic cyclic secondary amines involve both the above pathways.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Tesla BS-487C (80 MHz) and Bruker AC-200 (200 MHz) spectrometers from solutions in DMSO-d_6, chloroform-*d*, or acetonitrile-d_3; the chemical shifts were measured with an accuracy of ±0.5 Hz relative to HMDS as internal or external reference. The electron absorption spectra were obtained on a Specord M-40 two-beam spectrophotometer (dismountable quartz cells, automatic recorder) or on an SF-46 spectrophotometer (quartz cells); acetonitrile was used as solvent. The IR spectra were recorded on Specord 75IR and UR-20 spectrometers (LiF and NaCl prisms) from samples dispersed in mineral oil or pelleted with KBr. The products were isolated by column chromatography on silica gel L (100/250 μm, Czechia) using the Trappe eluotropic solvent series.

Molecular complex **I** was synthesized by the procedure described in [3].

1-(*p*-Chlorophenylamino)-3-methyl-2,4-dinitro-1,3-butadiene (IIa). A solution of 1.17 g (9 mmol) of *p*-chloroaniline in 20 ml of acetonitrile was added to a suspension of 0.90 g (3 mmol) of complex **I** in 20 ml of acetonitrile. The mixture was heated under reflux until it became homogeneous, the solution was concentrated, and the resulting oily substance was treated with chloroform. The precipitate was filtered off and washed with chloroform. Yield 0.30 g (27%). Dark yellow crystals, mp 165–166°C; published data [6]: mp 167–168°C; no depression of the melting point was observed on mixing with an authentic sample [6]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: *Z*,*Z* isomer: 2.31 (3H, CH_3), 7.59 (4H, C_6H_4), 7.67 (1H, 4-H), 7.80 (1H, 1-H), 11.37 (1H, NH); *E*,*Z* isomer: 2.31 (3H, CH_3), 7.59 (4H, C_6H_4), 7.67 (1H, 4-H), 8.32 (1H, 1-H), 9.89 (1H, NH); *Z*,*E* isomer: 2.54 (3H, CH_3), 7.59 (4H, C_6H_4), 7.72 (1H, 4-H), 7.80 (1H, 1-H), 11.37 (1H, NH); *E*,*E* isomer: 2.54 (3H, CH_3), 7.59 (4H, C_6H_4), 7.72 (1H, 4-H), 8.32 (1H, 1-H), 9.89 (1H, NH).

1-(*p*-Chlorophenylamino)-3-methyl-2,4-dinitro-1,3-butadiene (IIa) and 1-(*p*-chlorophenylamino)-2-

nitro-3-nitromethyl-1,3-butadiene (IIIa). A solution of 0.78 g (6 mmol) of *p*-chloroaniline in 20 ml of ethanol and 0.5 ml of triethylamine were added in succession to a suspension of 0.90 g (3 mmol) of complex **I** in 20 ml of ethanol. The mixture was stirred for 55 h, and the precipitate was filtered off, washed with ethanol and diethyl ether, and dried in air. Yield 0.21 g (25%). The product was a crystalline mixture of isomers **IIa** and **IIIa** with mp 140–145°C; isomer ratio **IIa**–**IIIa** 1:4 (according to the ^{1}H NMR data).

1-(*p*-Chlorophenylamino)-3-methyl-2,4-dinitro-1,3-butadiene (IIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: *Z*,*Z* isomer: 2.31 (3H, CH_3), 7.59 (4H, C_6H_4), 7.67 (1H, 4-H), 7.80 (1H, 1-H), 11.37 (1H, NH); *E*,*Z* isomer: 2.31 (3H, CH_3), 7.59 (4H, C_6H_4), 7.67 (1H, 4-H), 8.32 (1H, 1-H), 9.89 (1H, NH); *Z*,*E* isomer: 2.54 (3H, CH_3), 7.59 (4H, C_6H_4), 7.72 (1H, 4-H), 7.80 (1H, 1-H), 11.37 (1H, NH); *E*,*E* isomer: 2.54 (3H, CH_3), 7.59 (4H, C_6H_4), 7.72 (1H, 4-H), 8.32 (1H, 1-H), 9.89 (1H, NH).

1-(*p*-Chlorophenylamino)-2-nitro-3-nitromethyl-1,3-butadiene (IIIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: *Z* isomer: 5.62 (2H, CH_2NO_2), 5.79 (1H, H'), 5.92 (1H, H''), 7.59 (4H, C_6H_4), 7.67 (1H, 1-H), 11.37 (1H, NH); *E* isomer: 5.62 (2H, CH_2NO_2), 5.79 (1H, H'), 5.92 (1H, H''), 7.59 (4H, C_6H_4), 8.12 (1H, 1-H), 9.89 (1H, NH).

3-Methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid triethylammonium salt (IVa). A solution of 0.91 g (9 mmol, 1.20 ml) of triethylamine in 15 ml of ethanol was added with stirring to a suspension of 0.90 g (3 mmol) of complex **I** in 25 ml of ethanol. After 2 h, the mixture was subjected to column chromatography. Elution with methanol afforded a highly hygroscopic viscous oily substance which partially crystallized on storage in a desiccator over calcium chloride. Yield 0.25 g (78%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37 (9H, $3CH_3$), 3.27 (6H, $3CH_2$), 5.35 (2H, $=CH_2$), 7.83 (1H, =CH). Found, %: N 13.46, 13.40. $C_{11}H_{19}N_3O_6S$. Calculated, %: N 13.08.

3-Methyl-2,4-dinitro-1-piperidino-1,3-butadiene (IIb), 2-nitro-3-nitromethyl-1-piperidino-1,3-butadiene (IIIb), and 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid piperidinium salt (IVb). A solution of 0.78 g (9 mmol, 0.90 ml) of piperidine in 15 ml of ethanol was added with stirring to a suspension of 0.90 g (3 mmol) of complex **I** in 25 ml of ethanol. After 2 h, the mixture was subjected to chromatographic separation. Elution with benzene afforded 0.09 g (11%) of a mixture of isomers **IIb** and **IIIb** as a brown viscous oily substance (isomer ratio 1:4, according to the ^{1}H NMR data).

3-Methyl-2,4-dinitro-1-piperidino-1,3-butadiene (IIb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z*,*Z* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 2.10 (3H, CH_3), 3.43 (4H, $2CH_2$), 6.95 (1H, 4-H), 7.82 (1H, 1-H); *E*,*Z* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 2.10 (3H, CH_3), 3.43 (4H, $2CH_2$), 6.95 (1H, 4-H), 8.20 (1H, 1-H); *Z*,*E* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 2.37 (3H, CH_3), 3.43 (4H, $2CH_2$), 7.02 (1H, 4-H), 7.82 (1H, 1-H); *E*,*E* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 2.37 (3H, CH_3), 3.43 (4H, $2CH_2$), 7.02 (1H, 4-H), 8.20 (1H, 1-H).

2-Nitro-3-nitromethyl-1-piperidino-1,3-butadiene (IIIb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 3.43 (4H, $2CH_2$), 5.20 (2H, CH_2NO_2), 5.35 (1H, H'), 5.65 (1H, H''), 7.59 (1H, 1-H); *E* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 3.43 (4H, $2CH_2$), 5.20 (2H, CH_2NO_2), 5.35 (1H, H'), 5.65 (1H, H''), 8.07 (1H, 1-H).

By elution with chloroform we isolated 0.12 g (17%) of yellow crystalline diene **IIIb** with mp 120–122°C. IR spectrum (mineral oil), ν, cm^{-1}: 1550, 1360, 1240, 1190 (NO_2, $C=NO_2^-$); 1650, 1610 (C=C, $C=N^+$). UV spectrum (MeCN), λ_{max}, nm (ε): 360 (19500). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* izomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 3.43 (4H, $2CH_2$), 5.20 (2H, CH_2NO_2), 5.35 (1H, H'), 5.65 (1H, H''), 7.59 (1H, 1-H); *E* isomer: 1.18 (2H, CH_2), 1.60 (4H, $2CH_2$), 3.43 (4H, $2CH_2$), 5.20 (2H, CH_2NO_2), 5.35 (1H, H'), 5.65 (1H, H''), 8.07 (1H, 1-H). Found, %: C 50.02, 49.99; H 6.49, 6.50; N 16.72, 16.80. $C_{10}H_{15}N_3O_4$. Calculated, %: C 49.79; H 6.22; N 17.43.

By elution with methanol we isolated 0.54 g (58%) of light beige crystalline salt **IVb** with mp 130–132°C. IR spectrum (KBr), ν, cm^{-1}: 1560, 1360, 1280, 1210 ($=CNO_2$, $C=NO_2^-$); 1620 (C=C, $C=N^+$); 1320, 1180 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.62 (2H, CH_2), 1.85 (4H, $2CH_2$), 3.24 (4H, $2CH_2$), 5.12 (2H, $=CH_2$), 8.07 (1H, =CH). Found, %: C 39.30, 39.28; H 5.09, 5.02; N 13.70, 13.65. $C_{10}H_{15}N_3O_6S$. Calculated, %: C 39.34; H 4.92; N 13.77.

3-Methyl-2,4-dinitro-1-morpholino-1,3-butadiene (IIc), 2-nitro-3-nitromethyl-1-morpholino-1,3-butadiene (IIIc), and 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid morpholinium salt (IVc). A solution of 0.78 g (9 mmol, 0.78 ml) of morpholine in 15 ml of ethanol was added with stirring to a suspension of 0.90 g (3 mmol) of

complex **I** in 25 ml of ethanol. After 2 h, the mixture was subjected to chromatographic separation. Elution with chloroform gave 0.06 g (10%) of a mixture of isomers **IIc** and **IIIc** as a brown viscous oily substance (isomer ratio 1:4, according to the ^{1}H NMR data).

3-Methyl-2,4-dinitro-1-morpholino-1,3-butadiene (IIc). ^{1}H NMR spectrum (CD_3CN), δ, ppm: *Z*,*Z* izomer: 2.39 (3H, CH_3), 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 7.19 (1H, 4-H), 7.85 (1H, 1-H); *E*,*Z* isomer: 2.41 (3H, CH_3), 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 7.19 (1H, 4-H), 8.69 (1H, 1-H); *Z*,*E* isomer: 2.60 (3H, CH_3), 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 7.22 (1H, 4-H), 7.85 (1H, 1-H); *E*,*E* isomer: 2.62 (3H, CH_3), 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 7.22 (1H, 4-H), 8.69 (1H, 1-H).

2-Nitro-3-nitromethyl-1-morpholino-1,3-butadiene (IIIc). ^{1}H NMR spectrum (CD_3CN), δ, ppm: *Z* isomer: 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 5.31 (2H, CH_2NO_2), 5.47 (1H, H'), 5.76 (1H, H''), 7.63 (1H, 1-H); *E* isomer: 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 5.31 (2H, CH_2NO_2), 5.47 (1H, H'), 5.76 (1H, H''), 8.26 (1H, 1-H).

By elution with acetone we isolated 0.12 g (18%) of diene **IIIc** as yellow crystals with mp 118–120°C. IR spectrum (mineral oil), ν, cm^{-1}: 1550, 1350, 1240, 1180 (NO_2, $C=NO_2^-$); 1650, 1600 (C=C, $C=N^+$). UV spectrum (MeCN), λ_{max}, nm (ε): 360 (19000). ^{1}H NMR spectrum (CD_3CN), δ, ppm: *Z* isomer: 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 5.31 (2H, CH_2NO_2), 5.47 (1H, H'), 5.76 (1H, H''), 7.63 (1H, 1-H); *E* isomer: 3.57 (4H, $2CH_2$), 3.84 (4H, $2CH_2$), 5.31 (2H, CH_2NO_2), 5.47 (1H, H'), 5.76 (1H, H''), 8.26 (1H, 1-H). Found, %: C 44.52, 44.52; H 5.49, 5.53; N 17.48, 17.47. $C_9H_{13}N_3O_5$. Calculated, %: C 44.44; H 5.35; N 17.28.

By elution with metanol we isolated 0.51 g (55%) of salt **IVc** as light beige crystals with mp 140–142°C. IR spectrum (KBr), ν, cm^{-1}: 1550, 1360, 1280, 1220 ($=CNO_2$, $C=NO_2^-$); 1620 (C=C, $C=N^+$); 1330, 1180 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.29 (4H, $2CH_2$), 3.92 (4H, $2CH_2$), 5.07 (2H, $=CH_2$), 8.13 (1H, =CH). Found, %: C 35.11, 35.13; H 4.39, 4.35; N 13.60, 13.61. $C_9H_{13}N_3O_7S$. Calculated, %: C 35.18; H 4.23; N 13.68.

2-Nitro-3-nitromethyl-1-(1-piperazinyl)-1,3-butadiene (IIId) and 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid piperazinium salt (IVd). A solution of 0.78 g (9 mmol) of piperazine in 15 ml of ethanol was added with stirring to a suspension of 0.90 g (3 mmol) of complex **I** in 25 ml of ethanol. After 3 h, the mixture was subjected to chromatographic separation. Elution with acetone afforded 0.24 g (31%) of diene **IIId** as yellow crystals with mp 121–123°C. IR spectrum (mineral oil), ν, cm^{-1}: 1510, 1340, 1230, 1180 (NO_2, $C=NO_2^-$); 1630, 1600 (C=C, $C=N^+$). UV spectrum (MeCN), λ_{max}, nm (ε): 360 (17000). ^{1}H NMR spectrum (CD_3CN), δ, ppm: *Z* isomer: 2.64 (4H, $2CH_2$), 2.88 (4H, $2CH_2$), 4.98 (1H, H'), 5.06 (1H, H''), 7.60 (1H, $CH=NO_2^-$), 7.70 (1H, 1-H); *E* isomer: 2.64 (4H, $2CH_2$), 2.88 (4H, $2CH_2$), 4.98 (1H, H'), 5.06 (1H, H''), 7.60 (1H, $CH=NO_2^-$), 8.30 (1H, 1-H). Found, %: C 44.54, 44.55; H 5.59, 5.63; N 23.17, 23.47. $C_9H_{14}N_4O_4$. Calculated, %: C 44.63; H 5.79; N 23.14.

By elution with methanol we isolated 0.45 g (48%) of salt **IVd** as light yellow crystals with mp 150–152°C. IR spectrum (KBr), ν, cm^{-1}: 1550, 1360, 1260, 1220 ($=CNO_2$, $C=NO_2^-$); 1630 (C=C, $C=N^+$); 1340, 1180 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.13 (4H, $2CH_2$), 3.56 (4H, $2CH_2$), 5.11 (2H, $=CH_2$). Found, %: C 35.06, 35.10; H 4.65, 4.68; N 18.14, 18.15. $C_9H_{14}N_4O_6S$. Calculated, %: C 35.29; H 4.58; N 18.30.

1-(4-Methyl-1-piperazinyl)-2-nitro-3-nitromethyl-1,3-butadiene (IIIe) and 3-methylene-4-nitro-1,1-dioxo-2,3-dihydrothiophen-2-ylideneazinic acid 4-methylpiperazinium salt (IVe). A solution of 1.00 g (9.5 mmol) of *N*-methylpiperazine in 15 ml of ethanol was added with stirring to a suspension of 0.90 g (3 mmol) of complex **I** in 25 ml of ethanol. After 24 h, the mixture was subjected to chromatographic separation. Elution with acetone afforded 0.22 g (28%) of diene **IIIe** as light yellow crystals with mp 117–119°C. IR spectrum (mineral oil), ν, cm^{-1}: 1550, 1360, 1250, 1190 (NO_2, $C=NO_2^-$); 1640, 1600 (C=C, $C=N^+$). UV spectrum (MeCN), λ_{max}, nm (ε): 360 (16500). ^{1}H NMR spectrum (CD_3CN), δ, ppm: *Z* isomer: 2.60–2.80 (11H, $4CH_2$, CH_3), 5.10 (1H, H'), 5.20 (1H, H''), 7.20 (1H, 1-H), 7.35 (1H, $CH=NO_2^-$); *E* isomer: 2.60–2.80 (11H, $4CH_2$, CH_3), 5.10 (1H, H'), 5.20 (1H, H''), 7.35 (1H, $CH=NO_2^-$), 8.15 (1H, 1-H). Found, %: C 46.79, 46.85; H 6.29, 6.20; N 21.87, 21.90. $C_{10}H_{16}N_4O_4$. Calculated, %: C 46.88; H 6.25; N 21.88.

By elution with methanol we isolated 0.42 g (45%) of salt **IVe** as beige crystals with mp 145–147°C. IR spectrum (KBr), ν, cm^{-1}: 1550, 1360, 1270, 1240 ($=CNO_2$, $C=NO_2^-$); 1630 (C=C, $C=N^+$); 1340, 1180 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.50 (3H, CH_3), 2.70–3.10 (8H, $4CH_2$), 4.90 (2H, $=CH_2$), 8.20 (1H, =CH). Found, %: C 37.68, 37.72; H 5.36, 5.35; N 17.42, 17.49. $C_{10}H_{16}N_4O_6S$. Calculated, %: C 37.50; H 5.00; N 17.50.

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