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Solvatochromism of Heteroaromatic Compounds: XVII.[1] Effect of Aprotic Inert Solvents on the Structure of 2-(2,2-Dicyanovinyl-1-methylthio)-5-methylpyrrole

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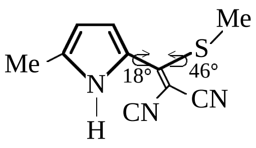
Abstract—The effect of aprotic inert media on the conformational structure of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole was studied by UV, NMR, and IR spectroscopy. Chloroform and less polar solvents stabilize only one of the four conformers. In more polar media, there is a dynamic equilibrium between all the possible conformers of the title compound. The state of the equilibrium depends both on the solvent and on the temperature.

In our previous work [1] we performed a theoretical study of the conformational structure of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole (see scheme). Nonempirical quantum-chemical calculations (HF/6-31G*) with allowance for nonspecific solvation in the framework of the Onsager model showed that the rotational isomerism of 2-(2,2-dicyanovinyl-1-methylthio)- 5-methylpyrrole in aprotic inert media is best experimentally studied in terms of such conformation-dependent characteristics of the molecule as the NH vibration frequency and the energy of the long-wave electronic transition involving redistribution of electron density.



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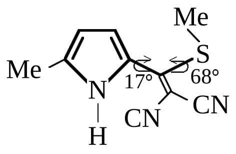

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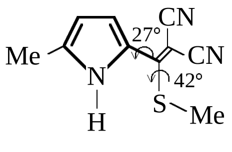

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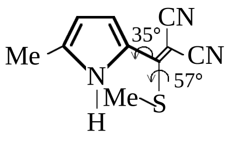

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The aim of the present work was to study the conformational isomerism of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert media by UV, NMR, and IR spectroscopy.

Solvatochromism of the long-wave band in the electronic absorption spectrum of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole. The empirical basis for the utilization of solvatochromistic information in the qualitative conformational analysis of compounds whose conformers have different ground-state dipole moments has been laid in [2, 3]. The essence of this approach is as follows. When one conformer is prevailing in a solution, the dependence of the position of its absorption maximum in the UV spectrum on the polarity/polarizability of the aprotic inert medium, measured by the general Kamlet–Taft π^*, is described by Eq. (1).

$$\nu_{\max} = \nu^0_{\max} + c\pi^*. \qquad (1)$$

If, as the polarity of the medium is varied, a conformer with another dipole moment appears in the solution, relation (1) is violated.

Data on the solvatochromism of the long-wave absorption band in the UV spectrum of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert media are given in Table 1. The effects of the medium are quantitatively described in terms of Eq. (1), where π^* is the parameter of the medium, measuring its ability to stabilize the dipole moments of solutes and $\nu^0_{\max}$ is $\nu_{\max}$ in a fully inert solvent (π^* 0). Linear regression analysis showed that the solvents used have notably different π^* values. At $\pi^* \le 0.65$ (Fig. 1, Table 1, nos. 1–9), the following equation relating $\nu_{\max}$ to π^* was obtained:

$$\nu_{\max} = (25550 \pm 20) - (1420 \pm 50)\pi^*;$$
$$r\ 0.995,\ s\ 40,\ n\ 9. \qquad (2)$$

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

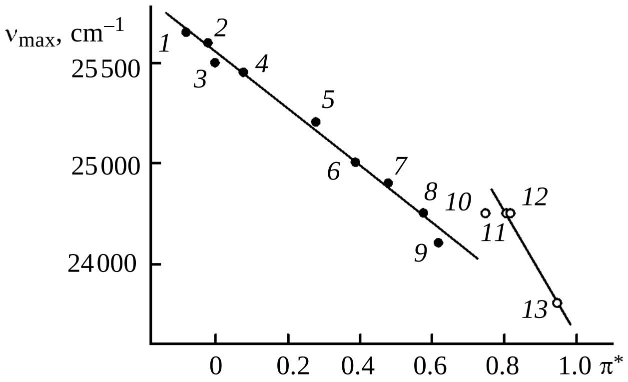

Fig. 1. Solvatochromism of the long-wave absorption band of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert media. The solvent numbering is given in Table 1.

The observation of a linear dependence with a high correlation coefficient suggests prevalence in these media of only one of the conformers. In more polar media ($\pi^* \geq 0.7$), there are considerable, much exceeding the experimental error (~50 cm^{-1}), deviations (~300 cm^{-1}) from the regression line (2) (Fig. 1, Table 1, nos. 10–13), which implies a change of the state of the conformational equilibrium. This conclusion is consistent with our theoretical data [1] for the gas phase and 1,2-dichloroethane. These data show that, in a medium with the dielectric constant ε 10.9, the largest energy gap between the conformers is much reduced (from 1.9 to ~0.5 kcal/mol), i.e. the molecule of the pyrrole studied in such rather polar solvents as 1,2-dibromoethane, 1,2-dichloroethane, dichloromethane, and 1,1,2,2-tetrachloroethane (Table 1, nos. 10–13) can exist as an ensemble of four conformers. Unfortunately, by UV spectroscopy we can firmly establish neither the structure of the prevailing isomer nor the composition of the complex conformational mixture in solvents with different abilities to nonspecific solvation. To solve this problem, we invoked NMR and IR spectroscopy.

Table 1. Solvatochromism of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert solvents

No.	Solvent	π^{*a}	ν_{max}, cm^{-1}
1	Hexane	–0.08	25650
2	Heptane	–0.02	25600
3	Cyclohexane	0.00	25500
4	Dodecane	0.08	25450
5	Carbon tetrachloride	0.28	25200
6	1-Butyl chloride	0.39	25000
7	1-Butyl bromide	0.48	24900
8	Chloroform	0.58	24750
9	Pentachloroethane	0.62	24600
10	1,2-Dibromomethane	0.75	24750
11	1,2-Dichloroethane	0.81	24750
12	Dichloromethane	0.82	24750
13	1,1,2,2-Tetrachloroethane	0.95	24300

[a] The Kamlet–Taft parameters were taken from [4, 5].

Rotational isomerism of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert media. As we showed in [1], the most suitable IR spectral range for studies on the rotational isomerism of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole is the range of NH stretching vibrations. The spectrum in the weakly polar chloroform (ε 4.7, π^* 0.58) shows a narrow single symmetric ν_{NH} band at 3433 cm^{-1}. This band belongs to one of the conformers most stable in chloroform: *sp,ac* or *sp,sc* [1]. A mixture of these conformers is also possible, since they are indistinguishable both by the IR and UV spectra. The other two conformers (*ap,ac* and *ac,sc*) cannot be observed in the IR spectrum. According to the calculations, they are less favored energetically. Moreover, since chloroform satisfies Eq. (2), the population of the *ap,ac* and *ac,sc* forms in this solvent is very low. To find out, whether one or two conformers are present in chloroform, we used NMR spectroscopy. The ^{1}H NMR spectrum of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in $CDCl_3$ revealed only one conformer [δ, ppm: 2.38 s (S–CH_3), 2.62 s (CH_3), 6.19 d (C^3H), 7.21 d (C^4H), 9.06 br.s (NH)]. In the NOESY spectrum we found a cross peak indicative of through-space coupling between the 3-H and 4-H atoms of the pyrrole ring. This result suggests that the most stable in $CDCl_3$ is the *sp,ac* conformer.

In going from chloroform to 1,1,2,2-tetrachloroethane (ε 8.2, π^* 0.95), dichloromethane (ε 8.9, π^* 0.82), and 1,2-dichloroethane (ε 10.9, π^* 0.81), the NH band (Fig. 2) shaply and systematically broadens and shifts red (Table 2). Moreover, it gets asymmetric, temperature-sensitive, and acquires a low- or a high-frequency shoulder (Fig. 3). Thus, the IR data point that there are several conformers in these solvents, which has close NH vibration bands. Attempted resolution of these bands by lowering the temperature failed. Therefore, we made use of deconvolution of the total contour into components (Table 2). One of them (high-frequency) was assigned to a mixture of the *sp,ac*, *sp,sc*, and *ap,ac* conformers which in solutions, according to theoretical speculations [1], have close ν_{NH} values. The low-frequency component is unambiguously assignable to the *ac,sc* conformer. One more experimental evidence for this assignment comes from the following results. The position and

Table 2. Dependence of characteristics of the NH vibration band on the polarity of inert solvent and temperature

Solvent	t, °C	ε^a	$\nu_{obs}^{(1)}$, cm^{-1}	$\nu^{(1)}$, cm^{-1}	$\Delta\nu_{1/2}^{(1)}$, cm^{-1}	$\nu_{obs}^{(2)}$, cm^{-1}	$\nu^{(2)}$, cm^{-1}	$\Delta\nu_{1/2}^{(2)}$, cm^{-1}
1,1,2,2-Tetrachloroethane	21	8.2	3430–3424	3432 ± 4	19 ± 2	3430–3424	3419 ± 3	33 ± 1
	–7		3424	3425 ± 3	21 ± 3	3416 sh	3418 ± 1	37 ± 1
	–17		3424	3420 ± 2	31 ± 4	3416	3416 ± 4	48 ± 17
Dichloromethane	21	8.9	~3420	3428 ± 1	26 ± 2	~3420	3408 ± 5	28 ± 1
	–19		3420 sh	3424 ± 2	28 ± 3	~3417	3405 ± 4	26 ± 1
	–53		3419 sh	3422 ± 1	26 ± 2	3408	3402 ± 3	26 ± 1
	–63		sh	3422 ± 2	27 ± 3	3408	3402 ± 3	26 ± 1
	–77		sh	3419 ± 4	53 ± 6	3408	3407 ± 1	31 ± 1
	–89	15.9	sh	3413 ± 2	44 ± 5	3406	3405 ± 4	27 ± 2
1,2-Dichloroethane	22	10.9	3410 sh	3414 ± 3	38 ± 4	3400	3390 ± 2	30 ± 1
	11		3420 sh	3417 ± 3	33 ± 4	3401	3391 ± 3	30 ± 1
	–3		3420 sh	3417 ± 3	34 ± 4	3393	3390 ± 2	29 ± 1

[a] Data of [6].

half-width of the low-frequency band ($\nu^{(2)}$) are solvent-dependent but temperature-independent (Table 2). The characteristics of the high-frequency band, by contrast, vary with solvent and temperature. Consequently, the high-frequency component is a superposition of closely located absorption bands of several conformers.

Thus, the results of independent experimental

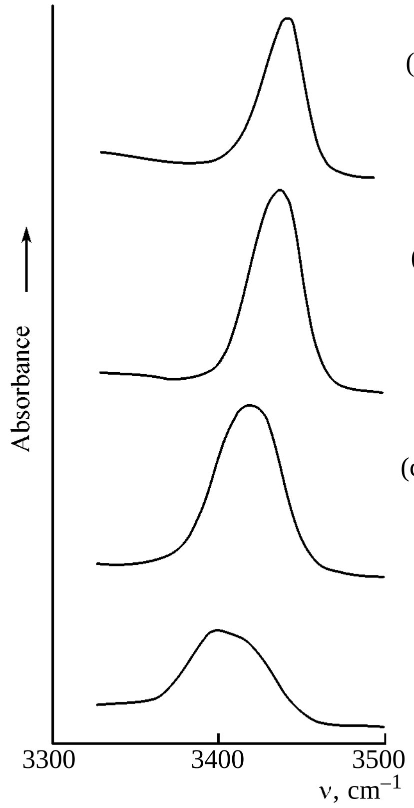

Fig. 2. Solvatochromism of the NH vibration frequency in the IR spectrum of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole. Solvent: (a) chloroform, (b) 1,1,2,2-tetrachloroethane, (c) dichloromethane, and (d) 1,2-dichloroethane.

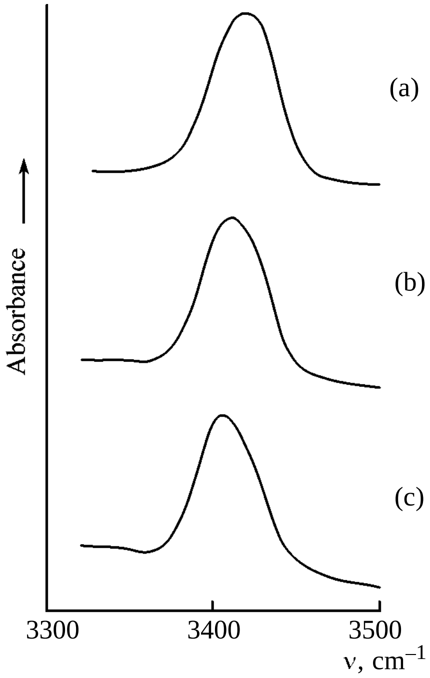

Fig. 3. Dependence of the shape and position of the NH vibration band in the IR spectrum of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in dichloromethane on temperature. Temperature, °C: (a) 22, (b) –53, and (c) –89°C.

methods (UV, NMR, and IR spectroscopy) show that in inert media there is a dynamic conformational equilibrium between all the possible conformers of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole, whose position is both solvent- and temperature-dependent. In media with $\pi^* \leq 0.65$, only the *sp,ac* isomer is stabilized. In higher polarity media ($\pi^* > 0.7$), an ensemble of the four conformers is present.

EXPERIMENTAL

The UV spectra of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole in aprotic inert solvents were measured on a Specord UV-Vis spectrophotometer at 22–25°C. The IR spectra in a series of inert media were obtained on a Specord IR-75 spectrophotometer. The ^{1}H NMR spectra were run on a Varian VXR-500S spectrometer (500 MHz); pulse 90°, relaxation delay 4 s, solvent $CDCl_3$. Two-dimensional ^{1}H NMR technique (NOESY) was also used.

2-(2,2-Dicyanocinyl-1-methylthio)-5-methylpyrrole. To a suspension of 0.59 g of malononitrile and 0.5 g of KOH in 30 ml of DMSO, stirred for 0.5 h at room temperature, we added 1 g of methyl 2-methylpyrrole-2-carbodithioate obtained by the procedure in [7]. The reaction mixture was heated for 1.5 h at 110°C, cooled to room temperature, and, after addition of 0.85 g of MeI, stirred for 2 h and then poured in acidified water (100 ml). The crystals that formed were filtered off, washed with water, and dried to obtain 0.7 g (59%) of 2-(2,2-dicyanovinyl-1-methylthio)-5-methylpyrrole, mp 138°C (from ethanol).

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