Conclusions

The analysis of the NMR spectra of specifically deuterated tetrahydrofuranmethanol, methyl β-D-ribofuranoside, methyl β-D-2-deoxyribofuranoside, and the sugar acetal 5-phosphates has permitted some important conclusions to be reached about the solution conformations of nucleosides and nucleotides: (1) in the unsubstituted sugars and their phosphates, the preferred sugar pucker is the 3′-endo and not the 2′-endo, demonstrating that the heterocyclic base has an important influence on this flexible portion of the structure; (2) in the unsubstituted sugars and their phosphates, the gauche–gauche rotamer about the C_4–C_5 bond does not predominate as in the nucleosides and nucleotides, but rather the two rotamers in which the vicinal C–O bonds are gauche to one another are about equally favored, and this rotational distribution can be described by consideration of a phenomenological V_2 potential; (3) the observed predominant occurrence of the gauche–gauche rotamer about the $C_{4'}$–$C_{5'}$ bond in nucleosides and nucleotides is presumably the result of an interaction between the substituent on $C_{5'}$ and the heterocyclic base, further favoring the gauche–gauche rotamer and which perhaps can occur only by a shift in the 2′-endo-3′-endo equilibrium; and (4) the rotameric distribution about the C_5–O_5 bonds in furanoside 5-phosphates is the same as is observed in nucleotides, even though the sugar ring pucker and rotameric distribution about the C_4–C_5 bond are different, indicating that these conformational degrees of freedom in nucleosides and nucleotides may not be intimately interdependent.

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Conformational Study of 1,2-Dimethylhexahydropyridazine by Variable-Temperature Photoelectron Spectroscopy[1]

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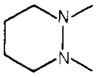
Abstract: Variable-temperature photoelectron spectroscopy (VTPES) measurements show that the diequatorial (lone pairs diaxial) conformation of 1,2-dimethylhexahydropyridazine is 1.20 ± 0.08 kcal/mol more stable than the axial,equatorial (lone pairs gauche) conformation. This energy difference is only 0.4 kcal/mol in solution, and the larger value in the vapor phase is attributed to the greater polarity of the axial,equatorial conformation.

Introduction

The photoelectron (PE) spectra of hydrazines show two low-energy ionization bands, caused by ionization from the symmetric and antisymmetric lone-pair combination orbitals. The separation of these bands (Δ) has been found to be sensitive to the lone-pair–lone-pair dihedral angle θ,[3,4] varying from about 2.3 eV when θ is near 0 or 180° and the lone-pair interaction is large to about 0.5 eV when θ is near 90°. The PE spectrum of 1,2-dimethylhexahydropyridazine (**1**) shows three bands in the lone-pair region,[3b,4b] two large ones separated by 2.3 eV, with a smaller band between them. The relatively rigid chair six-membered ring causes **1** to exist in conformations with well-defined θ, **lee** ($\theta \sim 180°$), **lae** ($\theta \sim 60°$), and (in principle) **laa** ($\theta \sim 60°$), depending on the relative configurations of the two nitrogens. The large bands were assigned to conformation **lee** and the smaller band to the higher energy lone-pair ionization of **lae**/**laa**; the lowest energy **lee** and **lae**/**laa** bands overlap and are not resolved. When Gaussian curves were fitted to the PE spectrum of **1**, it was estimated that the bands due to **lee** were about three times as intense as the **lae**/**lee** peaks.[4c] Thus **lee** was claimed to predominate the conformational mixture for **1**, but the possibility of significantly different band size for different conformations precluded accurate determination of the relative amounts of conformations.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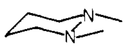
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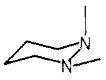
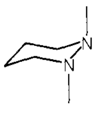

lae


laa

It was later shown by variable-temperature ^{13}C NMR work[5] that although **lee** does predominate in solution, K_{eq} = [**lee**]/[**lae**] is only about 1.4 at room temperature, with a $\Delta E°$ of −0.4 kcal/mol. In this paper we report measurement of the vapor phase $\Delta E°$, using the method of variable-temperature PE spectroscopy (VTPES),[6] so that the solution and vapor-phase conformational

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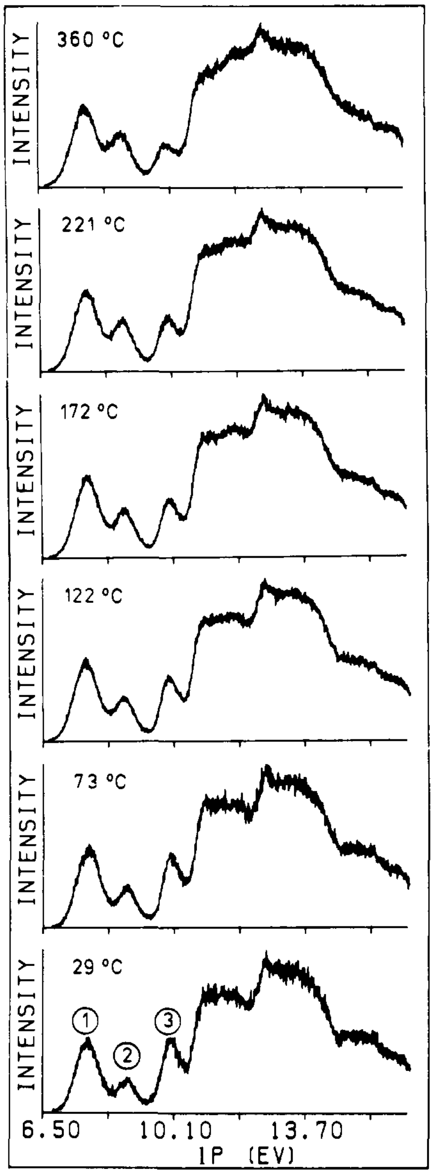

Figure 1. Photoelectron spectra of 1,2-dimethylhexahydropyridazine at six selected temperatures (29, 73, 122, 172, 221, and 360 °C).

equilibria for **1** may be compared.

Experimental Section

The variable-temperature photoelectron spectral (VTPES) measurements as well as the photoelectron spectral pyrolysis experiments were made by using previously[6a,e,h] described experimental setups. Each spectrum consists of 1024 data points averaged over 512 single scans with 4-ms sample time at each point. The spectra are calibrated with an acetylene/nitrogen mixture. The resolution $E/\Delta E$ was about 220, corresponding to a half-width of the argon signal of 25 meV. The computer analysis of the spectra was performed as outlined previously.[6h]

1 was prepared as previously described[7] and purified by preparative VPC, using a 15% XF.1150 on 60–80 mesh Chromosorb W column, before use.

Results and Discussion

Figure 1 presents the photoelectron spectra at various temperatures below 400 °C (as recorded with the aforementioned VTPES setup). Obviously, the intensity of band 2 increases and the intensity of band 3 decreases with increasing temperature. Figure 2 displays the relative peak heights h_3/h_2 and h_3/h_1 (solid lines) of the VTPES bands as a function of temperature. Both ratios decrease as expected. In addition, Figure 2 shows the corresponding ratios of the PES bands as obtained with the aforementioned photoelectron spectral pyrolysis setup (dashed lines). These ratios do not decrease, but instead sharply increase at about 400 °C, indicating rather exactly the temperature where **1** thermally decays. Accordingly, **1** does not decompose up to 400 °C and the VTPES changes of Figure 1 and **2** must be due to some internal reversible thermal process.

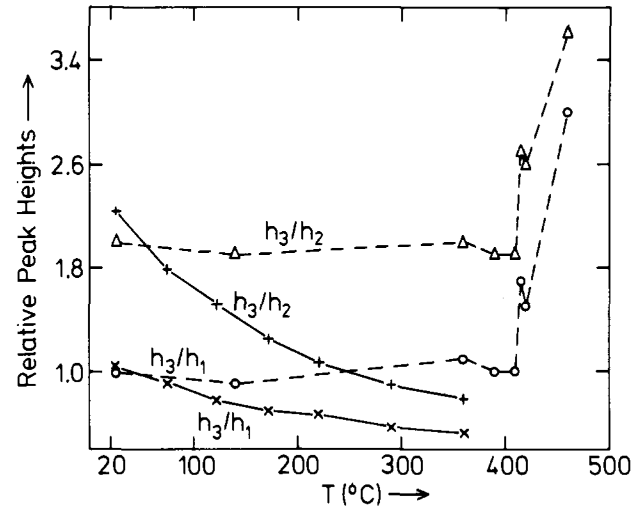

Figure 2. Relative peak heights in the photoelectron spectra of 1,2-dimethylhexahydropyridazine taken at various temperatures when applying the VTPES technique (solid lines) and taken at room temperature after external pyrolysis as a function of pyrolysis temperature (dashed lines).

In the earlier PES work[3,4] it was noted that the PE bands for **lae** and **laa** would be expected to fall on top of each other, and the minor conformation observed (band 2 and part of band 1) was assigned as **lae**/**laa**. There is, however, no evidence from the ^{13}C NMR work[5] that **laa** is populated detectably. This is hardly surprising, because the only reason **lae** can be detected is that the gauche ($\theta \sim 60°$) arrangement of its lone pairs is electronically preferred to the anti ($\theta \sim 180°$) lone pairs of **lee**. **lae** is sterically destabilized by the 1,3-diaxial MeN,CH interactions of the *axial* methyl group. This steric destabilization of **lae** should be larger than that for axial *N*-methylpiperidine relative to its equatorial form (the shorter NN and CN than CC bondlengths require closer MeN,CH approach), which is estimated to be 2.5–3.0 kcal/mol.[8] Because the electronic stabilization of **lae** and **laa** should be similar due to similar values for θ, **laa** ought to lie greater than about 3 kcal/mol in energy than **lae**, and hence not be significantly populated.

The spectra of Figure 1 show that the less stable conformation **lae** (which gives rise to band 2) can be significantly populated at the expense of **lee** (which gives rise to band 3). It is one of the strengths of the VTPES method that the results can be quantitatively analyzed to determine the energy difference between conformers in the gas phase.[6c,d,h,i] Note especially that such an analysis is independent of any cross section considerations in the present case.[5]

Following the preceding arguments[6h,i] the energy difference $\Delta E° = E°_{ee} - E°_{ae}$ is accessible from

$$\ln (I_3/I_2) = -\Delta E°/RT + \text{constant} \qquad (1)$$

I_3/I_1 is the relative band intensity of respective bands 3 and 2, R the gas constant, and T the absolute temperature.

The relative intensities I_3/I_2 for the temperature applied were determined from the areas of Gaussians fitted to the spectra over the range 6.5–11.2 eV.[6h,i] Four symmetrical Gaussians were used. Each Gaussian is determined by three parameters: its position (i.e., the band maximum), its peak height, and its half-width (i.e., the fwhm). Background was simulated by a base line with height

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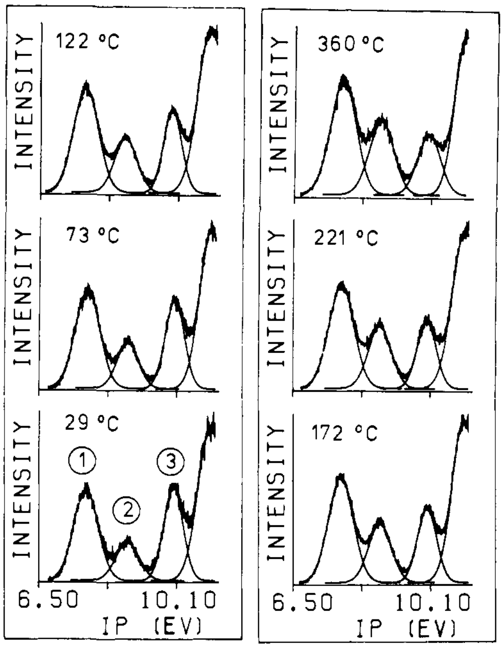


Figure 3. Gaussian curve-fitted photoelectron spectra of 1,2-dimethylhexahydropyridazine at six selected temperatures (29, 73, 122, 172, 221, and 360 °C).

Table I. Conformational Energy Differences for 1,2-Dihaloethane in Vapor and Liquid Phase

compound	$E°$(anti) − $E°$(gauche), kcal/mol vapor	liquid
$ClCH_2CH_2Cl$	−1.2	0.0
$BrCH_2CH_2Br$	−1.6	−0.7
$BrCH_2CH_2Cl$	−1.5	−0.5

being determined by the count rate prior to the first spectral band. This parameter was kept fixed and the remaining 12 parameters were determined in a nonlinear least-squares fit to the spectral trace. As judged from the standard deviations, the Gaussian simulation technique to photoelectron spectra (GSPES)[6h] worked excellently in the present case (cf. Figure 3). The data of the fit are, for the ionization potentials in eV (given with standard deviation), 7.75 ± 0.03, 8.79 ± 0.03, and 10.01 ± 0.02 for bands 1–3 for all temperatures applied and, for the relative band intentisites I_3/I_2 as a function of temperature, 1.98 ± 0.02 at 29 °C, 1.67 ± 0.03 at 73 °C, 1.24 ± 0.01 at 122 °C, 1.07 ± 0.01 at 172 °C, 0.90 ± 0.01 at 221 °C, 0.74 ± 0.01 at 291 °C, and 0.77 ± 0.02 at 360 °C.

From a plot of ln (I_3/I_2) vs. $1/T$ (Figure 4) $\Delta E°$ is found to be −1.20 ± 0.08 kcal/mol. This gas-phase value differs substantially from that in solution (by about 0.8 kcal/mol), although **lee** is favored in both cases.

The most reasonable explanation for the greater relative stability of **lee** over **lae** in the vapor phase than in solution is dipolar destabilization of **lae** caused by its gauche lone pairs. Conformation **lee**, with anti lone pairs, should have only a small dipole moment induced by the difference between methyl and normal alkyl substitution, but the dipole moment of **lae** is appreciable. Jones, Katritzky, and co-workers[9] determined the dipole moment of **1** to be 1.49 D (in cyclohexane) at room temperature, and since **1** is now known to exist about 40% as **lae** and 60% as **lee** (in acetone),[5] μ(**lae**) is in the range 3.7–3.0 D assuming that μ(**lee**) is in the range 0 (as previously assumed[9])–0.5 D. The energy difference between anti and gauche 1,2-dihaloethane conformations is structurally completely analogous to that between **lee** and

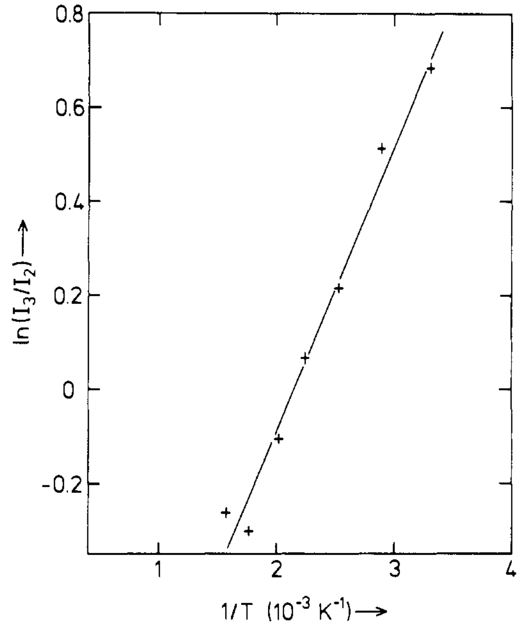
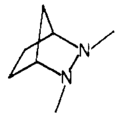
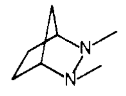


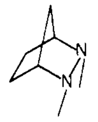
Figure 4. Plot of ln (I_3/I_2) vs. $1/T$ for 1,2-dimethylhexahydropyridazine over the temperature range 20–400 °C.

lae, and literature data[10] are summarized in Table I. Not only is the change in energy difference upon changing phase very similar for the dichloro compound **1** but the dipole moment of gauche 1,2-dichloromethane, 3.2 D,[11] is close to that estimated above for **lae**. It is generally accepted[10,11] that the favoring of the polar gauche form relative to the nonpolar anti form in solution is caused by the difference in dielectric between a vacuum and a liquid.

We also attempted VTPES measurements to estimate how high in energy the syn conformations of **2** lie above **2**-anti, which is


2-anti


2-syn$_1$


2-syn$_2$

the only conformation which can be seen by NMR.[12] The anti–syn energy gap is of particular interest in connection with the reverse Diels–Alder reactivity of syn and anti bicyclic tetrahydropyridazines.[13] Because of the difference in θ for syn and anti forms, the syn conformations should be detectable by PE spectroscopy. Unfortunately, no band for syn conformations of **2** was detected up to 400 °C, and thermal decomposition precluded experiments at higher tempertures.

Conclusion

The unusually good PE band resolution for the two conformations of **1** leads to the measurement of $\Delta E°$ for **1** being the most precise VTPES measurement yet reported, and it is also the first application of VTPES to a nonrotational conformational interconversion. The vapor-phase/liquid-phase energy differene in $\Delta E°$ of 0.8 kcal/mol is very similar to that for 1,2-dichloroethane, and the dipole moments of the gauche forms are also similar, both a little over 3 D. Potential stabilization of the more polar gauche form relative to the anti form in solution is the likely

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explanation in both cases. A similar change in ΔE° (anti–gauche) upon going from the vapor phase to solution is to be expected for other hydrazines, and should be employed if PE estimates of conformational mixtures are to be used in the rationalization of experiments conducted in solution.

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Time-Resolved Resonance Raman Spectroscopy: The Excited Triplet State of *all-trans*-β-Carotene

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Contribution from the Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark. Received March 5, 1980

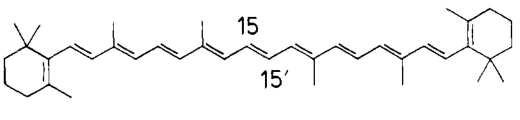
Abstract: The lowest excited triplet state of *all-trans*-β-carotene produced by pulse radiolysis has been studied by time-resolved resonance Raman spectroscopy. Six transient Raman bands at 965, 1009, 1125, 1188, 1236, and 1496 cm^{-1} were observed. The assignment of these transient bands to the triplet state of β-carotene is based on measurements of the dependence of the intensity upon irradiation dose and time. The Raman intensity was found to have the same dose and time dependence as the transient optical absorbance. The spectrum is discussed in detail, and it is concluded that the C=C double bond order is decreased in the triplet state and that the molecule may be substantially twisted, presumably at the 15,15′ bond, in the triplet state. The downward shift of the strong band in the C–C stretching region to 1125 cm^{-1}, however, still remains unexplained.

Introduction

The study of excited states of conjugated polyenes such as carotenes is of considerable interest in the understanding of photosynthesis. Previous studies of the lowest excited triplet state of *all-trans*-β-carotene in vitro include flash photolysis[1,2] and pulse radiolysis[3–5] experiments. All of these are based on the observation of a very strong transient optical absorption in the 510–530-nm region, which is due to the lowest triplet–triplet transition in β-carotene.

β-Carotene and related polyenes are also known to exhibit extremely strong enhancement in resonance Raman scattering. A large number of workers[6–15] have reported on different aspects of the resonance Raman spectrum of the ground state of β-carotene.

A few years ago, the technique of resonance Raman spectroscopy was extended by us to the study of short-lived radicals[16,17] and excited triplet states;[18] other groups[19–23] have reported on similar work. Recently Woodruff and co-workers[24] published the first time-resolved resonance Raman spectrum of the lowest triplet state of *all-trans*-β-carotene using pulse radiolysis. These authors detected three vibrational bands at 1495, 1126, and 1014 cm^{-1}, which were correlated to the ground-state in-phase double bond C=C stretching mode at 1521 cm^{-1}, the C—C in-plane single bond stretching mode at 1157 cm^{-1}, and a C—H in-plane bending mode at 1005 cm^{-1}, with the respective shifts when going to the triplet state. We report here a study under similar conditions essentially confirming the results of Woodruff and co-workers, but additionally finding three vibrational bands of the transient excited state at 965, 1188, and 1236 cm^{-1} and giving details with respect to the dependence of the vibrational spectra on time and the delivered irradiation dose.



ALL - trans β - CAROTENE

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