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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on his 70th anniversary

^{13}C–^{13}C Spin–Spin Coupling Constants in Structural Studies: XLIII. Stereochemical Study on Functionalized 3-Iminopyrrolizines

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Abstract—Three 1-ethylsulfanyl-3-imino-3*H*-pyrrolizine-2-carboxamides were synthesized by intramolecular cyclization of substituted (2*Z*)-2-cyano-3-ethylsulfanyl-3-(1*H*-pyrrol-2-yl)prop-2-enamides. The products were assigned *syn* configuration at the C=N bond and preferential *s-cis* orientation of the carbamoyl group on the basis of the experimental ^{13}C–^{13}C coupling constants and high-level nonempirical quantum-chemical calculations.

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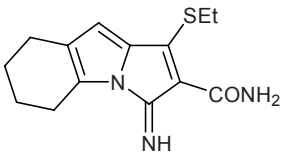
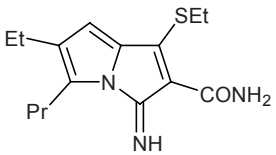
Pyrrolizine and indolizine alkaloids isolated from numerous macro- and microorganisms and plants constitute a huge class of natural compounds exhibiting versatile biological activity [1]. Pyrrolizine derivatives are used as antiinflammatory, analgesic [2, 3], and antitumor agents [4], as well as nonsteroidal enzyme inhibitors [5]. In addition, functionalized pyrrolizines are key building blocks in the synthesis of various heterocyclic compounds [6].

One of the most widely used methods for the preparation of pyrrolizines, in particular of their 3-imino derivatives, is intramolecular cyclization of 2-(2-cyanovinyl)pyrroles in the presence of nucleophiles [6–12]. For example, 2-(2,2-dicyano-1-ethylsulfanylvinyl)pyrroles in the presence of secondary amines undergo intramolecular cyclization to 1-ethylsulfanyl-3-iminopyrrolizines, and the subsequent fast replacement of the ethylsulfanyl group gives the corresponding 1-amino-2-cyano-3-imino-3*H*-pyrrolizines [8, 10–12]. 2-(2-Carbamoyl-2-cyano-1-ethylsulfanylvinyl)pyrroles react with primary and secondary amines, yielding 2-(1-amino-2-carbamoyl-2-cyanovinyl)pyrroles or products of their intramolecular cyclization involving either the cyano or carbamoyl group, 1-amino-3-imino-3*H*-pyrrolizine-2-carboxamides or 1-amino-3-oxo-3*H*-pyrrolizine-2-carbonitriles [11, 12].

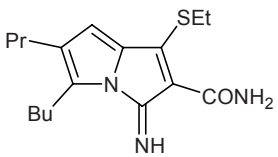
Taking into account the synthetic potential of iminopyrrolizines as building blocks for stereodependent heterocyclizations leading to fused polycyclic compounds, determination of their configuration and conformation is an important problem. In the present work we assigned configuration of the exocyclic double C=N bond in 1-ethylsulfanyl-3-imino-3*H*-pyrrolizine-2-carboxamides **Ia**–**Ic** and determined the preferential rotational conformation of the carbamoyl



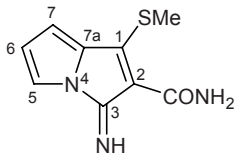
Ia



Ib

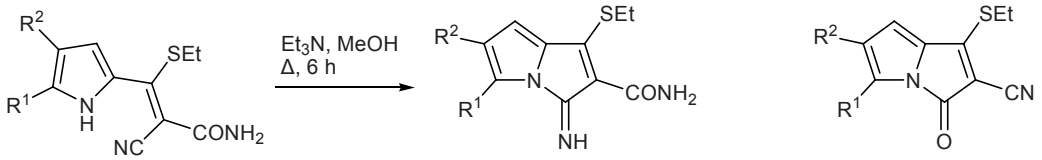


Ic



Id

Scheme 1.



$R^1R^2 = (CH_2)_4$ (**a**); R^1 = Pr, R^2 = Et (**b**); R^1 = Bu, R^2 = Pr (**c**).

group on C^2 in the simplest model iminopyrrolizine **Id** on the basis of the NMR data and results of high-level quantum-chemical calculations.

Pyrrolizines **Ia**–**Ic** were synthesized by intramolecular cyclization of the corresponding (2*Z*)-2-cyano-3-ethylsulfanyl-3-(1*H*-pyrrol-2-yl)prop-2-enamides (Scheme 1). It is known that the cyclization of 2-(2,2-dicyano-1-ethylsulfanylvinyl)-4,5,6,7-tetrahydroindole in the presence of a catalytic amount of triethylamine (methanol, 15 min under reflux) gives 1-ethylsulfanyl-3-imino-4,5,6,7-tetrahydroindolizine-2-carbonitrile in high yield [9]. 2-Cyano-3-ethylsulfanyl-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)prop-2-enamide undergoes cyclization much more difficultly [11]. The reason is that the carbamoyl group in the initial indole is oriented *syn* with respect to the pyrrole NH group (according to the NMR data); furthermore, the reaction is reversible. It was possible to direct the process toward formation of pyrrolizine **Ia** by removing the product from the reaction zone by filtration.

The cyclization of 2-cyano-3-ethylsulfanyl-3-(1*H*-pyrrol-2-yl)prop-2-enamides having alkyl substituents in positions *4* and *5* of the pyrrole ring occurred in a similar way. In these cases, the equilibrium cannot be displaced toward formation of the target products, for compounds **Ib** and **Ic** are readily soluble in methanol. Pyrrolizines **Ib** and **Ic** were separated from the initial pyrroles by preparative thin-layer chromatography, and their yields were 20 and 30%, respectively. Despite poor yields, the reaction was chemoselective: among two functional groups capable of participating in the cyclization (carbamoyl and cyano), only the cyano group was involved (no structures like **A** were detected in the reaction mixtures).

Pyrrolizines **Ia**–**Ic** were isolated as bright red crystalline substances. Their IR spectra contained absorption bands due to stretching vibrations of N–H and C=N bonds at 3149–3380 and 1650–1655 cm^{-1}, respectively. The amide carbonyl group gave rise to absorption at 1600–1605 cm^{-1} (amide I band). Analysis of the ^1H and ^{13}C NMR spectra of compounds **Ia**–**Ic** showed that they exist in solution as single isomers. However, two groups of signals were present due to restricted rotation about the partially double C(O)–N bond, i.e., iminopyrrolizines **Ia**–**Ic** are mixtures of two rotamers that are slowly converted into each other on the NMR time scale (Scheme 2).

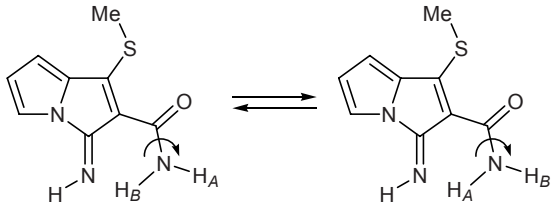
Signals from protons on the amide nitrogen atom, occupying *s-cis* and *s-trans* positions with respect to

Calculated (SOPPA) coupling constants $J(C^1,C^2)$ and $J(C^2,C^3)$ (Hz) for model 3-imino-1-methylsulfanyl-3*H*-pyrrolizine-2-carboxamide (**Id**)

Coupling constant	Isomer	Rotamer	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J_{calc}	J_{exp} [b]
$J(C^1,C^2)$	*Z* (*syn*)	*s-cis*	0.33	–7.48	2.6	74.39	69.84	70.0
		s-trans	0.33	–7.81	3.24	72.79	68.55	
	E (*anti*)	*s-cis*	0.34	–7.27	2.19	72.85	68.11	
		s-trans	0.33	–7.42	2.72	79.97	75.60	
$J(C^2,C^3)$	*Z* (*syn*)	*s-cis*	0.39	–2.24	0.82	70.69	69.66	67.0
		s-trans	0.39	–2.05	1.03	77.54	76.91	
	E (*anti*)	*s-cis*	0.39	–2.04	0.84	59.70	58.89	
		s-trans	0.39	–1.82	1.02	62.51	62.10	

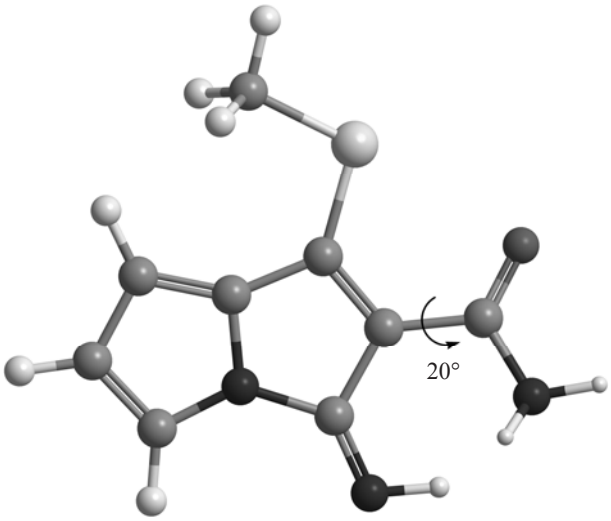
[a] For denotations of the rotamers, see Fig. 1.
[b] Data for compound **Ic**.

Scheme 2.

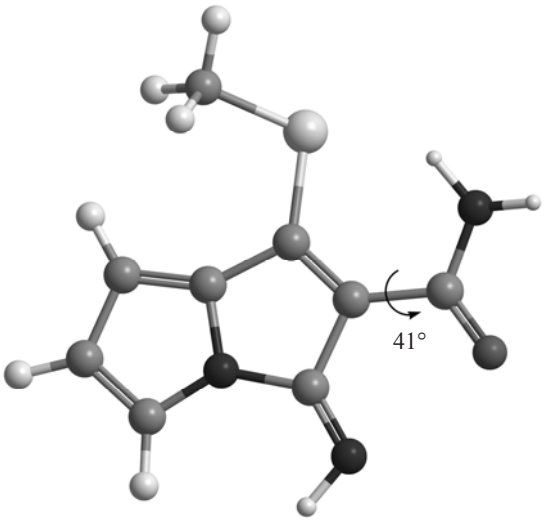


the C=O bond in different rotamers, were assigned using two-dimensional NOESY technique. The steric structure of compounds **Ia**–**Ic** was determined with the aid of various NMR techniques, including homo- and heteronuclear NOESY, HSQC, HMBC, and INADEQUATE experiments. In addition, high-level nonempirical calculations of $^{13}C–^{13}C$ coupling constants were performed, and the results were compared with the experimental data. As model structure for theoretical calculations we used compound **Id** having a methylsulfanyl instead of ethylsulfanyl group in position *1* and no substituents in positions *5* and *6*.

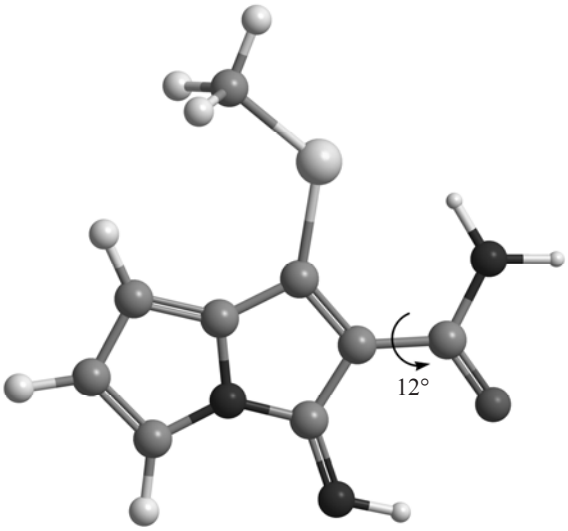
The configuration of the exocyclic C=N bond in compounds **Ia**–**Ic** was assigned by comparing the experimental and calculated $^{13}C–^{13}C$ coupling constants. As we showed previously, the $^{13}C–^{13}C$ coupling constants in the NMR spectra of Schiff bases [13] and oximes [14] strongly depend on the orientation of the



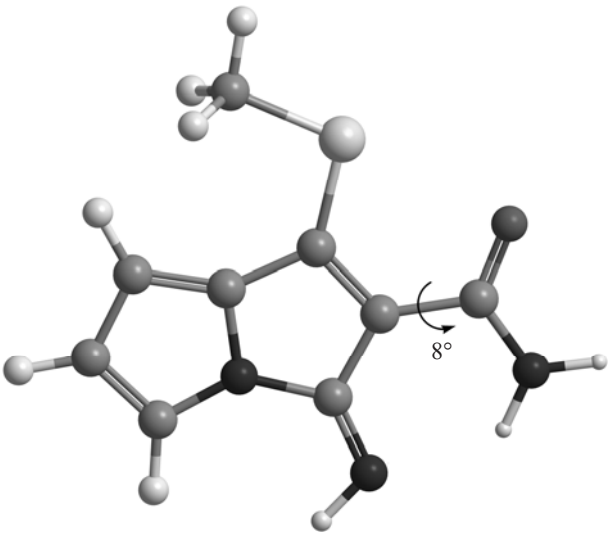
E-s-cis (2.4 kcal/mol)



Z-s-trans (11.8 kcal/mol)



E-s-trans (0.6 kcal/mol)



Z-s-cis (0.0 kcal/mol)

Fig. 1. Equilibrium conformations of the *E* and *Z* isomers of 3-imino-1-methylsulfanyl-3*H*-pyrrolizine-2-carboxamide (**Id**), optimized by the MP2/6-311G** method. The relative total energies are given in parentheses. Angular deviations of the carbamoyl group from the heteroring plane are shown with arrows.

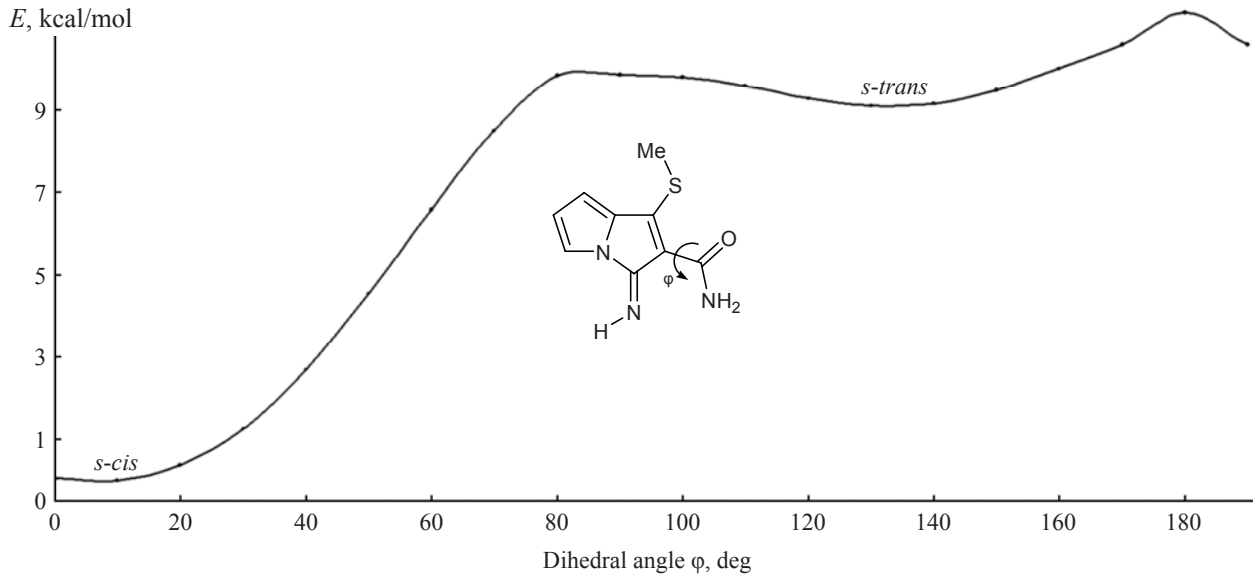


Fig. 2. Potential curve for internal rotation in model 3-imino-1-methylsulfanyl-3*H*-pyrrolizine-2-carboxamide (**Id**), calculated at the MP2/6-311G* level with optimization of geometric parameters in each rotational point (φ = 0° corresponds to the *s-cis* orientation of the carbamoyl group).

lone electron pair (LEP) on the C=N nitrogen atom. Sharp differences in the direct ^{13}C–^{13}C coupling constants of the C=N carbon atom between stereoisomers of Schiff bases are related to several factors: through-space interaction between the nitrogen LEP and the neighboring bond oriented *cis* with respect to the LEP, electron density transfer from the LEP orbital to the antibonding orbital of the *trans*-oriented bond (n_σ–σ* interaction), and stereospecific contribution of inner electrons in the interacting atoms. The nature of this effect was discussed in detail in some theoretical studies [15], and it is widely used for assignment of configuration of various Schiff bases [13].

The calculated coupling constants $J(C^2,C^3)$ for the *E* and *Z* isomers of model iminopyrrolizine **Id** differ by more than 10 Hz (see table); therefore, the configuration of compounds **Ia**–**Ic** can be unambiguously assigned on the basis of the experimental J_{CC} values. As follows from the experimental data, iminopyrrolizines **Ia**–**Ic** are characterized by *Z* configuration of the exocyclic C=N bond, which is consistent with the theoretical data on their relative thermodynamic stability. The *Z* isomer of **Id** having the most favorable conformation of the carbamoyl group is more stable than the *E* isomer by 2.4 kcal/mol (Fig. 1). In order to determine the most favorable conformation of the carbamoyl group on C^2 we calculated angular dependences of the total energy of model iminopyrrolizine **Id** upon rotation of the carbamoyl group and plotted potential curves for internal rotation using the MP2/6-311G* method with optimization of geometric parameters for each rotamer (Fig. 2).

The potential curve for internal rotation in molecule **Id** includes two energy minima at φ ≈ 10 and 140°, which correspond to the *s-cis* and *s-trans* conformers, respectively, and two maxima at φ ≈ 90 and 180° corresponding to transition states for internal rotation of the carbamoyl group about the C^2–C(O) bond (Fig. 2). Stable conformers were localized by searching for stationary points in the φ regions of ~10 and 140° by the MP2/6-311G** method. We thus have found two conformers, *s-cis* (φ = 8°) and *s-trans* (φ = 139°), whose optimized structures are shown in Fig. 1. It should be noted that the most favorable *Z-s-cis* conformer is almost planar and that the *Z-s-trans* conformer having a higher energy appreciably deviates from the planar structure (the dihedral angle between the carbamoyl group and pyrrolizine plane is 41°).

The nature of all conformers of compound **Id** and transition states was determined by analysis of normal harmonic vibrations. All vibrational frequencies of all conformers were found to be real numbers, while the vibrational spectra of all localized transition states each contained one imaginary frequency.

Especially valuable information on rotational conformers of iminopyrrolizines can be obtained from the coupling constants $J(C^1,C^2)$ and $J(C^2,C^3)$. According to the calculation data, these constants are sensitive to mutual orientation of the corresponding carbon–carbon

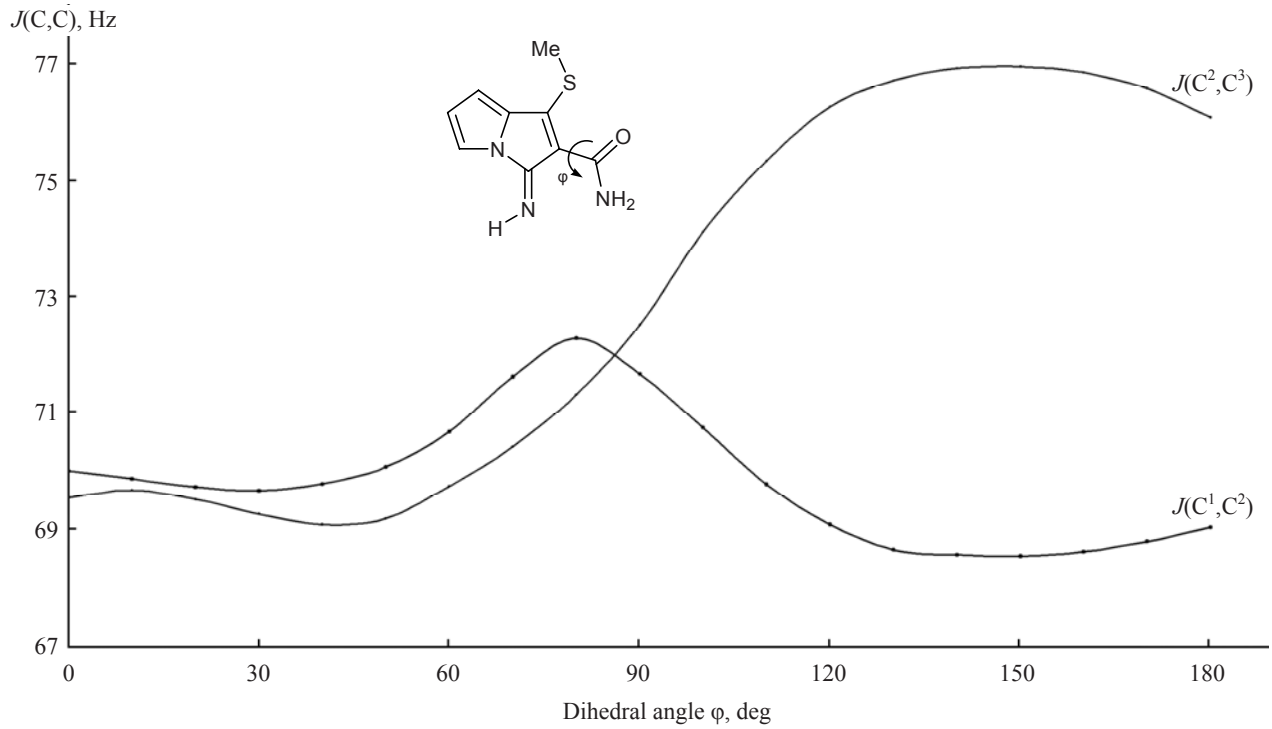
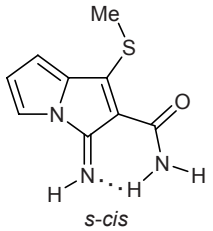


Fig. 3. Plots of the coupling constants $J(C^1,C^2)$ and $J(C^2,C^3)$ versus dihedral angle between the carbamoyl group and the heteroring plane in model 3-imino-1-methylsulfanyl-3*H*-pyrrolizine-2-carboxamide (**Id**), calculated in terms of the second-order polarization propagator approximation (SOPPA) with optimization of geometric parameters in each rotational point at the MP2/6-311G* level.

bonds and C=O bond in the amide fragment (Fig. 3). Rotation of the carbamoyl group in the φ range from 0 to 180° is accompanied by insignificant variation of the $J(C^1,C^2)$ value (about 2 Hz) which passes through a maximum at φ ≈ 85°. This is related to increase in the π order of the C^1–C^2 bond in the conformer with orthogonal orientation of the carbamoyl group with respect to the iminopyrrolizine plane. On the other hand, the coupling constant $J(C^2,C^3)$ shows a pronounced angular dependence: it increases by almost 8 Hz in going from the *s-cis* to *s-trans* conformer (Fig. 3). The observed dependence originates from the fact that the lone electron pair on the imino nitrogen atom in the *s-cis* conformer is involved in intramolecular hydrogen bond with protons in the amide group (see below), so that it does not contribute to the coupling constant for the neighboring C^2–C^3 bond (cf. [13–15]). When the carbamoyl group declines from the plane of the iminopyrrolizine fragment, the intramolecular hydrogen bond is broken, and the nitrogen LEP provides a positive contribution to the coupling constant $J(C^2,C^3)$, i.e., the latter increases in going to the orthogonal conformer. Further increase of $J(C^2,C^3)$ in going from the orthogonal (φ = 90°) to *s-trans* conformer (φ = 180°) results from hyperconjugation involving bonding orbitals of the C^2–C^3 and C^2–C(O) bonds and antibonding orbital of the C=O bond. This interaction gives rise to orientational contribution of the C=O bond to ^{13}C–^{13}C coupling constants for the neighboring bonds [16].

Thus the pronounced dependence of the calculated coupling constant $J(C^2,C^3)$ on the steric structure of model pyrrolizine **Id**, related to rotation of the carbamoyl group on C^2 with respect to the pyrrolizine plane (see table), allowed us to unambiguously assign *s-cis* orientation of the carbamoyl group in iminopyrrolizines **Ia**–**Ic**.



s-cis

EXPERIMENTAL

The NMR spectra were recorded at 25°C from 10% solutions in $CDCl_3$ on Bruker DPX-400 and Avance-400 spectrometers (400.13 MHz for ^1H and 100.61 MHz for ^{13}C) using hexamethyldisiloxane as

internal reference. The ^{13}C–^{13}C coupling constants were measured using INADEQUATE pulse sequence with the following parameters: spectrum width 6 kHz, pulse duration 13.5 μs, pulse delay 4 s, FID acquisition time 4 s, digital resolution 0.1 Hz per point, accumulation time 6 to 24 h. The ^{13}C–^{1}H coupling constants were determined from the proton-coupled ^{13}C NMR spectra with periodical broad-band decoupling from protons during pulse delays using the above spectral parameters.

Quantum-chemical calculations were performed with the aid of GAMESS [17] and DALTON programs [18]. The geometric parameters were optimized, and the total energies were calculated, in terms of the Moeller–Plesset second-order perturbation theory (MP2/6-311G**); the ^{13}C–^{13}C coupling constants were calculated using the second-order polarization propagator approximation (SOPPA) with standard or modified basis sets (for detailed specification, see [19]).

The synthesis and properties of 3-imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-2-carboxamide (**Ia**) were reported in [11]. ^{13}C NMR spectrum, δ_C, ppm: 112.76 (C^2), 113.91 (C^6), 125.93 (C^5), 129.45 (C^7), 131.21 (C^4), 155.58 (C^3), 157.79 (C^1), 165.15 (CO); ^{13}C–^{13}C coupling constants: $J(C^1,C^2)$ = 71.6, $J(C^2,C^3)$ = 67.6 Hz.

3-Imino-6-ethyl-1-ethylsulfanyl-5-propyl-3*H*-pyrrolizine-2-carboxamide (Ib). A solution of 0.50 g (1.7 mmol) of (*Z*)-2-cyano-3-(4-ethyl-5-propyl-1*H*-pyrrol-2-yl)-3-ethylsulfanylprop-2-enamide in 10 ml of methanol containing 0.5 ml of triethylamine was heated for 6 h under reflux. The solvent was removed, and the residue was subjected to preparative thin-layer chromatography on Al_2O_3 using petroleum ether (bp 40–70°C)–diethyl ether (1:5) as eluent to isolate 0.10 g (20%) of compound **Ib** with mp 140–142°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3409, 3342, 3153, 2957, 2929, 2867, 1655, 1636, 1602, 1487, 1420, 1373, 1217, 1169, 1153, 1116, 1103, 1050, 800, 591. ^1H NMR spectrum, δ, ppm: 1.00 t (6H, CH_3, J = 7.6 Hz), 1.14 t (2H, CH_2, J = 7.5 Hz), 1.42 t (3H, C**H**$_3$CH$_2$S, J = 7.4 Hz), 1.65 m (2H, CH_2), 2.35 q (2H, CH_2, J = 7.4 Hz), 2.67 t (2H, CH_2, J = 7.5 Hz), 3.19 q (2H, CH_2S, J = 7.4 Hz), 5.35 br.s (1H, $CONH_2$), 6.19 s (1H, 3-H), 7.85 s (1H, HN=), 8.57 br.s (1H, $CONH_2$). ^{13}C NMR spectrum, δ_C, ppm: 113.14 (C^2), 113.79 (C^6), 127.09 (C^5), 130.70 (C^7), 131.38 (C^4), 155.51 (C^3), 157.10 (C^1), 165.17 (CO); ^{13}C–^{13}C coupling constants: $J(C^1,C^2)$ = 71.1, $J(C^2,C^3)$ = 68.3 Hz. Found, %: C 61.96; H 7.16; N 14.54; S 10.85. $C_{15}H_{21}N_3OS$. Calculated, %: C 61.83; H 7.26; N 14.42; S 11.00.

5-Butyl-1-ethylsulfanyl-3-imino-6-propyl-3*H*-pyrrolizine-2-carboxamide (Ic) was synthesized in a similar way from 0.50 g (1.6 mmol) of (*Z*)-3-(5-butyl-4-propyl-1*H*-pyrrol-2-yl)-2-cyano-3-ethylsulfanylprop-2-enamide. Yield 0.15 g (30%), mp 124–126°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3349, 3314, 3157, 2934, 2868, 2841, 1651, 1600, 1481, 1449, 1371, 1348, 1283, 1255, 1214, 1180, 1138, 1014, 846, 796, 768, 725, 675. ^1H NMR spectrum, δ, ppm: 0.87 m (6H, CH_3), 0.94 m (4H, CH_2), 1.41 t (5H, CH_2, C**H**$_3$CH$_2$S, J = 7.3 Hz), 2.29 t (2H, CH_2, J = 7.5 Hz), 2.68 t (2H, CH_2, J = 7.6 Hz), 3.18 q (2H, CH_2S, J = 7.3 Hz), 5.32 br.s (1H, $CONH_2$), 6.16 s (1H, 3-H), 7.84 s (1H, HN=), 8.57 br.s (1H, $CONH_2$). ^{13}C NMR spectrum, δ_C, ppm: 113.02 (C^2), 113.89 (C^6), 127.78 (C^5), 131.01 (C^7), 131.82 (C^4), 155.10 (C^3), 157.03 (C^1), 165.19 (CO); ^{13}C–^{13}C coupling constants: $J(C^1,C^2)$ = 70.0, $J(C^2,C^3)$ = 67.0 Hz. Found, %: C 63.86; H 7.69; N 13.35; S 9.84. $C_{17}H_{25}N_3OS$. Calculated, %: C 63.92; H 7.89; N 13.15; S 10.04.

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