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Solvatochromism of Heteroaromatic Compounds: XVI.[1] Theoretical Study of the Effect of Nonspecific Solvation on the Rotational Isomerism and Spectral Characteristics of 2-[2,2-Dicyano-1-(methylthio)vinyl]-5-methylpyrrole

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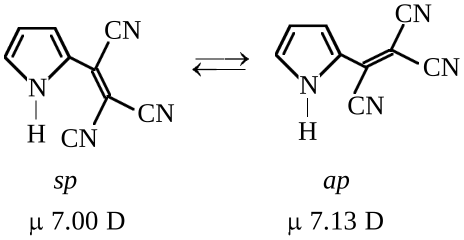
Abstract—The effect of nonspecific solvation of the relative stability of rotational isomers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole was studied theoretically (HF/6-31G*) in terms of the Onsager model. In the free form this compound exists as an ensemble of four nonplanar C, N, S rotamers, the largest energy gap between which being no more than 2 kcal/mol. The effects of media whose generalized parameters correspond to chloroform and 1,2-dichlroethane reduce this gap to 0.7 and 0.5 kcal/mol. The vibration spectra of the rotamers and characteristics of the $\pi \to \pi^*$ electronic transitions with intramolecular charge redistribution were calculated. Prospects of experimental studies of the solvatochromism and conformational isomerism of the title compound were discussed.

In one of our previous communications we considered the effect of nonspecific solvation on the conformational structure of 2-(1,2,2-tricyanovinyl)pyrrole [2]. This pyrrol has one internal rotation axis and can exist as a mixture of two stable rotamers. According to nonempirical quantum-chemical calculations, the rotamers of 2-(1,2,2-tricyanovinyl)pyrrole are planar in the free state and has close dipole moments (Scheme 1).

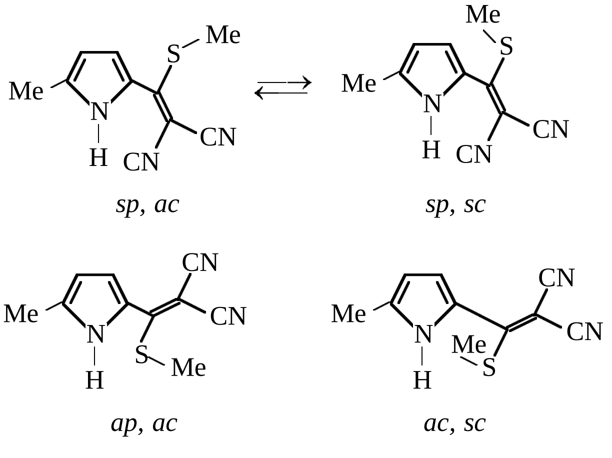
Scheme 1.



As a result, as deduced from the solvatochromism of the long-wave absorption band of 2-(1,2,2-tricyanovinyl)pyrrole in aprotic intert media [2], nonspecific solvation exerts no effect on the conformational equilibrium which is shifted to the *sp* form.

Replacement of one of the C≡N groups by C–Me gives 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole, a compound which, having two internal rotation axes, is much more complex conformationally (four rotamers) (Scheme 2).

Scheme 2.



From the structure of these rotamers we can expect that they have different dipole moments. In this case, nonspecific solvation will differently affect their stability. Such a complex conformational equilibrium is very difficult to thoroughly examine by means of one physicochemical method. Therefore, the main goal of the present work was to study the rotational isomerism of free 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole quantum-chemically and to reveal,

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[1] For communication XV, see [1].

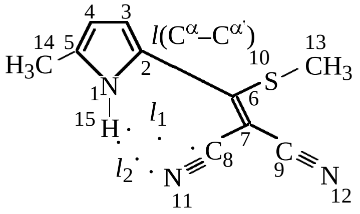
Table 1. Bond lengths (*d*) and bond angles (ω) in the *sp*,*ac* conformer of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole. Data of nonempirical quantum-chemical calculations (HF/6-31G*)

Bond	*d*, Å	Angle	ω, deg
N^1–C^2	1.382	$C^5N^1C^2$	110.3
C^2–C^3	1.381	$N^1C^2C^3$	106.3
C^3–C^4	1.401	$C^2C^3C^4$	108.0
C^4–C^5	1.375	$C^3C^4C^5$	107.3
N^1–C^5	1.343	$C^4C^5N^1$	108.2
C^2–C^6	1.442	$N^1C^2C^6$	125.0
C^6–C^7	1.365	$C^2C^6S^{10}$	112.9
C^7–C^8	1.436	$C^6C^7S^{10}$	121.9
C^7–C^9	1.434	$C^6C^7C^9$	123.3
C^8–N^{11}	1.138	$C^8C^7C^9$	114.0
C^9–N^{12}	1.137	$N^1H^{15}C^8$	113.3
C^6–S^{10}	1.774	$N^1H^{15}N^{11}$	133.5
S^{10}–C^{13}	1.819	$C^6S^{10}C^{13}$	105.5
C^5–C^{14}	1.496	$C^4C^5C^{14}$	130.2
N^1–H^{15}	0.994		

on the theoretical level, the role of specific solvation and its effect on the UV and IR spectra.

Quantum-chemical calculations of the structure, energy, and IR spectra of free conformers. It is commonly known that the population of conformers at a constant statistical factor is determined by their relative energies. Nonempirical calculations (HF/6-31G*) point to the prevalence, in the free molecule, of the *sp*,*ac* conformer (its geometric parameters are given in Table 1, and the atom numbering, in Scheme 3) which is 1 kcal/mol more favored by energy than its closest *sp*,*sc* conformer (Scheme 2). The energy gap separating the rest conformers from *sp*,*ac* is no larger than 1.9 kcal/mol (Table 2). Obviously, because of the stronger dipolarity of energetically less favorable forms (Table 2), the energy gap between the conformers will get narrower. Therefore, one may expect that all the conformers will be experimentally detected in solution.

Scheme 3.



sp, *ac* form

Let us consider in more detail the structure of the conformers. As follows from HF/6-31G* calculations, the rotamers all are nonplanar and have different dihedral angles. Let us denote the torsion angle of their exocyclic double bond with respect to the pyrrole ring plane by θ_1, and the torsion angle of the S–Me group with respect to the plane of the dicyanovinyl group, by θ_2. The calculated θ_1 and θ_2 angles are given in Table 2. As seen, even in the energetically favorable *sp* conformers the θ_1 angle in not zero. Conformers with the opposite orientation of the exocyclic double bond have an even larger torsion angle θ_1, and one of the conformers becomes *anticlinal* (*ac*). In the latter, the torsion angle of the double band is no larger than 30°. Most likely, the deviations from planarity are associated with nonbonded interactions between the NH bond atoms and the thiomethyl group. The largest θ_2 angle is characteristic of the pair of *synclinal* (*sp*,*sc* and *ac*,*sc*) conformers, which is also accounted by the interaction between the thiomethyl group and the CH or NH bonds of the pyrrole ring.

It should be noted that the energetic stability of the free rotamers varies in parallel with the interfragment $l(C^{\alpha}$–$C^{\alpha'})$ distance: *sp*,*ac* < *sp*,*sc* < *ap*,*ac* < *ac*,*sc* (Table 2). In its turn, the C^{α}–$C^{\alpha'}$ distance is directly related to the two torsion angles (the relation was obtained with the parameters of the nonequilibrium planar, by C, H, and S, form *sp*,*ap* form).

$$l(C^{\alpha}\text{–}C^{\alpha'}) = (1.428 \pm 0.002) + (4.3 \pm 0.4) \times 10^{-4}\theta_1 + (1.4 \pm 0.3) \times 10^{-4}\theta_2;\ r\ 0.982,\ s\ 5 \times 10^{-4},\ n\ 5.$$

As seen from the above relation, the interfragment distance is much more sensitive to the mutual orientation of the heteroring and dicyanovinyl fragment than to the deviation of the thiomethyl group from the plane of the latter. Consequently, the relative stability of the rotamers is primarily determined by a compromise between nonbonded and π-electron interactions between the unsaturated fragments of the 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole molecule (resonance component of the C^{α}–$C^{\alpha'}$ bond energy). The interaction of the lone electron pair of sulfur with the π-electron system exerts a much weaker effect. It was interesting to trace the trends in the equilibrium C=C bond length from rotamer to rotamer. Here the pattern is more intricate that in the above case, because *l*(C=C) experiences greater number of factors. One of them can be excluded from consideration, based on the data for the *sp*,*ac* and *ap*,*ac* conformers whose θ_2 angles differ from each other by only 4°. As follows from Table 2, the length of the exocyclic double bond decreases as θ_1 increases.

Table 2. Characteristics of the conformers of the free and solvated 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole. Data of nonempirical calculations (HF/6-31G*)

Conformer	ΔE, kcal/mol	ΔE_s[a], kcal/mol	θ_1, deg	θ_2, deg	l_1, Å	l_2, Å	l(N···S), Å	l(C=C), Å	$l(C^{\alpha}–C^{\alpha'})$, Å	ν_{NH}[b], cm^{-1}	$\nu_{C=C}$[b], cm^{-1}	μ, D
Gas phase												
sp,ac	0	0	18	46	2.347	2.474		1.365	1.442	3482	1475	5.94
sp,sc	1.00	0	17	68	2.349	2.438		1.358	1.445	3481	1509	7.52
ap,ac	1.43	0	27	42			2.997	1.360	1.446	3487	1510	8.14
ac,sc	1.83	0	35	57			3.104	1.361	1.451	3475	1543	9.03
Chloroform (ε 4.7)												
sp,ac	0	0.90	15	50	2.339	2.450		1.368	1.437	3481		6.78
sp,sc	0.47	1.43	19	64	2.374	2.486		1.360	1.441	3482		8.47
ap,ac	0.67	1.66	25	44			2.992	1.363	1.442	3483		9.08
ac,sc	0.67	2.06	27	42			3.104	1.354	1.447	3472		10.13
1,2-Dichloroethane (ε 10.9)												
sp,ac	0	1.14	14	51	2.336	2.453		1.368	1.436	3481		7.02
sp,sc	0.33	1.80	19	64	2.379	2.497		1.361	1.440	3483		8.71
ap,ac	0.48	2.09	24	44			2.991	1.366	1.440	3482		9.33
ac,sc	0.38	2.59	34	56			3.104	1.355	1.446	3472		10.42

[a] Energy of nonspecific solvation, estimated by the Onsager model. The Onsager radius of the conformers (6.1 Å) was estimated using the van der Waals radii [3]. [b] Scaled by a factor of 0.8929.

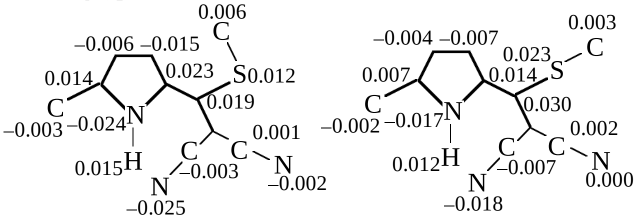
In the other set of conformers, *sp,ac* and *sp,sc*, where θ_1 ~ const, l(C=C) decreases with increasing θ_2. Probably, l(C=C) also depends on the two torsion angles; therewith, according to calculations, it is more sensitive to θ_1. The $C^{\alpha}–C^{\alpha'}$ and C=C bond lenghts, as would expected, vary in opposite directions. Consequently, the longer double bond and the shorter interfragment bond in the *sp,ac* rotamer (Table 2) are explained by stronger π-electron interaction between the pyrrole ring and the dicyanovinyl fragment at this molecular configuration.

As we theoretically showed in [2], in 2-(1,2,2-tricyanovinyl)pyrrole there is an intramolecular hydrogen bond involving the π system of the nitrile group. 2-[2,2-Dicyano-1-(methylthio)vinyl]-5-methylpyrrole may involve, depending on the equilibrium conformation, two types of intramolecular hydrogen bond: with an orthogonal π system of the terminal nitrile group (Scheme 3) or with the sulfur atom.

Let us focus initially on the *ap,ac* and *ac,sc* conformers. Their N···S distance (Table 2) in shorter by 0.25–0.35 Å on the sum of the van der Waals radii of nitrogen and sulfur, which might be considered evidence for an intramolecular H bond. However, the total charge on the sulfur atom in these forms is positive (~0.22*e*, by Mulliken). For this reason, the NH hydrogen cannot play the role of a bridge. In other words, the short N···S distances here are assignable to other, specifically conformational, factors.

The distances between the NH hydrogen and the atoms of the C≡N group (l_1 and l_2) in the pair of *sp* conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole (Table 2), too, is much shorter than the sum of the van der Waals radii (by 0.2–0.3 Å), and one of them is even shorter that in the *sp* conformer of 2-(1,2,2-tricyanovinyl)pyrrole (l_1 2.369, l_2 2.406 Å [2]). This suggests an intramolecular hydrogen bond but not unequivocally explains the shortened distance between the NH and C≡N fragments. A typical evidence for an H complex might be provided by the polarization of the bond involved in its formation. In our case, the *anti* forms of the molecule (*ac,sc* and *ap,ac*) may serve as a convenient reference point. Changes in the total charges on the C, N, and S atoms and the NH hydrogen in going from the *ac,sc* and *ap,ac* forms to the *syn* forms (*sp,sc* and *sp,ac*) are shown in Scheme 4. As seen, the NH bond is actually polarized.

Scheme 4.



Δq (*sp,sc* – *ac,sc*) Δq (*sp,ac* – *ap,ac*)

The conformational transition decreases the electron density on the bridging hydrogen atom and increases the electron density on the nitrogen atom. Moreover, in the *syn* forms, the nitrile group is also enriched in electron density, thus favoring electrostatic interactions stabilizing the *sp*,*sc* and *sp*,*ac* conformers. Thus, the relative energetic stability of the conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole is controlled by three types of interactions: nonbonded, π-electron, and intramolecular hydrogen bonding.

To reveal conformationally dependent stretching vibration frequencies, we performed vibrational computations (HF/6-31G*) for all conformers of the free molecule. The most perspective for experimental observations are the NH and C=C vibration frequencies of the dicyanovinyl fragment (Table 2). The lowest frequency vibration ν_{NH} is characteristic of the *ac*,*sc* conformer (3475 cm^{-1}). The NH vibration frequencies of the *sp* conformers are almost coincident. The highest vibration frequency is characteristic of the NH bond of the free *ap*,*ac* conformer (3487 cm^{-1}). The C=C vibration frequencies of the dicyanovinyl fragment vary quite differently. Thus, the *sp*,*sc* and *ap*,*ac* pair have equal C=C vibration frequencies. The highest $\nu_{C=C}$ is characteristic of the *ac*,*sc* conformer and the lowest, of the *sp*,*ac* conformer (Table 2). Unfortunately, the C=C vibration frequencies fall into the region of intrinsic absorption of most solvents. Therefore, NH vibration frequencies are more suitable for experimental studies on the rotational isomerism in solution.

Quantum-chemical calculations with account for nonspecific solvation. As noted above, the conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole have different dipole moments (μ). The lowest μ value is characteristic of the most stable, *sp*,*ac* conformer. Further μ order is quite unexpected: The less rotamer favored by energy, the higher its dipole moment (Table 2). Since, according to the known rule, polar media stronger stabilize conformers with high μ values, the energy gaps between the conformers will depend on the properties of the media.

To account for the effect of nonspecific solvation on the geometries, dipole moments, and relative stabilities of the conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole in terms of the Onsager model, we performed their nonempirical (HF/6-31G*) calculations for two aprotic inert solvents, chloroform (ε 4.7) and 1,2-dichloroethane (ε 10.9). The resulting data are given in Table 2. As seen, the *sp*,*ac* conformers still remains most favored by energy, while the energy gap separating it from the rest conformers gets much smaller. This tendency is most pronounced in 1,2-dichloroethane, where the conformers change their stability order: *sp*,*ac* > *sp*,*sc* > *ac*,*sc* > *ap*,*ac*. The reason for this result may lie in advanced increase in the solvation energies of polar conformers (Table 2).

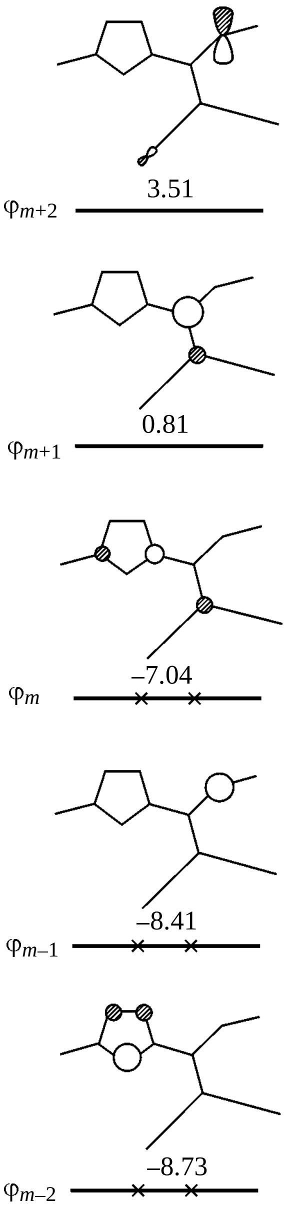
Analysis of the solvation-induced changes in the geometry of of the conformers led us to the following conclusions. The effect of the medium on θ_1 and θ_2 is very weak in all the conformers. Only slightly affected are also the double and interfragment bond lengths, as well as the N···S distance. The most sensitive to the effects of the medium are the nonbonded distances l_1 and l_2 (Scheme 3) in the *sp*,*ac* and *sp*,*sc* conformers. They change by 0.01–0.06 Å. In the *sp*,*ac* conformer, l_1 and l_2 are shortened in going from the gas phase to chloroform and further to 1,2-dichloroethane. The *sp*,*sc* conformer exhibits the opposite tendency: l_1 and l_2 increase with increasing solvation energy; simultaneously, θ_1 slightly increases. The increased l_1 and l_2 in the *sp*,*sc* conformer in solution compared with the gas phase should weaken the intramolecular hydrogen bond, thereby increasing NH absorption frequency. This increase is actually observed, but it is as small as 1–2 cm^{-1} (Table 2). The explanation is that the medium directly affects ν_{NH} (see data for the corresponding *anti* form in Table 2), decreasing it by 3 cm^{-1}. In other words, in the *sp*,*sc* conformer we deal with a compensation effect whose mechanism is as follows. When the intramolecular H complex gets weaker, the NH bond depolarizes, while when the polarity of the medium increases, it, by constrast, polarizes. Finally, the polarity of the NH bond in this conformer in a polar solvent slightly decreases.

Gas		$CHCl_3$		CH_2ClCH_2Cl	
N	H	N	H	N	H
–0.024	0.015	–0.021	0.010	–0.020	0.009

The l_1 and l_2 distances in the *sp*,*ac* conformer in going to solution change 2–3 times weaker than in the *sp*,*sc* conformer. Therewith, the polarization of the NH bond in the *sp*,*ac* conformer changes only slightly in a direction that suggests an inconsiderable decrease in ν_{NH} which agrees with the calculation results (Table 2).

Gas		$CHCl_3$		CH_2ClCH_2Cl	
N	H	N	H	N	H
–0.017	0.012	–0.025	0.007	–0.025	0.007

Unlike the gas phase, where only the two *sp* confomers have close NH vibration frequences, in chloro-



Orbital structure of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole as given by nonempirical calculations (HF/6-31G*).

form and 1,2-dichloroethane there are already three conformers (*sp*,*ac*, *sp*,*sc*, and *ap*,*ac*) with close ν_{NH} values. Consequently, experimentally, in the ν_{NH} range of the IR spectra in these solvents one will be able to identify the *ac*,*sc* conformer only, whereas the rest three conformers will give a composite band whose nature will require special consideration.

Under the action of nonspecific solvation, i.e. with increasing dielectric constant of the medium, the dipole moments of all the conformers increase. But the tendency for μ to increase in going from stable conformers to energetically less favorable is preserved (Table 2).

Orbital structure of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole and the nature of bands in its UV spectrum. As seen from data in Table 2, the medium-induced increment of dipole moment increases with increasing polarity of the ground electronic state. There are no reasons to expect that this regularity will be disturbed in the electronically excited state. Therefore, the strength of the nonspecific solvatochromic effect in the UV spectrum of a rotamer will depend on how much its dipole moments changes on excitation at the corresponding absorption band. In this connection, it is very important to determine the nature of long-wave electronic transitions.

The orbital diagram of the *sp*,*ac* conformer of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole is given in the figure. As seen from the figure, three highest occupied MOs and the lowest unoccupied MO of this rotamer (as well as of the other ones) are π-type orbitals, and the second unoccupied, a σ-type orbital. Nonempirical calculations of the UV spectrum of the *sp*,*ac* conformer showed (Table 3) that the long-wave absorption bands belong to $\pi\rightarrow\pi^*$ one-electron transitions and are rather strong. The first of them, $\varphi_m^2\rightarrow\varphi_{m+1}^0$ (electronic configuration of the locally excited state Ψ_m^{m+1}), involves interfragment redustribution of the orbital electron density from heteroring carbon atoms to the dicyanovinyl group. The second transition, $\varphi_{m-1}^2\rightarrow\varphi_{m+1}^0$ (Ψ_{m-1}^{m+1}), involves electron density transfer from the molecular orbital localized on the sulfur atom. The third transition is similar to the first one, but here the electron density gets lower primarily on the pyrrole nitrogen atom. Thus, the

Table 3. Characteristics of the $\pi\rightarrow\pi^*$ electronic transitions of certain conformers of free 2-[2,2-dicyano-1-(methylthio)-vinyl]-5-methylpyrrole. Calculated data [HF/6-31G*(CI)]

Confor-mer	ν, cm^{-1} [a]	*f*	Principal configurations[b]
sp,*ac*	27300	0.81	0.68 Ψ_m^{m+1}
	34200	0.21	0.64 Ψ_{m-1}^{m+1}
	38500	0.08	0.62 Ψ_{m-2}^{m+1}
ac,*sc*	27700	0.75	0.68 Ψ_m^{m+1}
	34900	0.09	0.44 Ψ_{m-1}^{m+1}
	39500	0.03	0.44 Ψ_{m-2}^{m+1}, 0.48 Ψ_{m-1}^{m+1}

[a] The given ν value corresponds to 0.75 ν[HF/6-31G*(CI)].

[b] The electronic configuration Ψ_i^j corresponds to the one-elec tron transition $\varphi_i^2\rightarrow\varphi_j^0$.

long-wave $\pi \to \pi^*$ transitions in the UV spectrum of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole should be classified as transitions involving intramolecular redistribution of electron density. As a rule, such transitions raise dipole moment, and, as a result, the compound studied will feature a pronounced positive solvatochromism. According to the calculation results, long-wave absorption bands are sensitive to molecular conformation. Thus, the electronic transitions of the *ac,sc* conformer are shifted blue with respect to those of the *sp,ac* conformer by 400–1000 cm^{-1}. Furthermore, the conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole have different polarities in the ground state (Table 2). Consequently, qualitative conformational analysis of this compound can be perfomed on the basis of medium-induced spectral shifts of its electronic absorption bands [4, 5]. Results of experimental studies on the conformational isomerism of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole will be reported in our further publications.

Calculational procedure. The energies and geometries of the conformers of 2-[2,2-dicyano-1-(methylthio)vinyl]-5-methylpyrrole, their dipole moments and IR and UV spectra in the gas phase and with account for solvation (in terms of the Onsager model) were obtained by nonempirical (HF/6-31G*) calculations with use of GAUSSIAN 98 [6].

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