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1,7-Dithioxo-Substituted Systems. Synthesis, Structure, and Photoconductivity of Bis(5,5-dimethyl-3-hydrazonocyclohex-1-enyl) Sulfide

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Abstract—Bis(5,5-dimethyl-3-hydrazonocyclohex-1-enyl) sulfide was synthesized by the reaction of bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfide or its oxygen analog with hydrazine. Conformational lability of the molecule of dihydrazone was studied by the DFT(B3LYP) method using expanded basis sets 6-311G and 6-311G(d,p). Analysis of vibration IR and Raman spectra of the most stable conformers of the isolated molecule of dihydrazone was performed at the harmonic approximation. Using the Onsager SCRF solvation model the absence of solvent effect on the relative stability of the conformers was shown. The photoconductivity of dihydrazone was studied. Low value of the ratio of photocurrent to dark current (J_p/J_d = 2.5–3.5) for dyhydrazone was assigned to the lability of its stereoelectronic structure, which was in line with the data of ^{1}H, ^{13}C, and ^{15}N NMR spectra.

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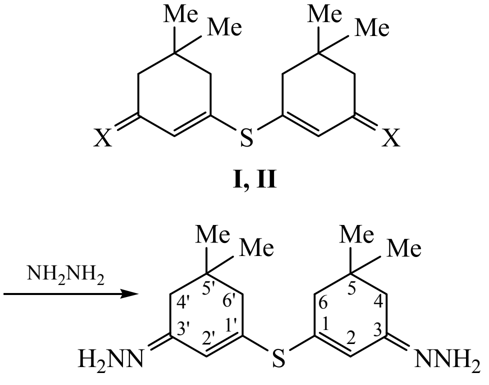
We have shown that compounds with the S=C–C=C–S–C=C–C=S structural fragment are promising in a search for solar energy converters [1]. In continuation of systematic studies in this direction in the series of functionally substituted α,β-unsaturated sulfides [2–5], in the present work the reaction of bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfide (**I**) and its oxygen analog, bis(5,5-dimethyl-3-oxocyclohex-1-enyl) sulfide (**II**) with hydrazine was studied and its stereoelectronic structure was investigated, in particular, in connection with the photoelectric properties of the obtained bis(5,5-dimethyl-3-hydrazonocyclohex-1-enyl) sulfide (**III**).

Reaction of dithioxosulfide (I) with hydrazine (the ratio of the reagents 1:2) in ethanol at –10 to –5°C is accompanied by active evolution of hydrogen sulfide and results in the formation of the earlier unknown bis (5,5-dimethyl-3-hydrazonocyclohex-1-enyl) sulfide (**III**) in 46% yield. Use of a 4-fold excess of hydrazine and increase of the reaction temperature to 0–5°C allowed to increase the yield of hydrazone **III** to ~80%. The same dihydrazone was obtained from dioxosulfide **II** and hydrazine, although in this case the reaction was more sluggish and should be carried out at room temperature.



X = S (**I**), O (**II**).

Dihydrazone **III**, unlike compounds **I** and **II**, is practically insoluble in conventional organic solvents. For analytical purposes, its low concentration solutions in DMSO and DMSO-d_6 were used.

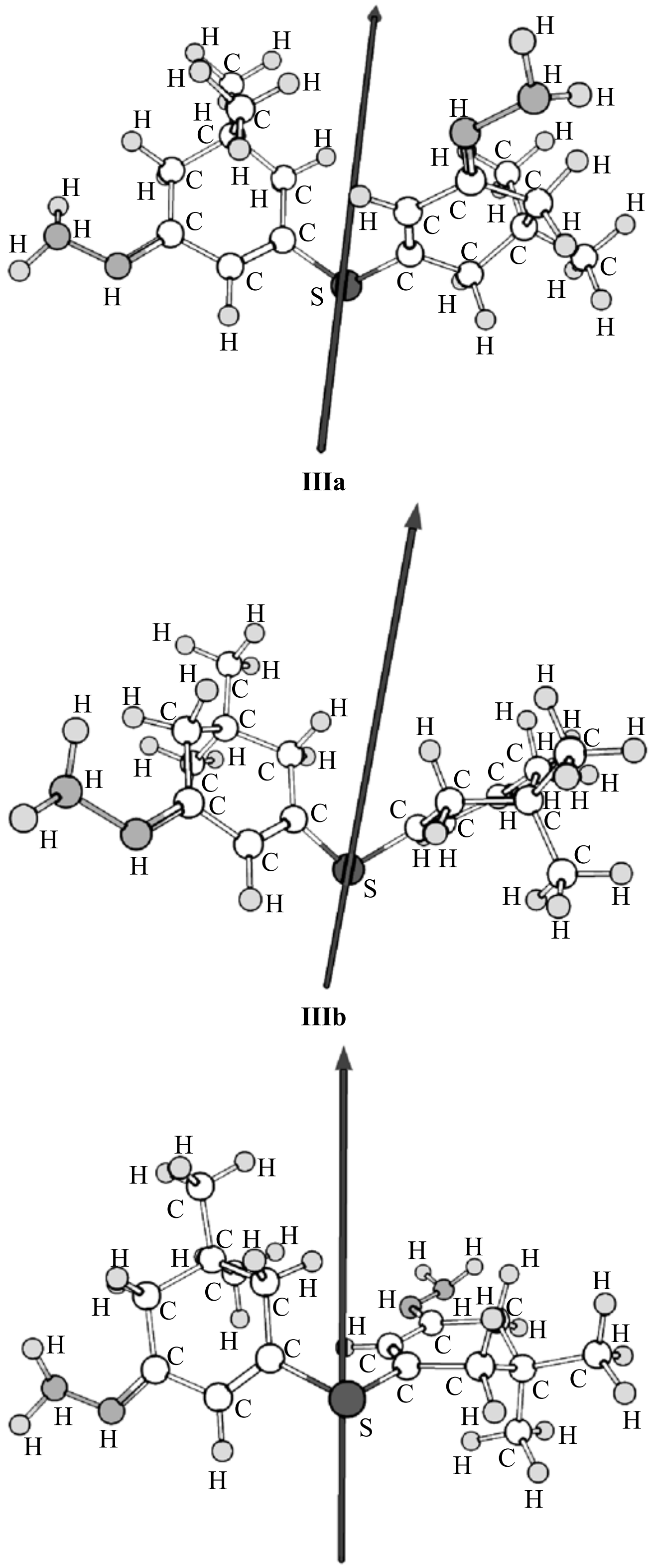
Molecule **III** contains important functional fragments of two types: divinyl sulfide group as the central unit and two hydrazone substituents, which can substantially change the conformational structure of compounds **I** and **II**. To analyze the peculiarities of stereoelectronic structure of dihydrazone **III**, we performed its conformational analysis using modern methods of quantum chemistry, experimental methods of IR and Raman spectroscopy, and the two-dimensional NMR spectroscopy.

The ^{1}H NMR spectrum of compound **III** in DMSO-d_6 contains narrow singlets of the NH_2 group protons (6.3 ppm), olefin protons (6.1 ppm), the protons of the ring CH_2 groups (2.11–2.13 ppm), and CH_3 groups (0.95 ppm). The absence of multiplet signals of the CH_2 and CH_3 group protons is indicative of fast reorientation of the molecule fragments leading to averaging of the signals. The values of chemical shifts in the ^{15}N NMR spectrum of the $C=N–NH_2$ fragment of compound **III** were obtained from the data of two-dimensional ^{1}H–^{15}N HMBC spectroscopy and are typical for the given structure (–47.5 ppm C=N).

Conformational nonuniformity of the molecule of dihydrazone **III** and the model system, bis(3-hydrazonocyclohex-1-enyl) sulfide (**IV**) having no methyl substituents in the six-membered rings, was studied by the DFT(B3LYP) method.

As for the earlier studied molecule of dithioxosulfide **I** [3], calculation of molecules **III** and its model **IV** in the gas phase predicts the preferable existence of nonplanar *cis-trans*-conformer (**IIIc**) (Fig. 1). The following order of relative stability of the conformers of dihydrazone **III** was found: E(**IIIc**) < E(**IIIb**) < E(**IIIa**). Moreover, in compound **III** two types of conformers are realized: less stable **IIIa** and the most stable (IIIc) with the exocyclic $C^{1'}=C^{2'}$ bond and the $C^{3'}=N–NH_2$ group arranged above and below the $C^{1'}SC^1$ plane, respectively. Unlike compound **I**, these conformers are not mirror images. The difference in their total energies is 4.53 kJ mol^{-1} and their dipole moments have different values and are oppositely directed (Fig. 1, Table 1).

The energy difference between the conformers **IIIa** and **IIIb** is substantially less, 0.66 kJ mol^{-1}. The obtained order of stability is retained for the model molecule **IV** that suggests negligible contribution of the methyl substituents into the energy of stabilization of the conformers. Variation of polarity of the medium to ε = 36 does not change the order of stability of the conformers.



IIIa

IIIb

IIIc

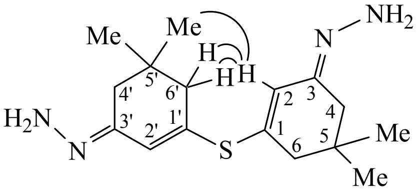
Fig. 1. Most stable conformers of dihydrazone **III** according to DFT(B3LYP)/6-311G(d,p) calculations.

Table 1. DFT(B3LYP)/6-311G(d,p) calculated total energies, energies of stabilization, dipole moments, dihedral and bond angles of stable conformers of dihydrazone **III**

Comp. no.	$-E_{tot}$, au	E_{stab}, kJ mol^{-1}	$\angle C^{2'}=C^{1'}SC^{1}$, deg	$\angle C^{1'}SC^{1}=C^{2}$, deg	$\angle CSC^{a}$, deg	μ, D
IIIa	−1242.72786	0	122.5	−19.3	105.3	3.2
IIIb	−1242.72813	−0.69	132.1	132.0	104.2	5.5
IIIc	−1242.72960	−4.55	−126.2	25.8	105.0	3.6

[a] C–S bond lengths in all conformers are close and equal to 1.785, 1.788, and 1.784 Å for conformers **IIIa**, **IIIb**, and **IIIc**, respectively.

The obtained theoretical results are in line with the data of the two-dimensional NMR spectroscopy for solutions of dihydrazone **III** in DMSO-d_6. 2D NOESY experiment allowed to establish the configuration of the $C=N–NH_2$ fragment from the presence of a cross peak between the signals of the NH_2 group protons and protons of $^{4(4')}CH_2$ groups. Besides in the 2D NOESY spectrum cross peaks are observed between the signals of the olefin proton $H^{2(2')}$ and protons of the $^{6(6')}CH_2$ and CH_3 groups in the 5(5') position (see scheme). The observed correlations are possible only for conformers **IIIa** and **IIIc**, which interconvert in the solution due to the rotation about the S–C bond.



Experimental study of the IR and Raman spectra of dihydrazone **III** in the solid state by the method of frustrated total internal reflection using the zinc selenide crystal in conjunction with quantum chemical analysis of vibration spectra allowed to reveal specific features of conformational equilibrium in the solid phase.

IR (Fig. 2) and Raman (Fig. 3) spectra of the most stable conformers **IIIa**, **IIIb** and **IIIc** of the molecule of dihydrazone **III** in the isolated state have been analyzed by the B3LYP/6-311G(d,p) harmonic vibration calculations. The conformers have C_s symmetry and each shows 135 normal modes of the A type symmetry in the theoretical spectra, which are active in the IR and Raman region.

The assignment of frequencies in the experimental vibration spectra was made on the basis of analysis of localization of theoretical vibrations, behavior of frequencies and intensities of vibrations in different media (gas phase, solvent with $\varepsilon = 36$ for model compound **IV**) and comparison of the experimental IR and Raman spectra in the solid phase and in the DMSO-d_6 solution. Method B3LYP/6-311G in approximation of the Onsager model revealed weak effect of the polar properties of the medium ($\varepsilon = 1–36$) on the vibration spectra of the conformers of the model compound **IV** ($\Delta\nu = 5$ cm^{-1}). Besides, in the IR spectra of dihydrazone **III** the experimental stretching vibrations of the NH_2 groups in the range of 3400–3000 cm^{-1} in the solid state and in the DMSO-d_6 solution coincide. This allowed us to use the data of theoretical calculations in the gas phase for analysis of vibration spectra of dihydrazone **III** in the solid state. Taking into account that calculations by the density matrix functional method lead to systematic overestimation of frequencies, the quality of calculations was estimated taking into account scaling factors (SF). In Table 2 the approximate forms, frequencies, and relative intensities of the conformationally sensitive vibrations and their scaling factors are given. The obtained values of SF characterize satisfactory the accuracy of calculation of the vibration spectra of compound **III** by the B3LYP/6-311G(d,p) method. This is clearly seen from the comparison of the theoretical and experimental vibration spectra (Figs. 2, 3).

According to the B3LYP/6-311G(d,p) calculations, three types of normal modes are characteristic by the form, namely, asymmetric and symmetric stretching vibrations of the NH_2 groups at 3650–3450 cm^{-1} and wagging vibrations ρ_ω of the NH_2 groups at 740–670 cm^{-1} (Table 2). They can be used for analytical appraisal of the conformational equilibrium since these very frequencies showed high sensitivity to conformational transformations. Two bands with different ratio of intensities are observed for conformers **IIIa** and **IIIc** ($I_{682} < I_{702}$ in the IR spectrum of the less stable conformer **IIIa** and $I_{687} > I_{726}$ in the IR spectrum of the most stable conformer **IIIc**), and one for conformer **IIIb** with equivalent $N–NH_2$ groups (Figs. 2, 3). A high-frequency band $\rho_\omega(NH_2)$ is due to wagging vibrations of the NH_2 group in the plane of atoms of the central fragment, a low-frequency band is

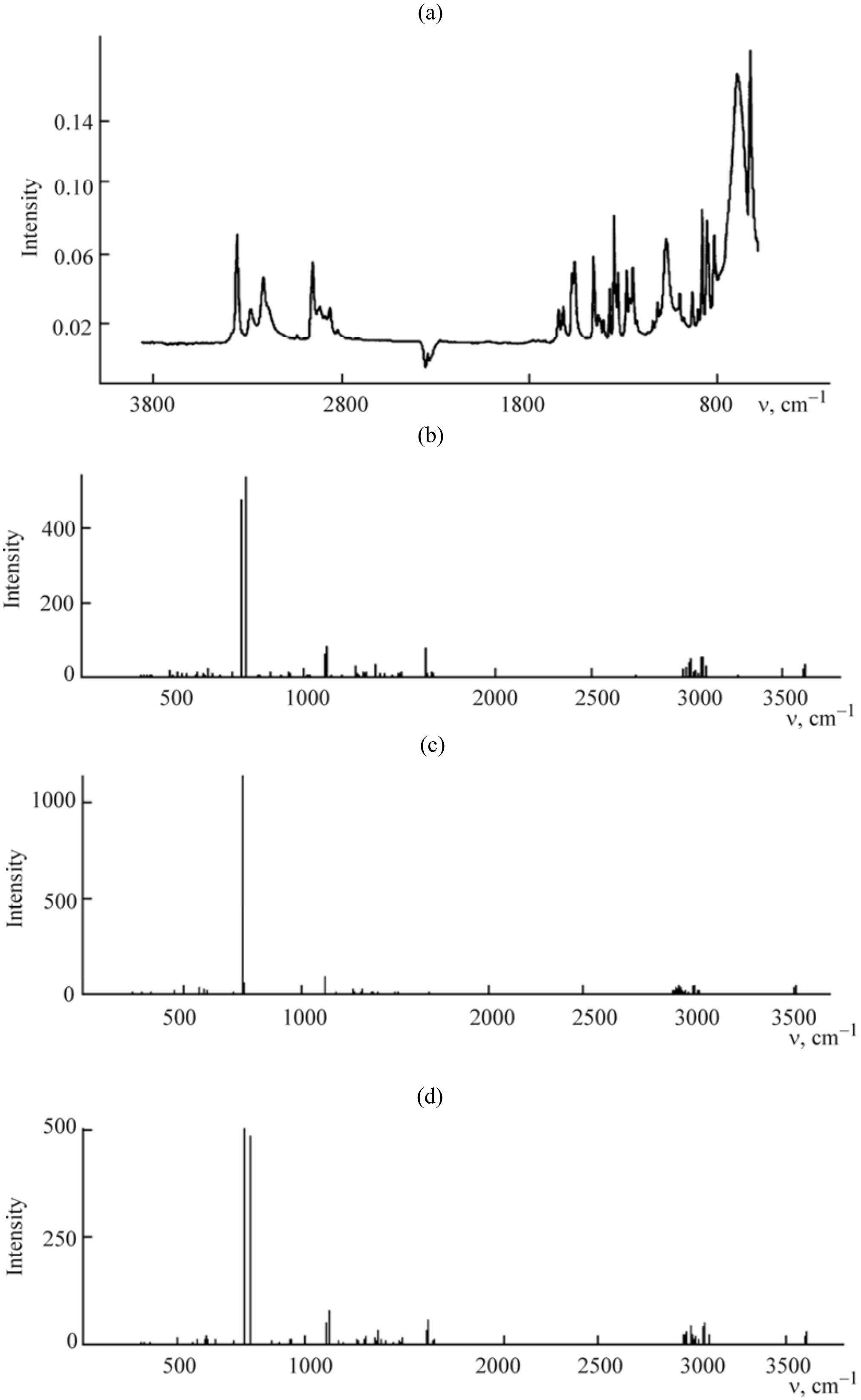


Fig. 2. Experimental IR-ATR spectrum of dihydrazone **III** in the solid state and B3LYP/6-311G(d,p) calculated IR spectra of conformers **IIIa**, **IIIb**, and **IIIc** in the gas phase.

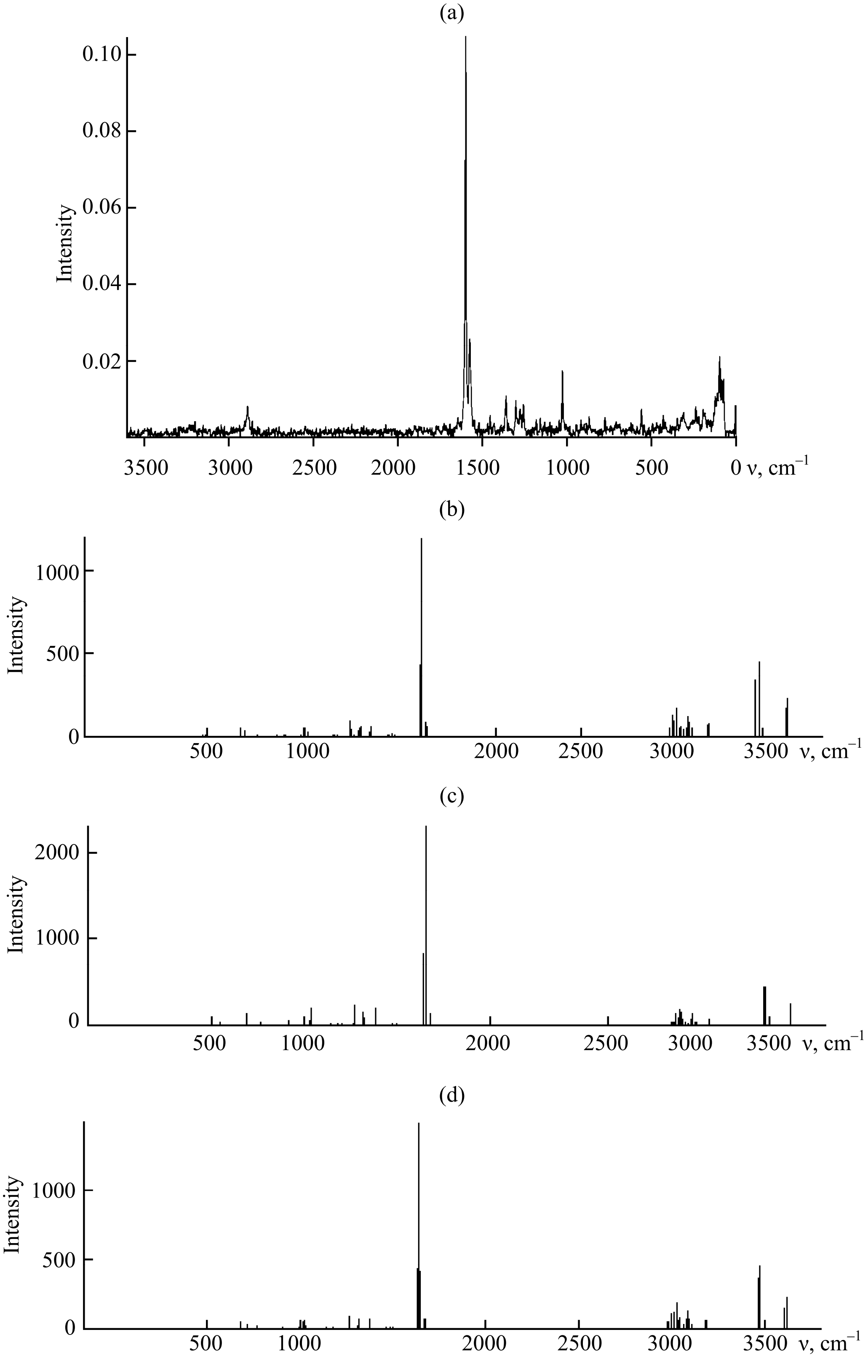


Fig. 3. Experimental Raman spectrum of dihydrazone **III** in the solid state and B3LYP/6-311G(d,p) calculated Raman spectra of conformers **IIIa**, **IIIb**, and **IIIc** in the gas phase.

due to vibrations of the out-of-plane NH_2 group. In the experimental IR-ATR spectrum of dihydrazone **III** in the solid phase the most intensive are two bands at 640 and 707 cm^{-1} with the ratio of intensities $I_{640} > I_{707}$, that allows to conclude on the stabilization of conformer **IIIc** in the solid phase. This is confirmed by the results of theoretical and experimental Raman spectra of compound **III** (Fig. 3, Table 2).

Analysis of the vibration spectra of dihydrazone **III** must take into account not only the possibility of existence of different conformers but also various associates with participation of the $N–NH_2$ groups. From this point of view it is interesting to note the absence of the stretching vibration bands of the NH_2 group in the Raman spectra, the presence of two additional broadened stretching vibration bands of the NH_2 group in the experimental IR spectrum in the range 3400–3200 cm^{-1}, and a strong broadening of the high-frequency band $\rho_\omega(NH_2)$ at 707 cm^{-1}. All together, these facts are indicative of the presence of NH-associates with participation of the out-of-plane NH_2 groups of conformer **IIIa** in the solid phase.

In the experimental Raman spectrum of dihydrazone **III** two very intense bands are observed. The most intense one is caused by stretching vibrations of the central fragment C=C–S–C=C with the *syn*-phase stretching of the double bonds, the less intense, by the stretching vibrations of atoms in the chain –N=C–C=C–S–C=C–C=N–. High intensity of the bands of these vibrations in the Raman spectrum proves the presence of a conjugated electronic system in the said fragments.

In this connection we expected that dihydrazone **III** should show high photoconductivity. It was found that in all spectral range the photocurrent is characterized by dependence on the applied voltage. For the samples with electrodes made of Al, Ag, and Au, the photocurrent is observed only when positive potential is applied to the lit electrode. This suggests that the main charge carriers in the studied sample of dihydrazone **III** are holes. Photoeffect is observed in the spectral region of the proper absorption (210–470 nm) of compound **III**. However, the efficiency of the photoeffect is low, the ratio of photocurrent (J_p) to the

Table 2. Calculated[a] and experimental characteristics of the conformationally sensitive bands in the IR and Raman spectra of dihydrazone **III**

Assignment	Calculated[a], ν, cm^{-1} (I, Km mol^{-1})			Experiment, ν, cm^{-1}	SF
	IIIa	**IIIb**	**IIIc**		
			IR spectra		
$\rho_\omega NH_2$	682 (472)	690 (1087)	687 (503)	640 v.s	0.94
$\rho_\omega[NH_2]'$	702 (534)		726 (487)	707 v.s	
$\nu_s NH_2$	3448 (4)	3473 (2)	3462 (1)	3195 sh	0.93
$\nu_s[NH_2]'$	3471 (2)	3482 (3)	3471 (2)	3221 m	
				3285 sh	
				3288 w	
$\nu_{as} NH_2$	3611 (20)	3616 (32)	3609 (20)	3361 m	
$\nu_{as}[NH_2]'$	3621 (32)	3617 (27)	3620 (32)		
			Raman spectra		
$\nu[N–N=C–C=C]_2–S$	1642 (428)	1642 (828)	1641(218)	1575 s	0.96
ν–C=C–S–C=C	1647 (1203)	1653 (2315)	1647 (1507)	1598 v.s	0.97
	syn-phase	*syn*-phase	*syn*-phase		
	1653 (401)		1654 (418)		
	anti-phase		*anti*-phase		
$\nu_s NH_2$	3447 (342)	3473 (437)	3461 (365)	–	
$\nu_s[NH_2]'$	3471 (449)	3482 (452)	3470 (455)	–	
$\nu_{as} NH_2$	3611 (176)	3616 (195)	3609 (155)	–	
$\nu_{as}[NH_2]'$	3621 (235)	3617 (255)	3620 (234)	–	

[a] DFT(B3LYP)/6-311G(d,p) method.

dark current (J_d) is J_p/J_d = 2.5–3.5. One of the reasons of low efficiency of photoeffect in the present case may be a possibility of dissipation of the absorbed energy connected with the lability of stereoelectronic structure of dihydrazone **III**. According to the rule of energy interval, the possible increase in the rate of internal conversion can be due to the presence of isomers. Therefore, apart from the decrease of the probability of photogeneration of positive charge carriers (holes) worsening of the conditions for their transport is also possible.

Therefore, by the B3LYP/6-311G(d,p) method in the gas phase the order of stability of the conformers of hydrazone **III** is determined: *E*(**IIIc**) < *E*(**IIIb**) < *E*(**IIIa**). The results of two-dimensional NMR spectroscopy (NOESY) are indicative of intercomversion of conformers **IIIa** and **IIIc** in the DMSO-d_6 solution. In the solid state, dihydrazone **III**, by the data of IR and Raman spectroscopy, exists predominantly in an NH-associated form. Lability of stereoelectronic structure of dihydrazone **III** can be considered as one of the main reasons explaining a low efficiency of the found photoeffect.

EXPERIMENTAL

IR spectra were registered on Fourier spectrometers IFS 25 in KBr pellets and in DMSO solutions (d = 0.0168 cm, c = 0.1 g ml^{-1}) and FT-IR Spectrum HE-3100 Varian in the solid state using the device of frustrated total internal reflection (ATR) on the SeZn crystal. Raman spectra in the solid state were obtained on a Fourier spectrometer FT-IR Vertex 70 Ram II. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker DPX 400 spectrometer [working frequency 400.1 (^{1}H), 100.4 (^{13}C), 40.5 (^{15}N) MHz], external standard HMDS. The reactions were followed and the purity of the obtained products checked by the TLC method on Silufol UV-254 plates, eluent chloroform–ethyl acetate, 3:1.

Bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfide **I** was synthesized according to [2]. Bis(5,5-dimethyl-3-oxocyclohex-1-enyl) sulfide **II** was prepared by the procedure [4].

Bis(5,5-dimethyl-3-hydrazonocyclohex-1-enyl)-sulfide (III). *a*. To a suspension of 0.31 g (1 mmol) of bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfide (**I**) in 18 ml of anhydrous ethanol a solution of 0.064 g (2 mmol) of hydrazine in 3 ml ethanol was added at stirring and continuous bubbling of argon at –10 to –5°C. The reaction mixture was stirred at this temperature for 4 h until the evolution of hydrogen sulfide ceased [test with solution of $Pb(OAc)_2$], filtered, the filtrate was partially evaporated. The precipitate formed was filtered off, washed with cold methanol, and dried in a vacuum. 0.14 g (46%) of dihydrazone **III** was obtained as strongly electrified cream powder with mp 174–176°C. IR spectrum, cm^{-1}: 3361 m, 3288 w, 3223 m, 3196 sh [$\nu(NH_2)$], 2959 m [$\nu(CH_3)$], 2922 w, 2868 w [$\nu(CH_2)$], 1655 w, 1631 w [ν(C=N–N)], 1584 m, 1571m [ν(C=C–S–C=C)], 707 v.s, 641 v.s [$\rho_\omega(NH_2)$]. Raman spectrum, ν, cm^{-1}: 3362 v.w (NH_2), 2891 v.w (CH_2), 1598 v.s, 1575 v.s (C=C–S–C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.95 s (12H, CH_3), 2.11 s (4H, $^{4,4'}CH_2$), 2.13 s (4H, $^{6,6'}CH_2$), 6.13 s (2H, 2HC=), 6.40 br.s (4H, $2NH_2$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.86 (CH_3), 31.56 (C^5, $C^{5'}$), 35.55 (C^6, $C^{6'}$), 43.96 (C^4, $C^{4'}$), 129.99 (C^2, $C^{2'}$), 131.17 (C^1, $C^{1'}$), 144.71 (C^3, $C^{3'}$). Found, %: C 62.11; H 8.45; N 17.88; S 10.83. $C_{16}H_{26}N_4S$. Calculated, %: C 62.75; H 8.50; N 18.30; S 10.46.

b. 0.1 g (0.3 mmol) of dithioxosulfide **I** and 0.04 g (1.2 mmol) of hydrazine in 5 ml of anhydrous ethanol were taken in the reaction carried out at 0–5°C during 4 h. The precipitate formed was filtered off, washed with cold alcohol, and dried in a vacuum. 0.07 g (78%) of compound **III** was obtained.

c. To the solution of 0.28 g (1 mmol) of bis(5,5-dimethyl-3-oxocyclohex-1-enyl) sulfide **II** in 13 ml of ethanol the solution of 0.096 g (3 mmol) of hydrazine in 2 ml of ethanol was added dropwise at stirring in an argon atmosphere at 0–5°C. The reaction mixture was stirred for 8 h at 20°C until the starting diketone **II** disappeared, filtered, the solvent removed in a vacuum. The solid residue was thoroughly washed with methanol and dried in vacuum. 0.12 g (39%) of dihydrazone **III** was obtained, its mp and the IR spectrum were identical to that from method *a*. Found, %: C 62.98; H 8.79; N 17.45; S 10.63. $C_{16}H_{26}N_4S$. Calculated, %: C 62.75; H 8.50; N 18.30; S 10.46.

Quantum chemical calculations were performed by the DFT(B3LYP) method and 6-311G, 6-311G(d,p) basis sets with full geometry optimization using GAUSSIAN-03W program package [6]. IR and Raman vibration spectra, total energies, zero point energies, dipole moments, and structures of the most stable conformers of compounds **III** and **IV** having the C_s symmetry were calculated. BSSE was not taken into account because of its negligible effect for extended basis sets [7].

The effect of polar medium (ε = 1–36) on the energy and structural characteristics, dipole moments, and vibration spectra of the conformers of the model compound **IV** was estimated using the Onsager model at the DFT(B3LYP)/6-311G level of theory.

Spectral distribution of photoconductivity of dihydrazone **III** was obtained on the unit earlier described by us [8], for the cells of the surface (raster) and volume (sandwich) types on quartz substrates. Aluminum and/or silver electrodes were deposited by thermal evaporation of the metal in a vacuum 5×10^{-4} Pa. To exclude the emission to vacuum in the case of volume cell, semitransparent bottom and nontransparent upper electrodes were used. Light transmission of the semitransparent electrode was 25–30%. The cells were made with symmetrical metal electrodes made of Al and Ag. The thickness of the sample was 3–4 μm. As a source of irradiation, xenon lamp DKsSh 1000 was used. All measurements were performed in a cryostate in a vacuum of 10^{-4} Pa.

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