

Thermochemistry of substituted pyrroles

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The heats of solution of a series of substituted pyrroles in benzene, carbon tetrachloride, chloroform, DMF, and pyridine were measured by a calorimetric method at 298.15 K. The influence of substituents in the pyrrole molecule on the energy parameters of solvation by organic solvents is discussed.

Key words: solvation, thermochemistry, substituted pyrroles.

Pyrrole is a structural element of the porphyrins, which include the organic components of the prosthetic group of blood hemoglobin heme, the green pigment of leaves chlorophyll, and other compounds. The necessity of studying the solvation of porphyrins, as well as their constituent fragments, is obvious in view of the fact that practically all processes which involve porphyrins occur in liquid media.

In this work derivatives of pyrrole-2-carboxylic acid (**1–12**) were investigated. Trialkylpyrroles **14** and **15** were obtained by decarboxylating **1** and **2**, and aldehydes **16** and **17** were obtained by formylating them. The heats

of solution in benzene, chloroform, DMF, pyridine, and partially in carbon tetrachloride were measured for the compounds obtained (Table 1).

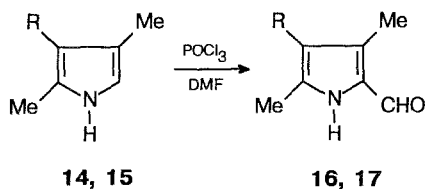
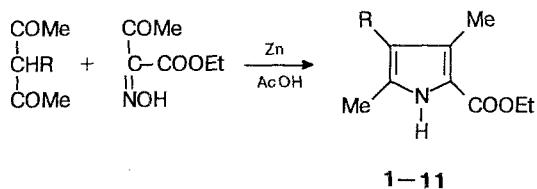
Experimental

Ethyl 3,4,5-trimethyl-2-pyrrolicarboxylate (1). To a solution of 198 mL (1.56 mol) of ethyl acetoacetate in 400 mL of acetic acid was gradually added a solution of 115.6 g (1.56 mol) of sodium nitrite in 250 mL of water with stirring, the temperature being kept below 40°C. The mixture was stirred for 1 h. The resulting solution of ethyl nitrosoacetoacetate was added with stirring and cooling to a solution of 178 g (1.56 mol) of 3-methyl-2,4-pentanedione in 600 mL of acetic acid with the simultaneous addition of 220 g of zinc dust (at a temperature below 90°C). The mixture was stirred on a boiling water bath for 1 h and poured into 6 L of water. Then it was held for 5 h, and the pyrrole obtained was filtered and dried. To separate the excess zinc dust, the product was dissolved in chloroform and filtered, the chloroform was distilled off, and the product was recrystallized from ethanol.

The following pyrroles were synthesized in a similar way:

Ethyl 3,5-dimethyl-4-ethyl-2-pyrrolicarboxylate (2) from 3-ethyl-2,4-pentanedione; **ethyl 3,5-dimethyl-4-propyl-2-pyrrolicarboxylate (3)** from 3-propyl-2,4-pentanedione; **ethyl 3,5-dimethyl-4-butyl-2-pyrrolicarboxylate (4)** from 3-butyl-2,4-pentanedione. Found (%): N, 6.28. $C_{13}H_{21}O_2$. Calculated (%): N, 6.27. **Ethyl 3,5-dimethyl-4-amyl-2-pyrrolicarboxylate (5)** from 3-pentyl-2,4-pentanedione; **ethyl 3,5-dimethyl-4-hexyl-2-pyrrolicarboxylate (6)** from 3-hexyl-2,4-pentanedione. Found (%): N, 5.60. $C_{15}H_{25}O_2$. Calculated (%): N, 5.57. **Ethyl 3,5-dimethyl-4-benzyl-2-pyrrolicarboxylate (7)** from 3-benzyl-2,4-pentanedione. Found (%): N, 5.42. $C_{16}H_{19}O_2$. Calculated (%): N, 5.44. **Ethyl 3,5-dimethyl-4-(2-methoxycarbonyl)ethyl-2-pyrrolicarboxylate (8)** from 3-(2-carbomethoxyethyl)-2,4-pentanedione; **ethyl 3,5-dimethyl-4-acetyl-2-pyrrolicarboxylate (9)** from acetylacetone; **diethyl 3,5-dimethyl-2,4-pyrroledicarboxylate (10)** from ethyl acetoacetate.

Ethyl 3,5-dimethyl-2-pyrrolicarboxylate (11). A solution of 50 g (0.209 mol) of diethyl 3,5-dimethyl-2,4-pyrroledicarboxylate in 100 mL of conc. H_2SO_4 was held at 40°C for 20 min and poured onto ice.¹ The precipitate was



R = H, Me, Et, Pr, Bu, C_5H_{11} , C_6H_{13} , CH_2Ph ,
COMe, COOEt, CH_2CH_2COOMe

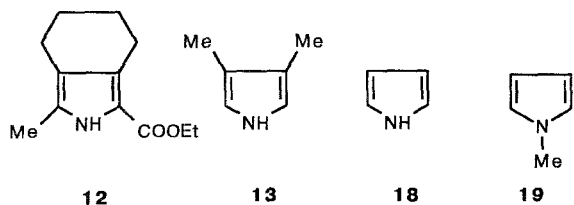


Table 1. Yields and some properties of substituted pyrroles

Compound	Yield (%)	Mp (°C) (literature data) or bp °C/p (Torr)	¹ H NMR spectrum, δ				
			NH	C(2)COOCH ₂ Me	C(3)—Me	C(4)—R	C(5)—Me
1	70	132(128 ¹)	9.00	4.16q; 1.18t	2.08	2.02 (Me)	1.75
2	60	96(95—96 ¹)	9.06	4.24q; 1.27t	2.21	2.31q; 0.97t (Et)	2.13
3	50	102(102 ¹)	9.00	4.25q; 1.27t	2.15	2.38t; 1.27m; 0.83t (Pr)	2.08
4	54	89	8.83	4.23q; 1.28t	2.20	2.28t; 1.28m; 0.95t (Bu)	2.13
5	45	73(71 ⁷)	9.83	4.10q; 1.23t	2.10	2.10m; 1.12m; 0.75t (S ₅ H ₁₁)	2.10
6	30	60	9.25	4.13q; 1.23t	2.13	2.27m; 1.23m; 0.83t (S ₆ H ₁₃)	2.13
7	47	127	9.83	4.19q; 1.23t	2.12	3.64s; 7.05s (SH ₂ Ph)	2.07
8	40	97(104 ¹)	9.67	4.13q 1.30t	2.17	2.50d; 2.33d; 3.50s (SH ₂ SH ₂ SOOMe)	2.17
9	50	143(143 ¹)	9.90	4.20q; 1.22t	2.50	2.35 (SOMe)	2.43
10	80	136(136 ¹)	10.07	4.17q; 1.27t	2.13	4.17q; 1.27t (SOOEt)	2.13
11	56 ^a , 50 ^b	123(125 ¹)	9.87	4.15q; 1.22t	2.17	5.62d (H)	2.11
12	33	107	9.50	4.10q; 1.30t	2.52m	2.28m 1.67m ^a	2.07
13	32	33(33 ¹) 65—66/14	7.17	6.18d ^b	1.88	1.88c	6.18d ^b
14	65	39(39 ¹) 71—72/11	7.08	1.98 ^c	1.83	1.77c	6.05s ^b
15	80	96—97/16	7.43	2.07 ^c	2.33m; 1.15t ^d	1.98s (Me)	6.10d ^b
16	73	146(147 ¹)	11.15	9.14s ^e	2.20	1.80s (Me)	2.13
17	75	106(105—106 ¹)	11.13	9.13s ^e	2.20	2.20m; 0.91t (Et)	2.15
18	50	130—132/760	7.62	6.50m ^b	6.13 ^b	6.13 ^b	6.50 ^b
19		120—121/760	3.37 ^c	6.30 ^b	5.88 ^a	5.88 ^a	6.30 ^b

^a (CH₂); ^b H; ^c Me; ^d Et; ^e CHO.

filtered, washed with water, and suspended in 1 L of water. The suspension was neutralized with 20 % NaOH to a weakly alkaline pH, and the precipitate was filtered off. The filtrate was acidified with dilute HCl (1:5), the precipitate of 2,4-dimethyl-5-ethoxycarbonyl-3-pyrrolecarboxylic acid was filtered, washed with water, and dried. The acid obtained was decarboxylated by heating at 230°C in an oil bath until the liberation of CO₂ ceased (about 2 h) and the product **11** was distilled in vacuum.

B. To a solution of 10.3 mL (0.1 mol) of acetylacetone in 30 mL of acetic acid and 10 mL of water was added a solution of 21.6 g (0.1 mol) of ethyl nitrosomalonate and sodium acetate (3:1) in 25 mL of acetic acid.² 25 g of zinc dust was gradually added with stirring and heating to 80°C. The mixture was further heated for 1 h in a boiling water bath and poured into 0.5 L of water. Then it was held overnight with cooling, the precipitate of product **11** was filtered, dried, and purified by recrystallization from ethanol. In a similar way **ethyl 5-methyl-3,4-tetramethylene-2-pyrrolecarboxylate (12)** was synthesized from 2-acetylcyclohexanone. Found (%): N, 6.78. C₁₂H₁₇O₂. Calculated (%): N, 6.76.

3,4-Dimethylpyrrole (13) was obtained according to the method in Ref.3.

2,3,4-Trimethylpyrrole (14). A mixture of 50 g (0.28 mol) of ethyl 3,4,5-trimethyl-2-pyrrolecarboxylate **1** with 50 g of KOH and 250 mL of ethylene glycol was boiled for 5 h with protection from air, cooled, diluted with water, and steam-distilled. The distillate was extracted with ether, the ether was evaporated, and the residue was distilled in vacuum.

2,4-Dimethyl-3-ethylpyrrole (15) was synthesized in a similar way from ethyl 3,5-dimethyl-4-ethyl-2-pyrrolecarboxylate **2** in the form of a colorless oil, which quickly darkened.

3,4,5-Trimethyl-2-pyrrolecarbaldehyde (16). To a solution of 10 g (0.052 mol) of 2,3,4-trimethylpyrrole in 75 mL of DMF was gradually added 12.5 mL of POCl₃ with stirring and cooling (the temperature was kept below 10°C). The mixture was stirred for 2 h at 20°C and poured into 300 mL of water. The aqueous solution was alkalized with 20 % NaOH under cooling, the precipitate of formylpyrrole **16** was filtered, washed with water, dried, and recrystallized from ethanol. **3,5-Dimethyl-4-ethyl-2-pyrrolecarbaldehyde (17)** was prepared in a similar way from **15**.

Unsubstituted pyrrole **18** was prepared according to a known procedure.⁴ 1-Methylpyrrole (**19**) from Fluka was distilled in vacuum. The yields and some properties of the pyrroles used are given in Table 1.

The ¹H NMR spectra of the compounds obtained were recorded with a Tesla BS-497 spectrometer in deuteriochloroform with hexamethyldisiloxane as an internal standard.

The solvents for the calorimetric experiments were prepared according to known procedures.⁵ Pyrroles with melting points lower than 50°C were freshly vacuum distilled, and the others were recrystallized from ethanol and dried in vacuum for 6 h at 50°C. Table 2 presents the experimental data obtained on a precision isothermal calorimeter⁶ at 298.15 K.

Results and Discussion

The heats of solution and solvation are related by the equation:

$$\Delta H_{\text{sol}} = \Delta H_{\text{solv}} + \Delta H_{\text{subl}}$$

where ΔH_{subl} is the heat of sublimation of the substance at a given temperature.

Table 2. Heats of solution (ΔH_{sol}) and transfer (ΔH_{trans}) of pyrroles (kJ mol^{-1})

Com- pound	Benzene ΔH_{sol}	Chloroform		DMF		Pyridine	
		ΔH_{sol}	$-\Delta H_{\text{trans}}$	ΔH_{sol}	$-\Delta H_{\text{trans}}$	ΔH_{sol}	$-\Delta H_{\text{trans}}$
1	29.4	17.5	11.9	16.9	12.5	15.7	13.7
2	31.2	20.3	10.9	19.3	11.9	19.1	13.1
3	31.8	21.8	10.0	22.6	9.2	20.3	11.5
4	37.5	25.2	12.3	26.3	11.2	23.6	13.9
5	31.0	20.5	10.5	21.2	9.8	19.7	11.3
6	42.1	30.8	11.3	33.4	8.7	28.4	13.7
7	33.3	23.8	9.5	23.8	9.5	19.6	13.7
8	32.9	18.5	14.4	17.3	15.6	20.2	12.7
9	37.7	21.6	16.1	23.9	13.8	28.8	16.9
10	42.9	26.9	16.0	27.3	15.6	25.9	17.0
11	33.9	24.5	9.4	22.2	11.7	20.6	13.3
12	29.5	18.2	11.3	18.5	11.0	14.9	14.6
13	5.6	-2.4	8.0	2.9	2.7	-	-
14	12.0	4.4	7.6	0.9	11.1	-	-
15	7.1	-1.8	8.9	-4.8	11.9	-4.7	11.8
16	27.8	15.5	12.3	17.6	10.2	14.6	13.2
17	31.3	15.8	15.5	18.4	12.9	-	-
18	4.3	0.8	3.5	-13.6	17.9	-8.9	13.2
19	0.8	-6.0	6.8	-0.8	1.6	-0.3	1.1

Note. The heats of solution were measured with an accuracy of $\pm 2.5\%$.

Since the heats of sublimation for pyrroles are unknown, it is useful to examine the heats of transfer ($\Delta H_{\text{trans}}^{\circ}$) from a standard solution to the solution under study, which reflect the differences in the solvating ability of solvents with respect to a given compound.⁸

$$\Delta H_{\text{trans}} = \Delta H_{\text{sol}(i)} - \Delta H_{\text{sol}(st)} = \Delta H_{\text{sol}(i)} - \Delta H_{\text{sol}(st)}$$

Benzene was chosen as the standard solvent, since it solvates pyrroles most weakly among all the solvents proposed (see Table 2).

Since the pyrrole molecule is an aromatic system, it is obvious that the following intermolecular interactions occur in the substance: interactions of π - π type, van der Waals interactions, and interactions due to hydrogen bonding. An increase in electron density in the heterocycle would probably lead to strengthening of the π - π interactions between the molecules, on the one hand, and to a decrease in the polarity of the N-H bond (an increase in basicity), on the other hand. At the same time the heats of solution of 1-methylpyrrole in benzene indicate that the replacement of the proton at the nitrogen atom by methyl results in a decrease in the energy of the intermolecular interactions (cf. ΔH_{sol} in benzene for **19** and **18**).

The transition from unsubstituted pyrrole **18** to the substituted pyrroles is accompanied by changes in the forces of intermolecular interactions and, as a consequence, changes are observed in the melting points (see Table 1). When pyrroles dissolve, solute-solvent and solvent-solvent interactions become active.

Let us consider the heats of solution of pyrroles in benzene in relation to the nature of the substituent. As can be seen from Table 2, compound **19** passes into

solution with the smallest energy expenditure. This attests to the low energy of the intermolecular interaction. In order to estimate the contribution of π - π interactions to the solvation of 1-methylpyrrole by benzene, we measured ΔH_{sol} in carbon tetrachloride ($\Delta H_{\text{sol}} = 1.27 \pm 0.02 \text{ kJ mol}^{-1}$). The heat of transfer is equal to 0.57 kJ mol^{-1} , i.e., the contribution of the π - π interactions to the solvation of 1-methylpyrrole is insignificant.

Upon passage from unsubstituted pyrrole **18** to the dimethyl and trimethyl-derivatives (**13,14**), the dissolution process becomes more endothermic, possibly due to enhancement of the π - π interactions, since a methyl group exhibits a $+I$ -effect. Introduction of an ethyl substituent instead of a methyl group into position 3 causes a decrease in the heat of solution in benzene from 12 to 7 kJ mol^{-1} , which may be correlated with the weakening of the crystal lattice in compound **15**.

Pyrrolecarboxaldehydes **16** and **17** dissolve with drastically increased endothermic effects. Introduction of a formyl group, which exhibits $-I$ and $-C$ induction effects, diminishes the electron density in the heterocycle, polarizes the N-H bond, and facilitates the formation of intermolecular H bonds in the crystal. Besides, the solvation of these pyrroles by benzene by means of π - π interactions decreases.

The variation of the heat of solution in compounds **1-12** can occur as a result of the variation of the substituent in position 4. Introduction of a carbethoxy group (compound **11**) deactivates the pyrrole ring through $-I$ and $-C$ effects somewhat more strongly than a formyl substituent does. The heats of solution in benzene increase monotonically for compounds **1-6**. This is probably attributable to the increase in the energy ex-

pended to form the cavity in benzene upon passage from CH_3 to C_6H_{13} , in spite of the fact that the crystal-lattice energy decreases along this series of pyrroles (Table 1). The benzyl substituent (compound **7**) exhibits a $-I$ effect, decreasing the π - π interactions of pyrrole rings, on the one hand, and increasing the π - π interactions of the benzene rings, on the other hand. As a whole, the energy characteristics of the dissolution and solvation of pyrrole with a benzyl substituent are similar to those of compound **11** without a substituent in position 4.

The $-I$ effect of the COCH_3 group and the presence of δ^- on the oxygen atom in acetylated pyrrole **9** favor the formation of an intermolecular H bond and strengthening of the crystal lattice (*cf.* melting points). As a result, the dissolution of compound **9** in benzene is a more endothermic process than that of **11**. The introduction of a second carboxy group in the pyrrole molecule (**10**) leads to further deactivation of the pyrrole ring and requires an additional energy expenditure to insert the substituent into the solvent. As a result, the heat of solution increases by almost 10 kJ mol^{-1} as compared with compound **11**.

The carbomethoxyethyl substituent in pyrrole **8** exhibits neither a $+I$ nor a $-I$ effect owing to the presence of an «insulator» in the form of a $-(\text{CH}_2)_2-$ fragment. Therefore, the heats of solution of compounds **8** and **11** in benzene are similar. Apparently, the energy expenditure for disrupting the solvent structure around this substituent and the energy gain due to the loosening of crystal lattice compensate each other. The heat of solution of compound **12** in benzene is almost equal to ΔH_{sol} of pyrrole **1** with CH_3 groups in positions 3 and 4. According to the melting points, the crystal lattice in **12** is more loosened than that in **1**; however, the energy expended to form a cavity in benzene is significantly greater.

Being a proton-donor solvent, chloroform can specifically solvate pyrroles by forming H bonds with electron-donor atoms. It is evident from Table 2 that ΔH_{trans} for the transfer of unsubstituted pyrrole **18** into chloroform is not large due to the universal solvent-solute interactions. The electron density on the nitrogen atom in 1-methylpyrrole **19** is considerably higher than in **1**. This promotes the solvation of **19** by chloroform by means of H-bond formation, the energy gain due to solvation being about 3 kJ mol^{-1} as compared with pyrrole **18**. The introduction of methyl and ethyl substituents into positions 2, 3, and 4 of compounds **13**–**15** results in an increase in electron density in the ring and facilitates solvation by means of H-bond formation.

The prerequisites for the preferential solvation of the CHO groups by chloroform are satisfied in **16** and **17**. In fact, if the heats of transfer of the compounds without CHO substituent (**14** and **15**) into chloroform are subtracted from those for their formyl analogs (**16** and **17**, respectively), a value of 4.7 kJ mol^{-1} , i.e., the contribution of the formyl group to the solvation of a pyrrole

molecule, is obtained in both cases.

Table 3 presents the heats of solvation of pyrroles **1**–**10** relative to compound **11**. An analysis of the values given in Table 3 reveals the strong influence of the nature of the substituent in position 4 on the heats of solvation of pyrroles. For example, variation of the length of alkyl substituent from C_1 to C_6 affects the solvation in chloroform, as well as in DMF and pyridine. As can be seen from Table 3, the even and odd alkyl residues are energetically inequivalent. This may be due to the different configurational packing of even and odd alkyl chains. A hexyl substituent markedly decreases the heat of solvation of the respective pyrrole in DMF, probably through an interaction with C(5)-Me. This is an example of «intramolecular solvation», under which a portion of the energy is already released before the compound enters the solvent. Hence, the values of ΔH_{trans} of pyrrole **6** are low in all solvents (Table 2).

The introduction of a benzyl substituent, as has already been discussed for benzene, does not influence the heat of solvation in the case of chloroform and pyridine. In DMF, solvation does not even compensate the energy expended to form a cavity in the solvent. The oxygen-containing substituents in compounds **8**–**10** interact with chloroform to form H bonds, the energy gain being 5 – 7 kJ mol^{-1} . The tetramethylene substituent in compound **12** acts on the pyrrole ring similarly to the two methyl substituents in **1**.

As a dipolar solvent, dimethylformamide solvates pyrroles by interacting with positive charge carriers. Specifically, the interaction with the polarized N—H bond in unsubstituted pyrrole **18** is rather strong (about 18 kJ mol^{-1}). The introduction of the methyl group at the nitrogen atom in pyrrole **19** results in the absence of specific solvation by DMF ($\Delta H_{\text{trans}} = -1.6 \text{ kJ mol}^{-1}$). The same effect is observed in pyridine. The solvation

Table 3. Influence of the nature of the substituent on the relative heat of solvation (kJ mol^{-1})

Compound	Substituent R in position 4	$\Delta(\Delta H) = \Delta H_{\text{trans}(i)} - \Delta H_{\text{trans}(11)}$		
		Chloroform	DMF	Pyridine
1	Me	-2.5	-0.8	-0.4
2	Et	-1.5	-0.2	0.2
3	Pr	-0.6	2.5	1.8
4	Bu	-2.9	0.5	-0.6
5	C_5H_{11}	-1.1	1.9	2.0
6	C_6H_{13}	-1.9	3.0	-0.4
7	CH_2Ph	-0.1	2.2	-0.4
8	$(\text{CH}_2)_2\text{COOMe}$	-5.0	-3.9	0.6
9	COMe	-6.7	-2.1	-3.6
10	COOEt	-6.6	-3.9	-3.7

Note. $\Delta H_{\text{trans}(i)}$, heat of transfer of substituted pyrrole into the solvent. $\Delta H_{\text{trans}(11)}$, heat of transfer of **11** into the same solvent.

centers in pyridine are the lone pair at the nitrogen atom and the π system of the heterocycle.

Thus, the solvation of substituted pyrroles is determined by the nature of the solvent and the nature of the substituent in the aromatic ring.

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Synthesis and reactivity of metal-containing monomers 28*. Low-temperature radical polymerization of zinc, barium, magnesium, and lead acrylates under the action of organocobalt initiators**

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The polymerization of diacrylates of the nontransition metals Mg, Zn, Ba, and Pb, which proceeds at low temperatures (5–10°C) with the complexes of alkylcobalts with tridentate Schiff bases (RCo) as initiators, was studied. The radical mechanism of the process was proved with the aid of free radical scavengers. The polymerization kinetics is given by the equation $W_p = k [M] \cdot [RCo]^{0.75}$. The influence of the nature of the metal in the monomer and the alkyl ligand in the initiator on the polymerization process was discussed. Low temperatures promote the formation of polymers with high molecular weights and a predominantly syndiotactic structure. The effect of the steric hindrances arising during polymerization due to the formation of a three-dimensional cross-linked structure in the metal-containing polymer on the microstructure of polymer chain and on polymerization kinetics was considered.

Key words: metal-containing monomers, organocobalt initiator, low temperature polymerization, acrylates of nontransition metals.

The polymerization of metal-containing monomers (MCM's) is an effective one-step method for synthesizing polymers, in which each repeating unit contains one equivalent of the metal. The reactivity of MCM varies

greatly and covers the range from monomers which polymerize even during their synthesis or separation to those which are incapable of polymerization even under extremely severe conditions.

Special interest has been stimulated by the polymerization of MCM's at low temperatures, which generally permits suppression of the side processes and increases the molecular weight and stereoregularity of the polymers

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