Synthesis and IR spectra of 5-phenyl-2-(1-phenyl-2-trichloroacetylethenyl)pyrrole

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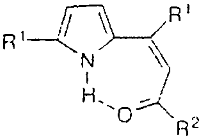
5-Phenyl-2-(1-phenyl-2-trichloroacetylethenyl)pyrrole was synthesized by the reaction of 2-phenylpyrrole with 1-phenyl-2-trichloroacetylacetylene on silicon oxide. The structure of an intramolecular proton-transfer H-complex was assigned to the title compound based on analysis of its IR spectra in solutions in the temperature range of 165—298 K.

Key words: 2-(2-acylethenyl)-5-phenylpyrroles, proton transfer, intramolecular H-complex, IR spectra.

Under particular conditions, the reactions of 2-phenylpyrrole with 2-acyl-1-phenylacetylenes afforded 2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles (**1a—c**)[1]:

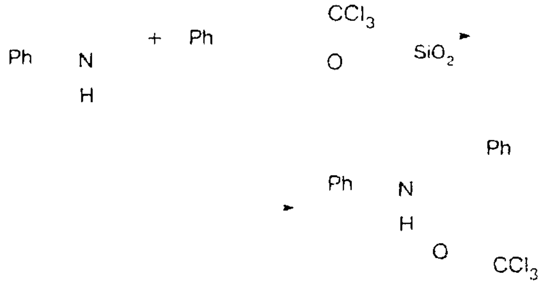


1a—c, **2a,b**

1a—c: $R^1 = R^2$ = Ph (**a**);
R^1 = Ph, R^2 = 2-thienyl (**b**), 2-furyl (**c**)
2a,b: R^1 = H; R^2 = Ph (**a**), 2-thienyl (**b**)

According to the results of ^{1}H NMR spectroscopy, these compounds exist exclusively as *Z* isomers in which the mutual arrangement of the carbonyl fragment and the olefin C=C bond corresponds to the *s-cis* conformation. Based on the large chemical shifts of the N—H protons (δ 14.7—14.8), it has been suggested[1] that the compounds have an intramolecular N—H...O=C bond. However, the IR spectra of both solid samples and solutions (CCl_4) of these compounds have no N—H stretching absorption bands in the region of 3150—3400 cm^{-1}. At the same time, the IR spectra of solutions of the *Z* isomers of 2-(2-benzoylethenyl)pyrroles (**2a,b**), which are structurally similar to compounds **1a—c**, have a broad ν_{NH} band at 3150—3180 cm^{-1}, which can be assigned to an intramolecular hydrogen bond. In addition, the signals for the NH protons in the ^{1}H NMR spectra of compounds **2a,b** are shifted downfield to a substantially lesser extent (δ 12.00—12.33).[2]

In the present work, we synthesized 5-phenyl-2-(1-phenyl-2-trichloroacetylethenyl)pyrrole (**3**) by the reaction of 2-phenylpyrrole with 1-phenyl-2-trichloroacetylacethylene. The reaction was carried out on silicon oxide. Unlike the reaction reported previously,[1] the reaction under consideration readily proceeded at room temperature.



3

With the aim of elucidating whether molecule **3** is analogous in structure to phenylpyrroles **1a—c** studied previously[1] and revealing the region of NH stretching vibrations for this type of molecules, we analyzed the IR spectra of compound **3**. It is known[3] that the IR spectra of compounds with H bonds recorded at nearly room temperatures do not necessarily show νNH and νOH bands due to their large width.[3] In addition, the corresponding bands can be substantially shifted to the low-frequency region depending on the strength of this bond. In this connection, the νNH absorption bands in the IR spectra of compound **3** were searched for in the region of 2200—4000 cm^{-1} both in the case of its solid samples and solutions, the temperature being varied in the range of 165—298 K.

The IR spectrum of a solid sample of compound **3** (a thin film precipitated from a solution in CH_2Cl_2) has a medium intensity stretching absorption band of the C=O group with the maximum at 1650 cm^{-1}, *i.e.*, the vibration frequency of this group is substantially lower than those in the case of chlorine-containing aromatic ketones

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(1700—1720 cm^{-1}).[4] The observed shift (Δν ~60 cm^{-1}) is an order of magnitude larger than the shifts observed upon formation of normal H-complexes of aldehydes or ketones with phenol (Δν ~3—10 cm^{-1}).[4] The νC=C vibration of the olefin group of the molecule is manifested as an intense absorption band with an unresolved structure at 1500 cm^{-1}. The intensity ratio of these two bands and the νC=O frequency are characteristic of molecular systems containing the *s-cis*-O=C—C=C fragment and an intramolecular hydrogen bond.[5]

It should be emphasized that the spectral characteristics of phenylpyrrole **3** are typical of this type of compounds. Thus, the spectrum of solid phenylpyrrole **1a** has the νC=O absorption band at 1615 cm^{-1}, which is 30 cm^{-1} lower than that in the spectrum of its analog without an H bond, *viz.*, of 2-(2-benzoyl-1-phenylethenyl)-1-ethyl-5-phenylpyrrole (**4**) (νC=O, 1645 cm^{-1}). However, the spectrum of compound **4** is characterized by the inverse ratio between the intensities of the absorption bands of the carbonyl (strong band) and olefin (medium band) groups, which is indicative of the *s-trans* conformation of the molecule, *i.e.*, this compound cannot be used as a model. In the spectrum of benzylideneacetophenone PhCH=CHC(O)Ph with the *s-cis* arrangement of the above-mentioned groups, the νC=O frequency reaches 1668 cm^{-1}.[6] The νC=O value in the spectrum of compound **1a** is 53 cm^{-1} lower than that in the spectrum of the above-mentioned isostructural analog.

The conclusions about the *Z*-isomeric form of compound **3**, the *s-cis* orientation of its carbonyl and olefin fragments, and the presence of an intramolecular H bond were also confirmed by analysis of the ^{1}H NMR spectra (see the Experimental section). The chemical shifts for the compound under study are virtually identical to those observed previously[1] for phenylpyrroles **1a—c**. In the IR spectra of compound **3**, the stretching absorption band of the associated NH group in the region of 3150—3400 cm^{-1} is also absent.

Detailed analysis of the IR spectrum of solid product **3** demonstrated that it is characterized by a substantial broadening of the weak absorption band in the region of νCH stretching vibrations of the phenyl rings with the center at 3065 cm^{-1} (Fig. 1, *a*). This fact suggests that the band overlaps with a broad absorption band caused by the νNH vibration. Such large low-frequency shifts are generally observed in proton-transfer H-complexes.[7] The integral intensities of these bands increase as the temperature decreases.[7] In this connection, we examined the IR spectrum of a solution of compound **3** in CS_2 containing 2 vol.% of $(CD_3)_2CO$ in the range from room temperature to the melting point of the binary solvent system. The presence of a small amount of more polar acetone-d$_6$ was used to prevent precipitation from the solution at low temperature. The spectrum of the solution under study has a low intensity band with a half-width of 230 cm^{-1} and the maximum at ~3100 cm^{-1} even at room temperature (Fig. 1, *b*). The precise position of the maximum is difficult to determine due to superposition of the νCH stretching vibration bands of the aromatic substituents (νCH = 3030, 3060, and 3075 cm^{-1}). The intensity of the broad band increases as the sample is cooled and it is most pronounced at 165 K (Fig. 1, *c*). In this case, the half-width of the band is 550 cm^{-1} and the maximum (at 3100 cm^{-1}) is clearly visible. The temperature changes are completely reversible. The position of the observed absorption band, the temperature dependence of its intensity, and the shape typical of charged molecules indicate that an intramolecular proton-transfer H-complex is present in solutions at low temperatures. Apparently, the large half-width of the band observed in the region characteristic of NH$^-$ and OH$^-$ stretching vibration frequencies is associated with a high amplitude of proton motion. The particular shape of this band calls for further theoretical investigation. Under the same conditions, the absorption band with the maximum at 3000 cm^{-1} is also clearly observed in the spectrum of compound **1a**. The frequencies and intensities of the absorption bands of the carbonyl groups in the spectra of the corresponding solutions of compounds **3** and **1a** remain virtually unchanged as the temperature decreases.

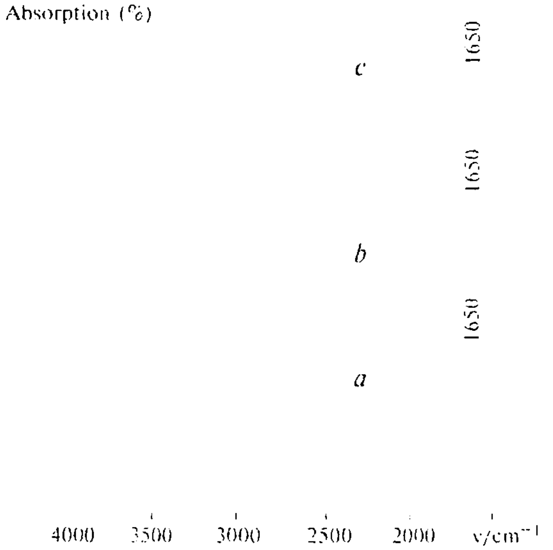

Fig. 1. IR spectra of 5-phenyl-2-(1-phenyl-2-trichloroacetylethenyl)pyrrole (**3**) as a solid sample (a film precipitated from a solution in CH_2Cl_2) (*a*) and a solution in CS_2 containing 2 vol.% of $(CD_3)_2CO$ at 298 K (*b*) and 165 K (*c*).

Experimental

The IR spectra of solid compound **3** and its solution in CS_2 containing 2% of $(CD_3)_2CO$ were measured on a Specord 75 IR spectrophotometer in the temperature range of 165—298 K. The ^{1}H NMR spectra were recorded on a Bruker DPX 250 instrument (250.13 MHz) in $CDCl_3$ with HMDS as the internal standard. 2-Phenylpyrrole was prepared according to the

Trofimov reaction[8] and purified by sublimation *in vacuo*, m.p. 129 °C.

5-Phenyl-2-(1-phenyl-2-trichloroacetylethenyl)pyrrole (3). 2-Phenylpyrrole (0.286 g, 2 mmol) and 1-phenyl-2-(trichloroacetyl)acetylene (0.495 g, 2 mmol) were triturated with silicon dioxide (100/160μ, 4 g) for 1 min. The reaction mixture was kept with periodic stirring at 20—25 °C for 1.5 h and then extracted with hexane. After removal of the hexane, the resinous residue was washed with ethanol. The bright-red precipitate of compound **3** that formed was isolated in a yield of 0.288 g (36.9%), m.p. 153—154 °C. ^{1}H NMR, δ: 6.50 and 6.77 (both dd, 1 H each, H(3) and H(4) of the pyrrole ring, $^3J_{H(3)-H(4)}$ = 4.3 Hz, $^4J_{H(3,4)-NH}$ = 2.4 Hz); 6.54 (s, 1 H, CH=); 7.31 (m, 1 H, *p*-H 5-Ph); 7.41—7.53 (m, 7 H, 1-Ph and 2 *m*-H 5-Ph); 7.80 (m, 2 H, 2 *o*-H 5-Ph); 13.74 (br.s, 1 H, N—H). Found (%): C, 62.03; H, 3.37; N, 3.44; Cl, 27.78. $C_{20}H_{14}Cl_3NO$. Calculated (%): C, 61.48; H, 3.61; N, 3.59; Cl, 27.22.

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