

Conformational Fingerprints in the IR and Raman Spectra of Oligoanilines: A Combined Theoretical and Experimental Study

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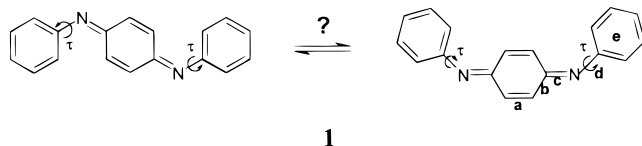
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MacDiarmid has pointed out recently¹ that conformational changes could play a major role in determining the properties of an important conducting polymer, polyaniline. For instance, *E/Z* isomerization might be at play when it is used as a chemical sensor.^{1a} However, correct determination of conformation has been challenging due to its relatively small effect on most properties. Vibrational properties can be useful in deducing the conformation of leucoemeraldine base, the fully reduced form of polyaniline,² as well as other molecular systems.³ As a model system, the imine form of a phenyl-end-capped dimer, **1**, has proven to be useful in understanding the



properties of imine-containing (pernigraniline form, PNB) oligo- and polyanilines.^{4,5} Local conformational information is critical in understanding the properties of oligoanilines and polyanilines.⁶

In this communication, vibrational properties of **1** have been studied with density functional theory (DFT)⁷ in combination with Baker et al.'s new force field scaling scheme.⁸ As a further approximation, we have evaluated polarizability derivatives using the HF/6-31G* method and combined it with B3LYP/6-31G* vibrational results in order to calculate Raman intensity efficiently. It is shown that, with the help of this new scaling scheme as well as our theoretical model systems, conformational

Table 1. Theoretical Geometric Data of **1**

	τ , deg	a, Å	b, Å	c, Å	d, Å	e, Å	E_{rel}^a
Z-nonplanar (C_2)	51.7 ^b	1.348	1.463	1.300	1.398	1.400	0.4
Z-planar (C_{2v})	0 ^c	1.350	1.461	1.306	1.391	1.401	9.9
E-nonplanar (C_i)	49.8 ^b	1.350	1.466	1.301	1.397	1.400	0
E-planar (C_{2h})	0 ^c	1.353	1.464	1.307	1.391	1.401	8.9
experiment ^d	53	1.33(1)	1.46(1)	1.32(1)	1.42(1)	1.37(1)	

^a Energies are relative to that of *E*-nonplanar conformation in kcal/mol. ^b Optimized. ^c Constrained. ^d X-ray data for the *E*-nonplanar conformation, taken from ref 12.

information (both planarity and *Z-E* conformation) can be deduced from the comparison of the theoretical predictions on model systems and experiments.

The imine form of the *N,N*-diphenyl-1,4-phenylene-diamine was prepared via the Zaghali and Shatnawi procedure.⁹ An orange powder was obtained, which was used in the Raman and IR experiments. Infrared absorption spectra were collected on an FTIR spectrometer (Nicolet 20 SXC) equipped with a DTGS detector using the KBr pellets technique. Raman spectra were obtained with the excitation lines in the visible range (457.9, 514.5, 676.4 nm) and were recorded using a microscope on a multichannel Jobin Yvon T64000 spectrometer connected to a CCD detector. The Raman spectra were registered at liquid nitrogen temperature (80 K), to avoid the problem of degradation. For the 1064 nm excitation wavelength, an FT-Raman Bruker RFS 100 spectrometer was used in a backscattering configuration.

In Table 1 we compare selected geometric and relative stability data of **1** for four model conformations and experiment. The theoretical calculations were performed with the B3LYP/6-31G* [Lee, Yang, and Parr's (LYP)¹⁰ correlation functional in combination with Becke's three parameter hybrid (B3)¹¹ exchange functional] DFT method. Torsional angles (τ) of the *Z* and *E* nonplanar models are predicted to be 51.7° and 49.8°, showing the influence of large van der Waals repulsions between adjacent hydrogen atoms. The agreement between the experimental and theoretical geometry is excellent.¹² Earlier calculations failed to predict the torsion correctly,¹³ because the MNDO-type calculations employed often fail to properly balance the subtle competition

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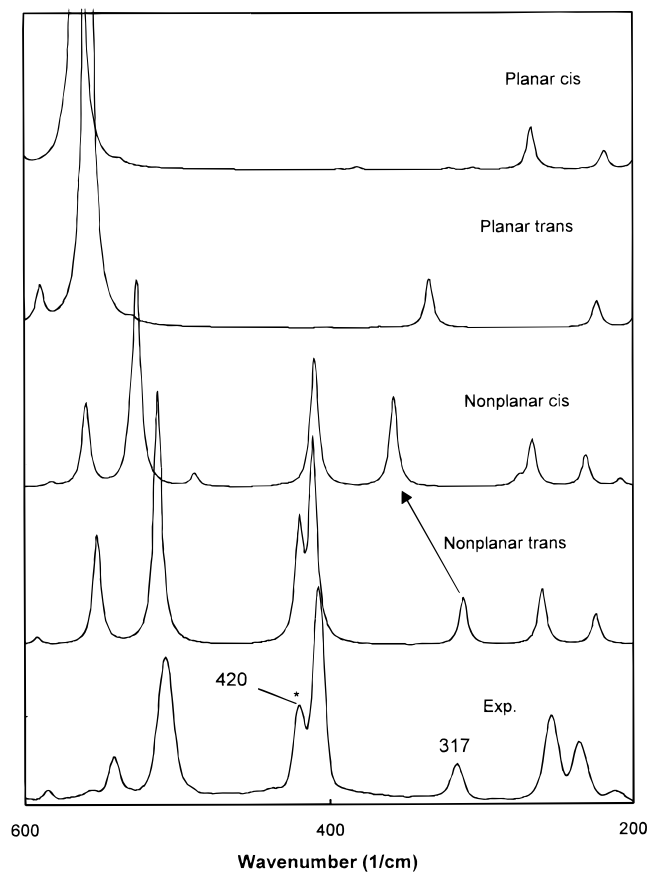


Figure 1. Experimental (bottom) and predicted Raman spectra of **1**. An arrow or an asterisk indicates a large frequency or intensity dispersion, respectively.

between π -electron delocalization and van der Waals repulsion. As expected, the difference between the two torsional angles of the two conformers is very small. Also, the bond lengths around the central quinonoid ring are not very sensitive to the torsional angles. All geometrical data indicate that the degree of conjugation between rings is quite independent of the *Z/E* isomerization and even rather independent of the torsional angles. Both *Z* and *E* planar conformers are predicted to be less stable by about 9 kcal/mol as compared to their nonplanar counterparts. The energy difference between the *Z* and *E* nonplanar conformers is a mere 0.4 kcal/mol, in concordance with the fact that both *Z* and *E* conformers have been observed earlier.¹⁴

Vibrational properties of **1** are predicted and compared with experiment in Figures 1 and 2. Since *Z/E* isomerization only moderately affects the molecular structure and the relative stability, it is expected that there should be no large vibrational frequency and intensity dispersion as a function of conformation except in the low-frequency region. This is indeed what we found. Therefore, only the low-frequency region is presented in Figures 1 and 2. A few bands do exhibit large frequency or intensity dispersions, as indicated by an arrow or a star, respectively. In the Raman spectrum, the observed peaks at 317 and 420 cm^{-1} are the characteristics of the nonplanar *E* conformer. These are attributed to the ring rotations and the C–N–C bending modes, thus explaining why these modes depend on the

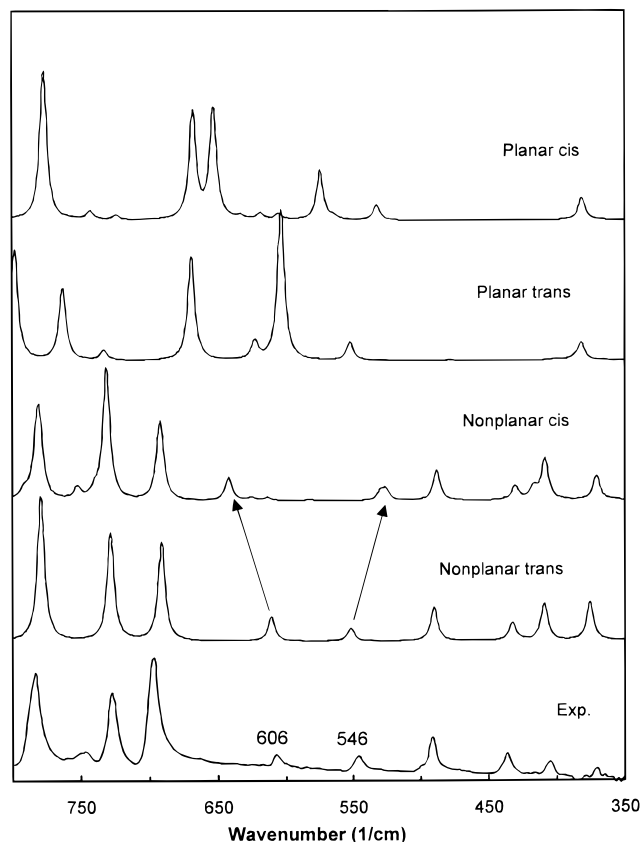


Figure 2. Experimental (bottom) and predicted infrared spectra of **1**. An arrow indicates a large frequency dispersion.

conformation. The two peaks are well-reproduced with the nonplanar *E* model, while the peak at 317 cm^{-1} is blue-shifted by 50 cm^{-1} and the peak at 420 cm^{-1} is missing in the case of the nonplanar *Z* model. Among the predicted spectra, that of the nonplanar *E* model is in excellent agreement with the experiment.

Similar conformation specific peaks can be identified in the predicted infrared spectra, as shown in Figure 2. Two peaks stand out: the 546 and 606 cm^{-1} peaks, both correspond to ring deformation modes. The former mode is more localized on the quinonoid ring, the latter on the benzene ring. The predicted spectrum of the nonplanar *E* model is in best agreement with the experiment. The 546 cm^{-1} peak is red-shifted, while the 606 cm^{-1} peak is blue-shifted in the nonplanar *Z* model.

Except these characteristic peaks, the rest of the spectrum is much less dependent on the conformation. (Tables of vibrational frequencies and the full vibrational assignments for the four models discussed in this paper are available as Supporting Information.)

We have made a special effort to locate the minority conformer in the Raman spectrum. There is a small peak at 361 cm^{-1} that could be assigned to the minority conformer (predicted band at 358 cm^{-1}) or to a weak band of the planar *E* conformation (predicted band at 367 cm^{-1}). The relative peak areas are for the 317 cm^{-1} and 361 cm^{-1} bands are 96% and 4%, respectively. Assuming that the scattering cross section for these bands are the same, we arrive at an estimate of maximum 4% abundance for the minority conformer. This number should be compared with the 3–4% sensitivity of the instrument. A similar analysis of the IR spectrum leads to the following results. Assuming that the 546 cm^{-1}

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peak corresponds to the majority, nonplanar *E* conformer, the sideband at 520 cm^{-1} has been identified as a possible signature of the minority, nonplanar *Z* conformer (theoretically predicted at 525 cm^{-1}). The area under this peak is about 5%, as compared to the 546 cm^{-1} majority peak. The IR detection limit is estimated at 2%.

Assuming similar intensities, and taken together with the Raman evidence, this interpretation is consistent with the presence of about 4–5% minority conformer.

On the basis of these observations, we conclude that the majority conformation of **1** is likely to be a nonplanar *E* conformer, although our calculated total energy values indicate that both the *Z* and *E* conformers ought to coexist. It is unclear at this point why the synthesis produces overwhelmingly the *E* rather than the minority *Z* conformer. The characteristic peaks identified in

this study will be used for attaining a better understanding the role of conformations in understanding properties and applications of oligoanilines and polyanilines.

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Supporting Information Available: Tables of vibrational frequencies and the full vibrational assignments for the four models discussed in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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