

0040-4039(95)00888-8

Synthesis and Characterization of Pyridine End-Capped Oligoazines

Eric C. Kesslen and William B. Euler* Department of Chemistry, University of Rhode Island, Kingston, RI 02881

Abstract:

A new group of controlled chain length oligoazine analogues with pyridine end groups are synthesized and characterized.

Introduction:

A new group of polyazine analogues have been synthesized by condensation of oligoazines having amino end groups with 2-pyridinecarboxaldehyde.¹



Methyl substituted oligoazines are linear, rigid, planar molecules with extended π systems² and lead to materials with interesting electronic and nonlinear optical properties. The pyridine end group should extend the conjugation length of the oligomer provided the dihedral angle between the main chain and the aromatic group is not too large.

Infrared Spectroscopy:

The band in these compounds seen at 1630 cm⁻¹ in 1 and at 1617 ± 1 cm⁻¹ in 2 through 5 are assigned to the C=N stretch. This compares to imine peaks found at about 1590 cm⁻¹ for amino capped oligoazines.^{2,3} The additional shift seen in the amino capped oligomers has been attributed to coupling of the imine bond to N-H rocking vibrations of the end groups and the results found here are consistent with that conclusion. This demonstrates that the conjugation length as measured by IR is limited to four imine bonds plus the contribution of the pyridine end groups. Since the C=N peaks in 2 through 5 do not change shape or position with chain length it is believed that the compounds are all in the same conformation in the solid state: single bonds anti and double bonds E, in accordance with previous work.²

¹H NMR Spectroscopy:

Proton NMR of compounds 1-5 show that the ring protons exhibit similar chemical shifts and splittings in all compounds with $\delta(H^1) = 8.7$ ppm, $\delta(H^2) = 7.5$ ppm, $\delta(H^3) = 7.9$ ppm and $\delta(H^4) = 8.1$ ppm and $J_{1.2} = 4.8$ Hz, $J_{1.3} = 1.6$ Hz, $J_{1.4} = 1.1$ Hz, $J_{2.3} = 7.8$ Hz, $J_{2.4} = 1.1$ Hz and $J_{3.4} = 7.3$ Hz, indicating that the pyridine ring is not coupled significantly to the azine chain.

The imine proton, H^5 , in compound 1 is seen as a singlet at 8.6 ppm while in compounds 2-5 H^5 is seen between 8.1 and 8.2 ppm. In an effort to decouple whether this is due to conjugation or the methyl groups the unsubstituted analogue of compound 2 was synthesized and the analogous imine proton was found at 8.4 ppm implying that the methyl groups on the bridge donate sufficient electron density into the bridge backbone to shield H^5 . Since compound 1 has no methyl groups H^5 is the least shielded. Thus in agreement with the IR, the conjugation length in the ground state as probed by NMR is quite limited.

Ultraviolet Spectroscopy:

Compound 1 shows three well defined bands at 260 nm ($\varepsilon = 14\ 000\ M^{-1}\ cm^{-1}$), 299 nm ($\varepsilon = 31\ 500\ M^{-1}\ cm^{-1}$) and 308 nm ($\varepsilon = 29\ 400\ M^{-1}\ cm^{-1}$) and a low energy shoulder at 325 nm. The peak at 260 nm is associated with transitions localized in the pyridine ring but the lower energy transitions must be between orbitals in the conjugated imine system. Compounds 2 through 5 have similar spectra with maxima at 300 nm ($\varepsilon = 40\ 000\ M^{-1}\ cm^{-1}$), 304 nm ($\varepsilon = 54\ 000\ M^{-1}\ cm^{-1}$), 308 nm ($\varepsilon = 60\ 400\ M^{-1}\ cm^{-1}$), and 306 nm ($\varepsilon = 61\ 500\ M^{-1}\ cm^{-1}$) respectively, as well as a lower energy shoulder. Based on the magnitude of the extinction coefficients these have been assigned $\pi \rightarrow \pi^*$ transitions. There is no evidence of $n \rightarrow \pi^*$ transitions.

The maxima in 1 are not regularly spaced so do not arise from a vibronic progression. All of the π molecular orbitals have either a_u or b_g symmetry (assuming C_{2h} symmetry) so two types of transitions are allowed, $a_u^2 \rightarrow a_u^1 b_g^{*1}$ and $b_g^2 \rightarrow b_g^1 a_u^{*1}$; both are ${}^1A_g \rightarrow {}^1B_u$. Increasing the amount of conjugation increases the number of allowed transitions which has the effect of widening and smoothing the manifold (i.e. band formation).

The changes in the low energy band as a function of the conjugation (the number of azine units) allows us to assign it as a transition centered in the azine linking units. With this series of molecules the effect of conjugation is clearly observable up to at least n = 4 as the graph below demonstrates, but spectroscopic shifts may no longer occur for n > 4 (there is insignificant data for an unambiguous determination). This suggests



Figure 1. A plot of band edge vs. the inverse of the number of azine units showing the typical linear behavior associated with increasing conjugation. 3

that conjugation in the excited state, as probed by the UV experiment, is significantly longer than the conjugation in the ground state as implied by the IR and NMR results.

Conclusion:

A series of polyazine analogues has been synthesized and characterized by infrared, ¹H NMR and UVvis spectroscopies. The results of analyses show that electronic properties can be tailored by altering the length of dihydrazone used in the synthesis. Spectroscopic results also show that delocalization in the excited state is larger than in the ground state. The pyridine end group is situated so that diimine metal complexes can be synthesized. Because of the apparent difference in conjugation lengths in the ground and excited states, such metal complexes should be interesting models for electron transfer theories.⁴

Acknowledgement is made to the US Army Research Office for partial support of this work.

References

- All compounds were synthesized by slow addition of the appropriate dihydrazone² (hydrazine for compound 1) into a stoichiometric amount of 2-pyridinecarboxaldehyde in 95% ethanol. Precipitation of solid was induced by cooling on an ice/salt bath. Compound 1. (n = 0) 77% yield. mp = 150°C. Anal. calcd for C₁₂H₁₀N₄: C, 68.56; H, 4.79; N, 26.65. Found: C,68.54; H, 5.02; N, 26.64. Compound 2. (n = 1) 51% yield. mp = 158-159°C. Anal. calcd. for C₁₆H₁₆N₆: C, 65.75; H, 5.52; N, 28.75. Found: C,65.40; H, 5.92; N, 28.75. Compound 3. (n = 2) 42% yield. Decomposed at 123-124°C. Anal. calcd for C₂₀H₂₂N₈: C, 64.23; H, 5.93; N, 29.96. Found: C, 63.40; H, 5.71; N, 29.80. Compound 4. (n = 3) 39% yield. Melting point, 135-137°C. Anal. calcd. for C₂₄H₂₈N₁₀: C, 63.13; H, 6.18; N, 30.68. Found: C, 63.06; H, 6.25; N, 30.78. Compound 5. (n = 4) 34% yield. Decomposition at 131-133°C. Anal. calcd. for C₂₈H₃₄N₁₂: C, 62.43; H, 6.36; N, 31.20. Found: C, 60.87; H, 6.39; N, 31.08. Infrared spectroscopy was done as potassium bromide pellets using a Perkin-Elmer 1650 FTIR. Ultraviolet spectroscopy was done on methanol solutions using a Perkin-Elmer Lambda 2 UV-vis spectrophotometer. NMR spectroscopy was done on d⁶ DMSO solutions (compound 4 was done in CDCL), using a Bruker AM 300 instrument.
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(Received in USA 25 April 1995; revised 16 May 1995; accepted 17 May 1995)