Conformational Influences on Electronic Spectra and Structure. Polymorphs of *N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline

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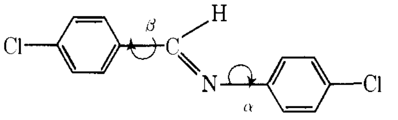
Abstract: *Conformational polymorphism,* in which a molecule adopts significantly different conformations in different crystal polymorphs, is exhibited by *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (**1**). Conformations observed in the two solids also differ somewhat from the most likely one in solution. Normal incidence reflection spectra and Kramers–Kronig transforms are reported for both crystal forms. Differences in electronic structure due to variations in conformation are manifested in the spectra and provide direct evidence for conformational influences on electronic structure and spectra. Bands in the Kramers–Kronig derived absorption spectra show a very good correspondence with the π electronic energy levels for nonplanar benzylideneaniline (BA) and a planar analogue as determined by previously reported photoelectron spectra.

Introduction

One fundamental question pertaining to conformationally flexible systems is, "How do the electronic structure and spectra change as a function of conformation?" The chemical literature provides very few examples of well-defined chemical systems wherein the molecular structure is known precisely for a number of different conformational arrangements and the consequent variations in electronic and spectral properties are measured and compared.

By utilizing a wide variety of physical techniques, many studies have been reported in the recent literature wherein solution and solid-state conformations have been investigated and compared, and in a number of cases significant differences have been found.[2a,b]

A less widely recognized phenomenon is that of conformational polymorphism, in which a flexible molecule crystallizes and assumes a different conformation in each of at least two distinct crystal structures. A previous paper[2c] described a methodology for utilizing this phenomenon to investigate the nature of crystal forces influencing molecular conformation for the dimorphs of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (**1**), in which the molecule adopts significantly different conformations in the two observed crystal structures. The observed high-energy planar conformation was shown to be stabilized by the triclinic lattice while in the orthorhombic form the two exocyclic angles, (α,β), adopt normal values of ±24.8°.



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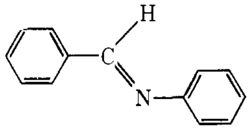
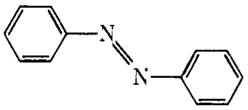
Of interest in this BA system is its apparently anomalous solution spectral properties compared to its isoelectronic analogue *trans*-azobenzene (AB) and *trans*-stilbene (S). The latter molecules are essentially planar (average rotation of ring 4°) in the solid[3] and nearly so (rotation ~30°) in the gas phase[4] and are assumed to be such in solution. There is overwhelming evidence that BA spectral differences arise from severe nonplanarity in solution.[5] BA is nonplanar in the solid and gas phase[6] and the close correspondence between the diffuse reflectance spectrum and solution spectrum of BA[7] supports this conclusion. The solution spectrum of **1** varies little from that of BA,[8,9] indicating that **1** is nonplanar in solution and that the chlorine substituents do not significantly perturb the electronic spectrum from that of benzylideneaniline. Hence the measurement of polarized crystal spectra for the two **1** forms, where the molecular conformations differ, provides a direct determination of the conformation–electronic structure relationship. A preliminary solid-state spectroscopic study on the triclinic form has been reported earlier.[10] This paper presents the results of a complete study on both polymorphs.



BA



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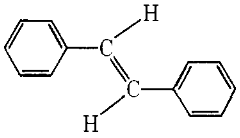

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Experimental Section

Synthesis of **1** and preparation of single crystals of the two polymorphs have been described previously.[8] The solution spectra for BA, A, and S were taken from Haselbach and Heilbronner.[9] That of **1** in cyclohexane was measured on a Cary 14 spectrophotometer. They are all shown in Figure 1.

Crystal faces were identified in the course of the full X-ray structure determinations and verified by optical goniometry in this spectroscopic study. The projection of the structure on the (001) face (Figure 2) is favorable for these polarized spectral measurements, since one extinction direction (I_{max}) is dominated almost exclusively by in-plane molecular transitions, while the second (I_{min}) gives essentially a measure of out of plane transitions.

The orthorhombic case is somewhat more complex owing to the translational inequivalency of the molecules comprising the contents of the unit cell. None of the crystal faces exhibited has projections as favorable as that given for the triclinic structure. Projections on the (010) and (110) faces studied here are given in Figure 3.

Experimental techniques for determining polarized single crystal reflection spectra are given elsewhere.[11] The spectra are shown in Figures 4 and 5. The polarized absorption spectra obtained via Kramers–Kronig transformation of the specular reflection spectra are given in Figures 6 and 7. In the transforms, both spectroscopic data, in particular PES, and molecular orbital calculations were used in fitting data. No obvious excitonic interactions are found for any of the 300 K crystal spectra.

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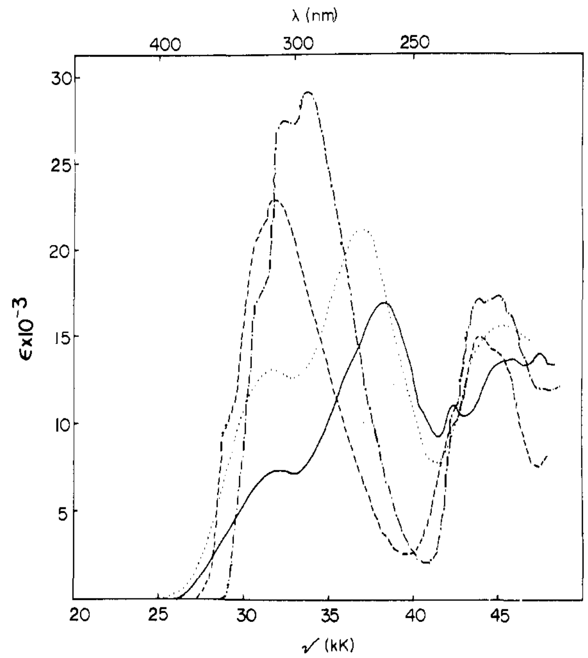

Figure 1. Absorption spectra in cyclohexane for *trans*-stilbene (S) (- · · · · ·); *trans*-azobenzene (A) (- - - - - -); benzylideneaniline (BA) (—); *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (**1**) (· · · · · ·).

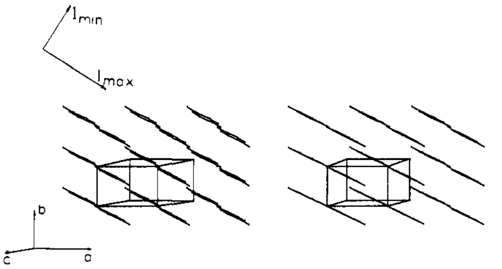

Figure 2. Stereoview of the projection on the (001) face of the triclinic structure of **1**. I_{max} and I_{min} are the extinction directions which were oriented parallel to the electric vector of the incident light for measurement of the reflection spectra

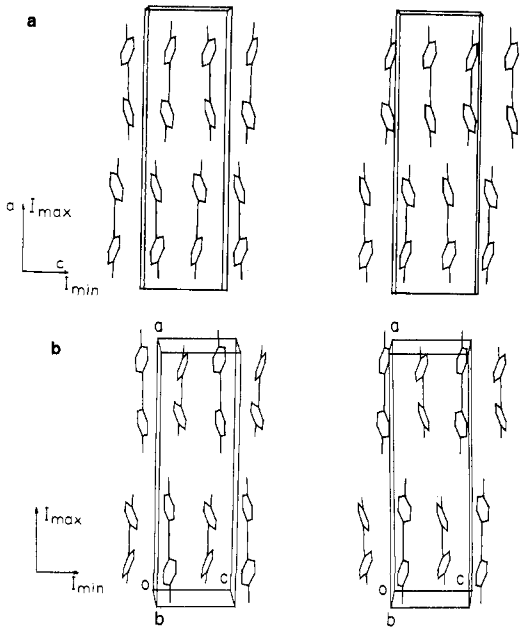

Figure 3. Stereoviews of the projections on the two faces of the orthorhombic structure of **1**. I_{min} and I_{max} have the same meaning as in Figure 2. (a) projection on (010) face; (b) projection on (110) face.

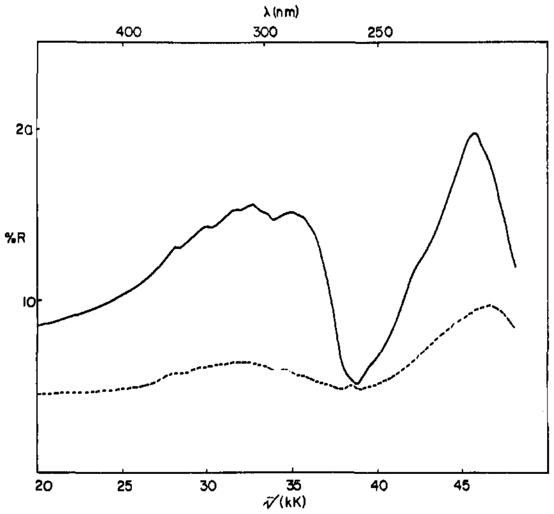

Figure 4. Reflection spectra at 298 K for light polarized parallel to the I_{max} (—) and I_{min} (- - - - - -) extinction directions on the (001) face of the triclinic form of **1**.

Discussion

The solution spectrum of **1** (Figure 1) has the characteristic features of the unsubstituted molecule with some minor perturbations. The intensities of both the shoulder at 3.15 μm^{-1} (1 μm^{-1} = 10 000 cm^{-1} = 10 kK) and the peak at 3.75 μm^{-1} are greater than in the parent compound and the latter is red shifted by about 0.1 μm^{-1}. However, the similarity of the solution spectrum of **1** with that of BA and the marked difference from those of S and A verify the presence of the nonplanar conformation of **1** in solution.

A large number of studies which employ a variety of means for forcing BA into a planar conformation have been reported in the literature.[5] The most stable nonplanar conformation is generally considered to be due to a competition between the repulsion between the hydrogen on the -CH=N- group and one of the ortho hydrogens on the aniline ring which is relieved by an out of plane rotation about the *N*-phenyl bond on the one hand and the stabilization of the out of plane conformation due to overlap between the lone pair electrons on the nitrogen and the π system on the aniline ring on the other hand.[12] Using these arguments, the energy difference between planar and nonplanar conformations for the free molecule has been estimated to be 1.5 kcal/mol on the basis of the sum of nonbonded interactions and simple Hückel molecular orbital considerations. Ab initio methods employing model compounds to investigate the energetics for CH-phenyl and *N*-phenyl yielded a similar difference between the planar conformation and a minimum energy conformation with $\alpha = 45°$, $\beta = 0°$.[13,14] A recent photoelectron spectroscopic (PES) study yielded an approximate value for α of 36° in the gas phase.[5] A more recent electron diffraction experiment[6b] gives $\alpha = 52°$, $\beta = 0$ and is in closer agreement with the calculations.

There have also been a large number of semiempirical molecular orbital studies which have attempted to correlate the spectral data with electronic structure. For the systems treated here, the validity of most of these studies, especially those employing CNDO/2, MINDO/2, and MINDO/3, has recently been questioned.[5] In particular, these methods fail to correctly predict the now fairly certain free molecule conformation, presumably owing to their failure to properly account for π systems connected by an essential single bond.[5] Therefore, we will not attempt here to correlate our spectral data directly with the results of these semiempirical studies. Rather, we will be concerned with the differences observed between the

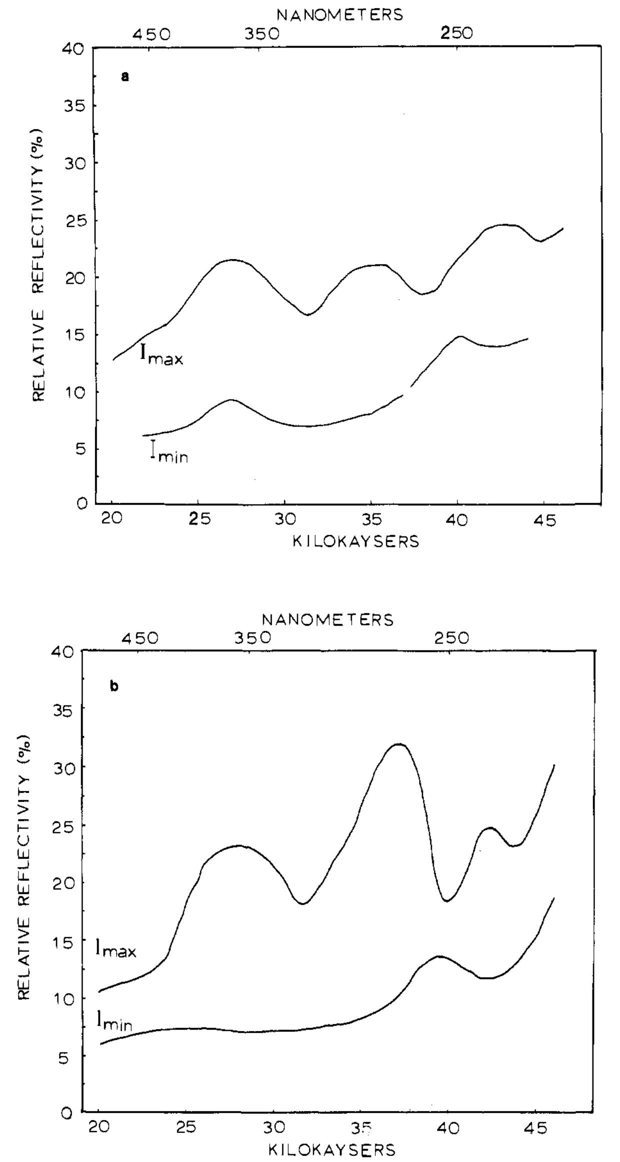

Figure 5. Reflection spectra at 298 K on two faces of the orthorhombic form of 1. (a) (010) face; (b) (110) face.

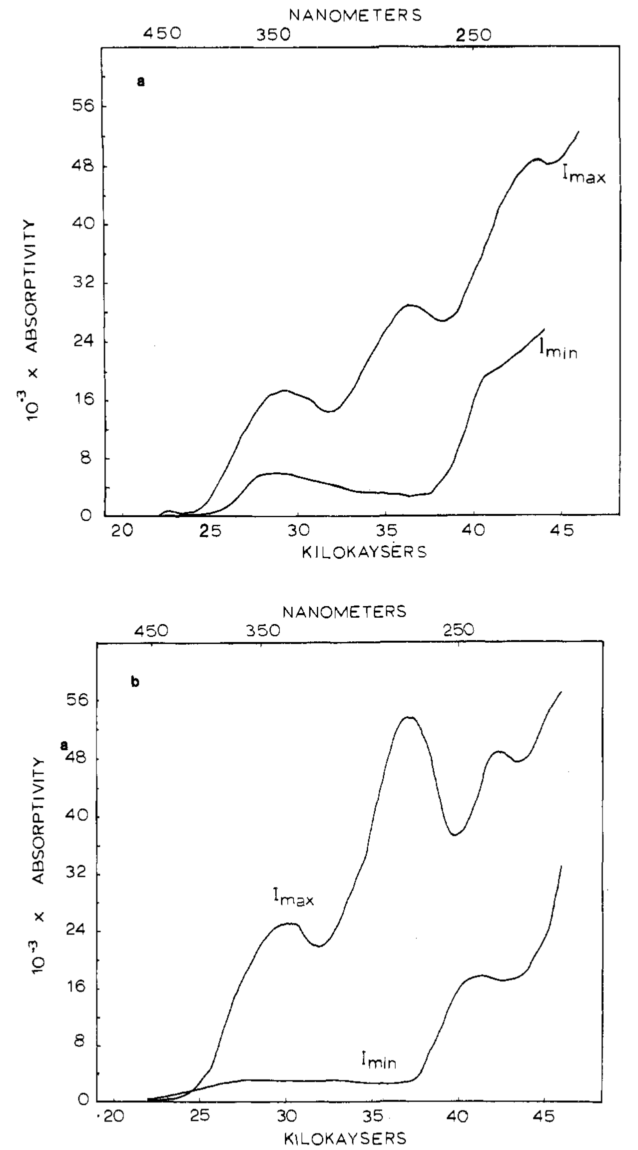

Figure 7. Kramers-Kronig transform of the reflection spectra on two faces of the orthorhombic form of 1. (a) (010) face; (b) (110) face.

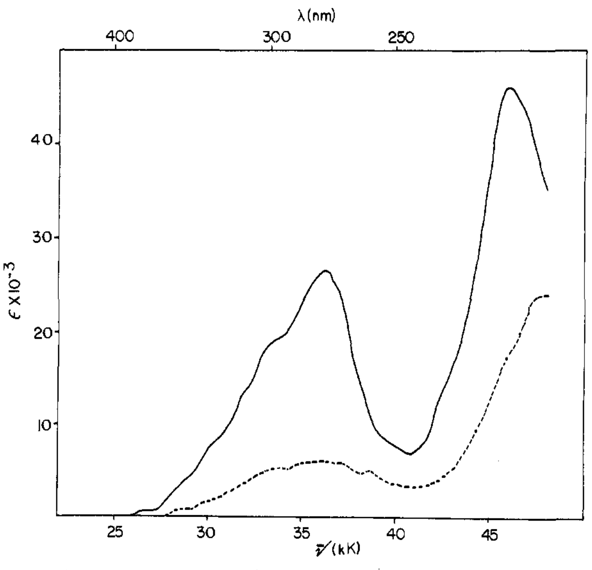

Figure 6. Kramers-Kronig transform of the reflection spectra on two faces of the triclinic form of 1. I_{max} (—); I_{min} (- - - - - -).

solution spectrum and those in the two different crystal forms. Furthermore, the various bands observed in the crystal spectra can be quite closely related to the energy levels obtained from the analysis of the PES of the molecule and, as a result, some probable assignments of the transitions may be made on the basis of this correlation.

The Triclinic Structure. The extinction directions on the (001) face (Figure 2) are such that along the I_{max} direction molecular excitation is almost exclusively in the molecular plane and nearly along the projection of the longest axis of the molecule (the vector connecting the two chlorine substituents). The I_{min} direction, on the other hand, has a very small projection on the molecular plane. The molecular symmetry for the planar molecule in this structure is essentially C_{2h} if the asymmetry induced by the -CH=N- bridge is disregarded. Assuming then that the molecular symmetry does approximate C_{2h}, observed transitions will be polarized either out of plane (z) or in plane, with no restrictions on the latter, since both in-plane molecular axes transform as the same irreducible representation. In A and S, it has been shown that the polarization of at least the major portion of the intense, low-energy transition is very nearly parallel to the long (para-para′) axis of the molecule.[15-17] As expected, the intense low-energy transition for planar **1** resembles those for A and S, and the

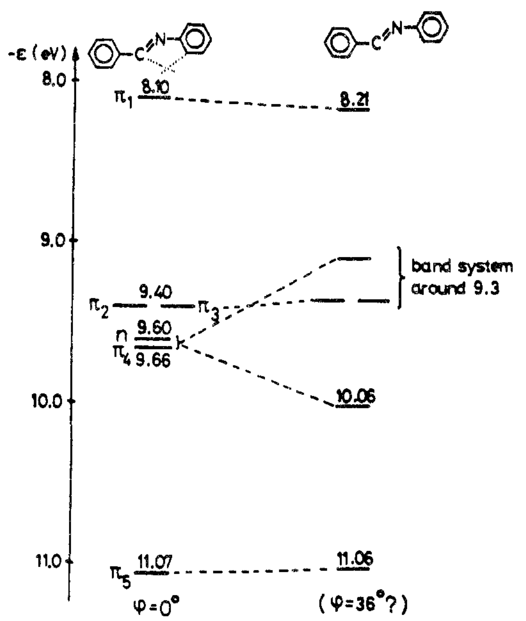

Figure 8. Correlation diagram for energy levels of **1** and **2** derived from the photoelectron spectrum. The figure is a condensation of Figure 2 of ref 5, which should be consulted for a full explanation of the assignment of energy levels (reproduced with permission from *Helvetica Chimica Acta*).

band fails to show the characteristic shape of BA in solution.

Furthermore, even at room temperature, the I_{max} direction exhibits significant vibrational structure on the red side of the low-energy band closely resembling the vibrational structure in both solution and low-resolution solid-state spectra of A and S. In the latter, this vibrational structure (1342 and 1599 cm^{-1}, respectively) has been assigned to a combination of the stretching mode of the central bridge atoms with the electronic transition polarized in nearly the same direction.[15] The vibrational spacing of ~1600 cm^{-1} found here, and absent in solution and in the orthorhombic structure, is additional evidence that in the planar molecule the low-energy side of the main absorption is due to a long-axis polarized $\pi^* \leftarrow \pi$ transition analogous to that found in A and S. The net result then is that the crystal forces present in this structure are sufficient to force **1** into the energetically unfavorable planar conformation, which in turn leads to an electronic spectrum resembling that of its planar isoelectronic analogues.

On energetic grounds, as well as the above assignment for the lowest energy transition, such a mechanism appears quite plausible. The energy levels of 3,3-dimethyl-2-phenylindolenine (**2**), a planar analogue of BA, have been determined by PES[5] and are shown in Figure 8. The lowest energy transition should originate from the π orbital at −8.1 eV (i.e., a $\pi^* \leftarrow \pi$ transition) and, in correspondence with arguments from above and earlier assignments,[14-16] would have a polarization along the long molecular axis. From the maximum in the absorption spectrum, the energy of this transition in the crystal is $\bar{\nu}_{max} \sim 3.63\ \mu m^{-1}$, which is probably close to the $(\pi\text{-}\pi^*)$ separation, but the precise value is somewhat in doubt owing to the large bandwidth and the presence of the vibronic structure. Bally et al.[5] have assigned the next broad peak in the PE spectrum of **2** (Figure 9) to four energy levels, $\pi_2 = \pi_3$ (−9.40 eV), n (−9.60 eV), and π_4 (−9.66 eV). The difference between this group (whose energy is given as 9.32 eV on the spectrum) and π_1 is about 1.05 μm^{-1}, which corresponds quite well with the separation of 0.93 μm^{-1} observed in the spectrum, especially considering the uncertainty in assigning an origin for the first broad band.

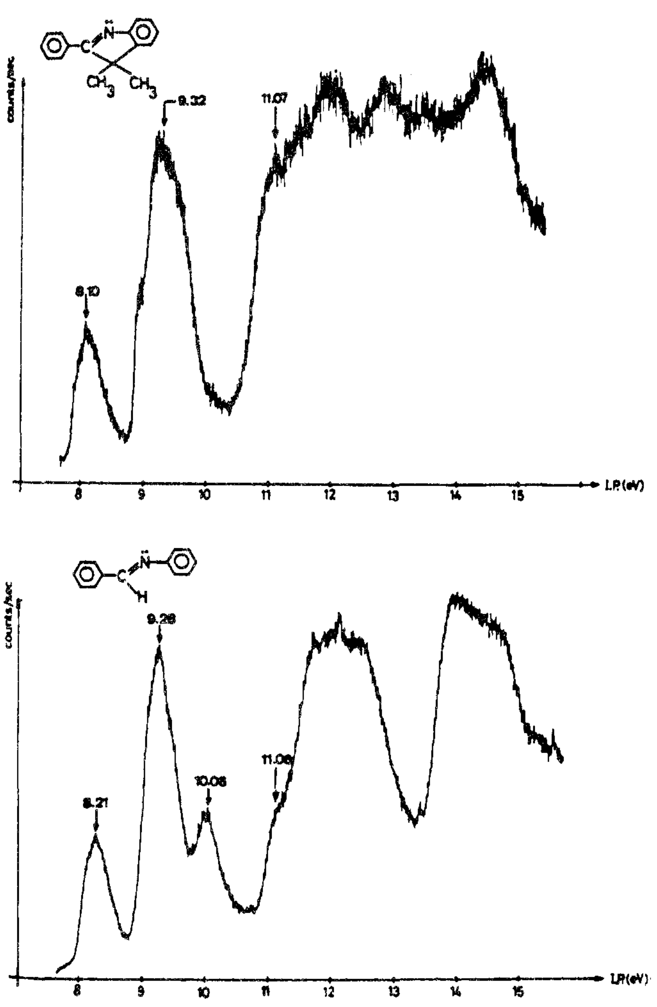

Figure 9. Photoelectron spectra of benzylideneaniline **1** and 3,3-dimethyl-2-phenylindolenine **2** (reproduced with permission from *Helvetica Chimica Acta*).

There is a shoulder in the PES of **2** at about 8.9 eV which would correspond to a transition energy of about 4.2 μm^{-1}, i.e., on the high-energy side of the first main band. Such a transition has been suggested by both theoretical and experimental studies in A and S and might be present here as well.[16,18-20]

Orthorhombic Structure. The derived absorption spectra of the nonplanar molecule in the orthorhombic crystal (Figure 7) can be directly correlated with the PES of BA. The lowest energy transition corresponds to excitation from the π_1 level at 8.21 eV to the lowest π^* level and appears to correspond to the familiar low-energy shoulder in the BA solution spectrum. The PES suggests that the next transition should be about 0.75 μm^{-1} higher in energy arising from excitation from a level assigned to n-π_4 by Bally et al.[5] Indeed on I_{max} of (010), this peak comes at 3.67 μm^{-1} (Δ from first peak = 1.40 μm^{-1}) and 4.24 μm^{-1} on (110) (Δ from first peak = 1.22 μm^{-1}).

Thus, the correspondence between the observed optical spectra in planar and nonplanar BA with the energy levels as measured by PES is very close. As has been pointed out in earlier work,[21,22] this is not usually expected since the difference of the singlet excited state energies $\Delta E = \Delta \mathrm{IP} - \Delta J + 2\Delta K$ where ΔIP is the difference of ionization potentials of the orbitals from which the transitions originate. ΔJ and ΔK are the differences in coulomb and exchange integrals associated with the two electronic transitions.[21,22] As shown above $\Delta E \approx \Delta \mathrm{IP}$ and thus $\Delta J + 2\Delta K \approx 0$ is implied. This requirement may, therefore, be used to test the validity of calculations on these systems. Unfortunately, the low symmetry of the molecule involved prevents a meaningful analysis on the basis of 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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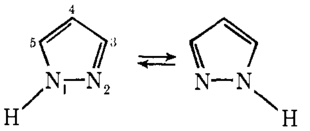
Abstract: The ^{13}C NMR shifts of all the carbons in pyrazole have been observed at room temperature. This paper reports the kinetic data available from the temperature-induced collapse of the C-3, C-5 NMR peaks. $\Delta G^{\ddagger} \simeq 14.8$ kcal/mol, $\Delta H^{\ddagger} \simeq 7.0$ kcal/mol, 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.



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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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