simple molecular orbital calculations. The aforementioned uncertainty in the applicability of previous quantum chemical calculations for A and S and especially for BA makes the definite assignment of these transitions to specific states tenuous at best. Moreover, differences in molecular symmetry between the free molecule (C_1) and those found in the two crystal structures (triclinic, site symmetry C_i; orthorhombic, site symmetry C_2) complicates this matter even further. Nevertheless, a good model for these systems should be capable of accounting for variations in electronic structure and spectra as a function of conformation and further studies of the type presented here should provide hard tests for theory.

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Proton Exchange and Temperature Studies of Pyrazole in Dimethyl-d_6 Sulfoxide by ^{13}C NMR

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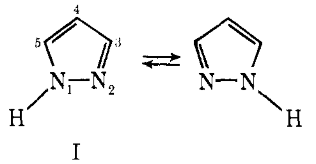
Abstract: The ^{13}C NMR shifts of all the carbons in pyrazole have been observed at room temperature. This paper reports the kinetic data available from the temperature-induced collapse of the C-3, C-5 NMR peaks. $\Delta G^{\ddagger} \simeq 14.8$ kcal/mol, $\Delta H^{\ddagger} \simeq 7.0$ kcal/mol, and $\Delta S^{\ddagger} \simeq -25.0$ cal/deg for the virtual tautomerism of pyrazole in Me_2SO-d_6. Temperature-induced ^{13}C shifts for the solvent and for pyrazole were also determined to be $+1.47 \times 10^{-3}$ and $+2.0 \times 10^{-3}$ ppm/deg for C-4 and the center of the C-3, C-5 peaks, respectively. The solvent shift for ^{13}C with temperature is $+11.59 \pm 10^{-3}$ ppm/deg for the CD_3 in Me_2SO-d_6 and $+3.22 \times 10^{-3}$ ppm/deg for the deuterium in Me_2SO-d_6. Rapid exchange of pyrazole observed earlier by several workers in the solvent Me_2SO-d_6 is attributed to acid impurities present in previous samples.

Chenon et al.[1] have studied the tautomerism of pyrazole in a variety of solvents including Me_2SO. Earlier, Saito et al.[2] observed the ^{14}N shifts of pyrazole in several solvents including Me_2SO. Elguero et al.[3] have also studied the tautomerism of a wide variety of compounds by the use of ^{13}C NMR methods. In each of these studies, such rapid proton exchange existed in Me_2SO that only an averaged resonance for C-3 and C-5 or N-1 and N-2 was observed even at 6 °C.[1] Only by a change of solvent to HMPT[1] was the slow-exchange spectrum observed at −17 and 33 °C where the peaks were broader, though still separated.

During experiments carried out independently of the above, ^{13}C NMR spectra of pyrazole in Me_2SO-d_6 were observed. At ambient probe temperature (29 °C), it was clearly seen that separate C-3 and C-5 resonances were visible. The present paper reports the results of a temperature study of the virtual equilibrium of I with its tautomer.



I

Results and Discussion

The ^{13}C NMR shifts of I dissolved in Me_2SO-d_6 are given in Table I.

It is apparent from the data presented that the proton exchange in pyrazole is slow on the NMR time scale and that the C-3 and C-5 peaks do not coalesce until the temperature is raised to 337 K (64 °C). The C-3 and C-5 assignments are made based on the work of Chenon et al.[1] As the temperature is increased from 283 to 337 K, the two peaks broaden and move closer together. Above 337 K, the single averaged peak narrows until at 355 K the width is 180 Hz. It is significant, in the light of previous work,[1] that the separation of the C-3 and C-5 peaks remains relatively constant at 10.3 ppm until the temperature is above 302 K (the ambient probe temperature). The peak separation noted by Chenon et al.[1] was 10.5 ppm in HMPT at −17 °C. This must be the actual separation of the two resonance positions for the slow exchange region of pyrazole.

Using gated decoupling, the coupling constants for C-4 were found to be $J_{CH} = 175.1_2$, $J_{CCH} = 10.1_1$ Hz; for C-3, $J_{CH} = 185.9_0$ Hz; and for C-5, $J_{CH} = 186.0_9$ Hz.

By utilizing the standard equations for exchange-broadened NMR lines,[4] one can calculate the data given in Table II.

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Table I. ^{13}C NMR Data Obtained for Pyrazole in Me_2SO-d_6

T, K	^{13}C chemical shift, ppm[b] C-5	C-3	C-4	averaged position C-3, C-5	C-3, C-5 line width,[a] Hz	C-3, C-5 separation, ppm
283	88.9	99.3	65.15	94.1	42.0	10.4
291	88.6	99.0	65.08	93.8	49.2	10.4
293	88.8	99.0	64.98	93.9	57.6	10.2
295	88.8	99.0	65.06	93.9	55.2	10.2
302	88.6	99.0	64.92	93.8	59.8	10.4
318	89.5	98.0	64.78	93.7	112.8	8.5
320	89.4	97.8	64.78	93.6	120.0	8.3
326	89.8	97.6	64.70	93.7	121.0	7.8
329	91.1	96.3	64.61	93.7	186.0	5.2
330	91.3	95.1	64.62	93.2	189.0	3.8
337	93.2		64.60	93.2	279.6	
355	93.7		64.43	93.7	180.0	

[a] Average line width at half height of the C-3 and C-5 peaks, ±1.5 Hz. [b] Chemical shift in parts per million relative to internal Me_2SO-d_6. Positive values are downfield shifts.

Table II. Kinetic Data for Pyrazole

T, K	$\tau \times 10^3$[a]	ln k
283	4.823	4.64
291	3.959	4.84
293	3.275	5.03
295	3.445	4.98
302	3.136	5.07
318	1.533	5.79
320	1.434	5.85
326	1.421	5.86
329	0.899	6.32
330	0.884	6.34
337	0.805	6.43

[a] Corrected for the "natural line width" as suggested[4] by using the line width of the C-4 peak.

Table III. ^{13}C NMR Shifts for Pyrazole in Various Solvents at 29 °C

sample	C-3	C-5	C-4	$\Delta\delta$, ppm
pyrazole in Me_2SO-d_6	88.6	99.0	64.92	10.4
pyrazole in Me_2SO-d_6 + 1.6 mol % H_2O	90.6	97.0	64.92	6.4
pyrazole in Me_2SO-d_6 + 1.6 mol % H_2O + 0.01 mL concd HCl	93.7		64.92	
pyrazole in acetone	90.8		61.90	

Plotting ln k vs. $1/T$ gives a linear plot which has a slope of $-3200°$ from which one can calculate $\Delta H^{\ddagger} \simeq -7.0$ kcal/mol (average) over the 80 °C temperature range studied. The value of $\Delta G^{\ddagger}$ obtained is 14.8 kcal/mol, which compares well with the value obtained earlier[1] for pyrazole in the solvent HMPT. These values result in a calculated $\Delta S^{\ddagger} \simeq -25.0$ cal/deg.

Further results obtained from the temperature data in Table I are the temperature shifts for the C-4 peak and the average resonance position of C-3 and C-5. Because of the breadth of the C-3 and C-5 peaks, these data are quite scattered. The C-4 peak is, however, quite sharp and a plot of peak position vs. temperature gives a linear plot with slope $-0.010\,125$ ppm/deg relative to Me_2SO-d_6. Because previously measured[5] temperature effects for ^{13}C have shown a positive linear character, the shift of Me_2SO-d_6 with temperature would be expected to have a slope greater than $+0.01$ ppm/deg. This appears to be reasonable because of the recorded values[5] for temperature shifts of methyl group carbons in a variety of compounds. Measuring the ^{13}C temperature shift of Me_2SO-d_6 by using a 90–10 (% by volume) mixture of Me_2SO-d_6 and benzene and comparing to the literature value for benzene[5] gave the true slope for Me_2SO-d_6 of $+11.59 \times 10^{-3}$ ppm/deg. This, in turn, means that the true value for C-4 in pyrazole is $+1.47 \times 10^{-3}$ ppm/deg. This value is quite small for a nitrogen heterocycle assuming that pyridine is normal.[5] The slope for the averaged peak, C-3, C-5, is $+2.0 \times 10^{-3}$ ppm/deg. This number is not as precise as the C-4 slope and all that can be said is that it appears to be larger than the C-4 value. The decrease in the effect of temperature on the carbon chemical shift as the distance from the nitrogen increases matches the trend found for the carbons in pyridine.[5] (Incidentally, the temperature shift of deuterium in Me_2SO-d_6 is found to be $+3.22 \times 10^{-3}$ ppm/deg.)

Finally, even when confronted with the evidence of slow proton exchange on the NMR time scale in these experiments, one cannot ignore the previous observations which have been made. As a quick test, a small amount of distilled water was added to a sample for which slow exchange had been observed and which had been warmed to the point of coalescence of the C-3 and C-5 peaks and beyond. After cooling (and reconfirmation of slow exchange), water was added to the extent of 0.01 mL to a 3-mL Me_2SO-d_6 sample (1.6 mol %). The data in Table III were obtained. Further, an introduction of 0.01 mL of concentrated HCl caused averaging of the C-3 and C-5 broad lines into a single, very sharp line with a height twice as great as the C-4 line. Dissolving pyrazole in acetone gave only an average C-3 and C-5 line as well as the C-4 peak. Thus, the introduction of significant amounts of water causes only a slight increase of the rate of proton exchange as indicated by the broadening of the C-3 and C-5 lines and the decrease in the separation of these lines. The addition of acid caused very rapid exchange.

Actually, similar results have been observed previously in a different, though similar, system.[6] In that case, H_2O was dissolved in liquid ammonia and the ^1H NMR spectrum observed. Concentrations of H_2O in ammonia as high as 50 mol % could be tolerated without losing the separate NH_3 and H_2O resonances and more than 24 mol % H_2O was required before the ^{14}N–H coupling was obscured due to exchange. The smallest trace of NH_4^+ (acid) produced complete averaging, however. Without knowing anything further about the previous work,[1-3] it must be concluded that impurities of some kind were present in those samples and it is suggested that those impurities were acidic.

Experimental Section

Pyrazole was supplied by Professor E. P. Papadopoulos of the Chemistry Department, University of New Mexico, Albuquerque, N. Mex. This material was not purified any further nor treated in any special way. Me_2SO-d_6 was supplied as Economy Grade by Bio-Rad Laboratories and not further treated. The samples of pyrazole were prepared by dissolving about 150 mg of pyrazole in 3 mL of Me_2SO-d_6 and sealing (freeze–thaw) in a 10-mm Pyrex test tube sealed to a length of 5-mm glass tubing. This sample tube was then placed inside a normal thin-walled 12-mm Pyrex NMR sample tube for use in the NMR.

Spectra were obtained using a Varian XL-100 NMR spectrometer fitted with a Nicolet TT-100 pulse system. Temperatures were maintained with a Varian Variable Temperature Controller and the temperatures were measured directly by replacing the sample with a mercury thermometer placed in a sample tube containing a small amount of H_2O for thermal contact.

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Solid-State Spectroelectrochemistry of Cross-Linked Donor Bound Polymer Films[1]

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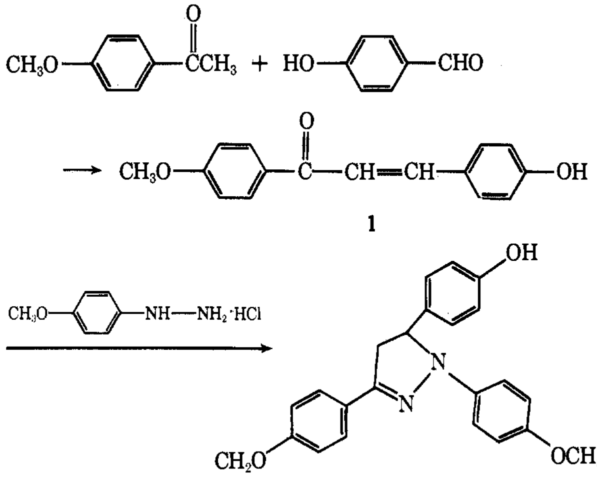
Abstract: A new electroactive material has been prepared by attaching the potassium salt of 1,3-di(*p*-methoxyphenyl)-5-(*p*-hydroxyphenyl)-Δ^2-pyrazoline to cross-linked chloromethylated polystyrene resins. The polymer can be readily coated from benzene suspensions onto metallic electrodes. At these modified electrodes, electrochemical charge transfer reactions are accompanied by large optical changes as pyrazoline cations are formed through the film bulk. Studies of the electrochemical and optical changes as a function of sweep rate and time indicate that electrons are transferred between monomeric pyrazoline species, and that the polymer matrix is characterized by a considerable degree of donor site flexibility.

Introduction

Recently the surface modification of electrode properties has attracted considerable attention. Most work has centered on the covalent binding of electroactive molecules to electrode surfaces,[2] a method which requires chemical pretreatment of the electrode surface and the use of special analytical techniques to characterize the small amounts (monolayer coverage or less) of material involved. In an alternate approach, films of electroactive polymers[3,4] have been physically adsorbed onto untreated electrode surfaces with the subsequent observation of electrochemical charge transfer. So far these polymeric films[3,4] have been kept *thin* (200 Å or less) to ensure efficient electronic and (charge compensating) ionic transport through the films. However, in this communication we describe a new class of electroactive donor materials based on porous, cross-linked polymer resins which provide a new means of modifying the electrochemical properties of electrodes. Since these materials are porous and can be readily coated onto substrates to form relatively thick films, the electrochemical charge-transfer processes are accompanied by easily detectable optical changes which are used to provide information on the mechanism of electron transport through these films.

Results

The electroactive material was prepared by attaching a suitably functionalized organic π donor of the triaryl Δ^2-pyrazoline class to a cross-linked polymer resin. The pyrazoline π donor was chosen because of its known ability[5] to be reversibly oxidized to stable, colored radical cations. The pyrazoline selected for attachment to the polymer resin was prepared[6] in two steps involving initial aldol condensation of *p*-methoxyacetophenone with *p*-hydroxybenzaldehyde to give a 4-hydroxy-4′-methoxychalcone (**1**). The chalcone is then reacted with *p*-methoxyphenylhydrazine hydrochloride to yield 1,3-di (*p*-methoxyphenyl)-5-(*p*-hydroxyphenyl)-Δ^2-pyrazoline (**2**) (see eq 1). The potassium salt of pyrazoline **2** was coupled to S-X1 chloromethylated polystyrene resin (5.4 mequiv/g, 1% cross-linked)[7] in refluxing dioxane–ethanol (4:1) under N_2. After reaction, about 85% of the chloromethylated sites were reacted[8] (i.e., 72% of the phenyl groups of the polystyrene resin have been coupled to pyrazoline). Spectroscopic measurements (IR and UV–vis: KBr) gave absorptions which were identical with those of the starting pyrazoline (**2**). In the IR, no alcohol absorption of monomer **2** was seen indicating that all of the donor pyrazoline was covalently bound to the polymer chain, and not present as the unreacted monomer.



(1)

Although this functionalized polymer is insoluble in common organic solvents by virtue of the internal cross-links present, it was discovered that films of the material could be cast onto a variety of substrates from a suspension in a swelling solvent such as benzene. The films were heterogeneous in character owing to the particulate nature of the polymer, porous, with a high surface area as observed by scanning electron microscopy, and with an average thickness[9] of 5–10 μ. When films of the pyrazoline copolymer coated onto Pt electrodes were examined for electrochemical response via cyclic voltamme-

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