respectively. Addition of (*S*)-**1a** and (*S*)-**1b** in THF[7] to *t*-BuLi (1 equiv) in THF at −105 °C and protonation of thus formed (*P*)-**2a** (3 min[11]) and (*P*)-**2b** (10 min[11]), respectively, at −105 °C with CF_3COOH in THF[7] led to (*S*)-**1a** (96%) with 87% ee[6c] and (*S*)-**1b** (98%) with 92% (93%[12]) ee,[6a,c] respectively. Thus deprotonation of (*S*)-**1a** and (*S*)-**1b** with *t*-BuLi in THF seems to be slightly more selective than with *n*-BuLi in THF/*n*-hexane. Allylation of (*P*)-**2a** and (*P*)-**2b**, which were generated as described above with *t*-BuLi, with allyl iodide (2 equiv) in THF[7] at −70 and −100 °C, respectively, gave after a reaction time of 300 min and 10 min, respectively, the homoallylic sulfones (*R*)-**3a**α (79%) with ≥95% ee[6d] and (*R*)-**3b**α (80%) with 92% (95%[12]) ee,[6a] respectively. Hydroxyalkylation of (*P*)-**2b**, generated from (*S*)-**1b** with *t*-BuLi at −105 °C (10 min[11]), with benzaldehyde (2 equiv) in THF[7] at −105 °C (10 min) delivered the hydroxy sulfones (*S*,*R*)-**3b**β and (*S*,*S*)-**3b**β (84%; 3:2), each with 92% (95%[12]) ee.[6a] The (*R*) configuration at the α-C atom was provisionally assigned to the sulfones **3a**α and **3b**α and the (*S*) configuration to the sulfone **3b**β since the alkylation of (*P*)-**2a** and (*P*)-**2b** should proceed with the same sense of asymmetric induction as the protonation (vide infra).

The above enantioselectivities are composites and stem from the two stereoselective processes deprotonation and either protonation or alkylation. It follows, from cryoscopy,[1,9] $^6Li\{^1H\}$ NOE spectroscopy,[1] ab initio calculations,[13,14] X-ray structure analysis,[1,4,9,10,15,16] and other studies[17] of α-sulfonyl carbanion salts, that (*P*)-**2a** and (*P*)-**2b** are most probably monomeric contact ion pairs in THF at low temperatures endowed with (a) a chiral conformation, which is due to a stabilization by $n_C-\sigma^*_{SR}$ hyperconjugation[13] and a minimization of torsional strain, (b) a pyramidalized and hence chiral α-C atom, and (c) *a THF-solvated Li atom which is bound to the O atoms but not to the* α*-C atom* as depicted in Scheme I. Enantioselective formation of (*P*)-**2a** and (*P*)-**2b** can be attributed to a preferential intermolecular deprotonation of (*S*)-**1a** and (*S*)-**1b**, respectively, in conformation II (Scheme I) primarily for steric and electronic[13,14] reasons. It remains to be determined if and to what extent selectivity is due to a prior coordination of *n*-BuLi or *t*-BuLi to the sulfonyl group (O–Li)[18] of (*S*)-**1a** and (*S*)-**1b** followed by an intramolecular deprotonation in conformation II[5] as proposed for other systems.[19] Enantioselective protonation and alkylation of (*P*)-**2a** and (*P*)-**2b** occurs preferentially syn to the O atoms and can be attributed to two major factors whose individual contribution is not apparent yet: (1) steric hindrance by the CR_3 group and (2) the pyramidalization of the α-C atom,[20,21] which originates from a relief of torsional strain between the alkyl groups and the O atoms in conjunction with a shallow pyramidalization potential.[10b,14] From crystal structure analysis of a monomeric and several dimeric α-sulfonyl carbanion salts containing THF[4,9] or other ethers as ligands,[10a,15,22] however, a severe shielding of the α-C atom by the syn-positioned THF molecule in disolvated (*P*)-**2a**/**b**·2THF is perceptible. Therefore it seems likely that monosolvated (*P*)-**2a**/**b**·THF (Scheme I), which could be in a fast equilibrium with (*P*)-**2a**/**b**·2THF, is the decisive species. In this case, however, intramolecular protonation and alkylation via prior coordination of the electrophile to the Li atom[23] could be the preferred reaction path. In order to probe this possibility in the case of the protonation, (*P*)-**2b** generated from (*S*)-**1b** with *n*-BuLi in THF at −105 °C was treated at −105 °C with HBF_4 in Et_2O.[7] Here, too, (*S*)-**1b** was isolated but with the slightly lower ee value of 82%.[6b]

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

(12) Value corrected for partial racemization of (*P*)-**2b**.
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Thermodynamic Analysis of β-Turn Formation in Pro-Ala, Pro-Gly, and Pro-Val Model Peptides in Methylene Chloride

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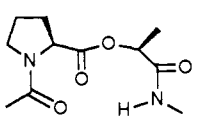
β-turns constitute the smallest common element of protein secondary structure[1] accounting for up to one-third of the residues in globular proteins.[2] Information on the intrinsic stability of such turns in various environments should provide insight on the origin of protein folding patterns. Although turn conformations have been detected within small linear peptides in numerous solvents,[3] only a few attempts have been made to quantify the extent of turn formation.[4] Thermodynamic relationships between folded and open peptide conformations have been explored computationally,[5] but not experimentally. We report a thermodynamic assessment of β-turn formation in Pro-Ala, Pro-Gly, and Pro-Val model peptides in methylene chloride solution.[6]

Figure 1 shows the temperature dependences of the amide proton chemical shifts ($\Delta\delta NH/\Delta T$) of Ac-L-Pro-L-Ala-NHMe (**1**) and two reference compounds, depsipeptides Ac-L-Pro-L-Lac-NHMe (**2**)[7] and c-$C_5H_9C(=O)$-Lac-NHMe (**3**), in CD_2Cl_2.



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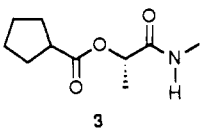

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(6) Abbreviations: Ala = alanine residue, Gly = glycine residue, Lac = lactic acid reside, Pro = proline residue, c-$C_5H_{11}C(=O)$ = cyclopentylcarbonyl.

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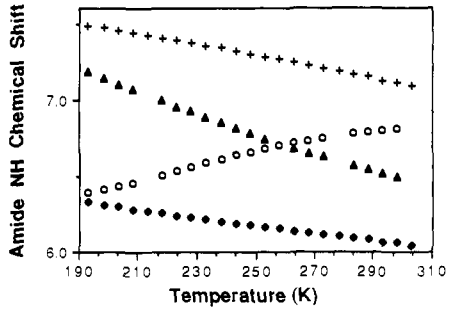


Figure 1. Temperature dependences of the amide proton ^1H NMR chemical shifts for **1**, Ala NH (○) and C-terminal N–H (▲), **2** (+), and **3** (◆) in CD_2Cl_2. The chemical shifts for **1** have been linearly extrapolated to infinite dilution, using data from 5, 2, 1, and 0.5 mM samples (only very small deviations were observed between these extrapolated values and the data obtained at 1 mM (see the supplementary material)). The data for **2** and **3** were obtained with 1 mM samples; no hydrogen-bonded N–H stretch signal could be observed for 1 mM **3** in CH_2Cl_2 by IR throughout this temperature range, and only a very small amount of non-hydrogen-bonded N–H stretch was detected for **2**. Samples were prepared and spectral data obtained as described in ref 14.

Under these conditions, equilibration among alternative intramolecularly hydrogen-bonded and non-hydrogen-bonded[8] states is rapid on the NMR time scale, and conformationally averaged δNH values are observed.[9] The $\Delta\delta NH/\Delta T$ data for **2** provide a good representation of the C-terminal NH of **1** in the internally C=O···H—N hydrogen-bonded β-turn state, because corresponding IR data[10] show that 10-membered hydrogen-bonded ring formation is nearly complete in CH_2Cl_2 (this observation is consistent with IR data for **2** in CCl_4 from Boussard et al.[7a]). Judged against this standard, the data for the C-terminal NH of **1** suggest that the β-turn folding pattern of this peptide is increasingly populated at lower temperatures. The positive $\Delta\delta NH/\Delta T$ of the Ala NH suggests that 7-membered-ring hydrogen bonding (γ-turn formation) across the proline residue occurs to an increasing extent as the temperature is raised.

Variable-temperature IR data for **1** in CH_2Cl_2 (Figure 2) are consistent with the hypothesis that β-turn formation is increasingly favored at lower temperatures. At 297 K, three distinct N—H stretch bands are observed. Previous studies of Pro-Ala derivatives have shown that the two bands at higher energy arise from N—H moieties not involved in C=O···H—N interactions, with the band at 3448 cm^{-1} assigned to the C-terminal N—H and the band at 3426 cm^{-1} assigned to the Ala N—H.[11] The broader band at 3360 cm^{-1} arises from intramolecular C=O···H—N interactions. At 205 K, the highest energy band has diminished substantially, indicating that there is relatively little C-terminal NH free of intramolecular hydrogen bonding; however, considerable Ala NH is non-hydrogen-bonded at the low temperature. Since very little hydrogen-bonded N—H stretch is detected for dilute c-C_5H_9C(=O)-Ala-NHMe (**4**) at 297 or 205 K in CH_2Cl_2,[10] we conclude from Figure 2b that intramolecular hydrogen bonding involving the C-terminal NH of **1** at 205 K occurs largely in the 10-membered ring (β-turn), rather than in a 7-membered ring (γ-turn) across the Ala residue.

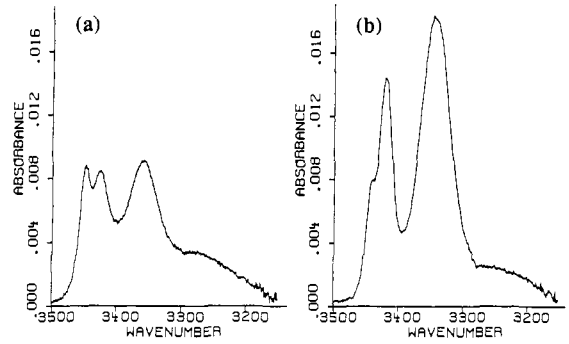
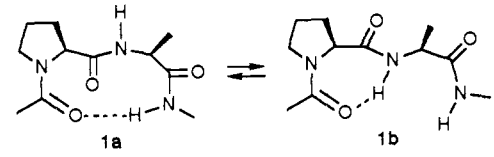


Figure 2. N–H stretch region FT-IR data for a 1 mM sample of **1** in CH_2Cl_2 minus the spectrum of pure CH_2Cl_2 at that temperature: (a) spectrum at 297 K, absorption maxima at 3448, 3426, and 3360 cm^{-1}; (b) spectrum at 205 K, absorption maxima at 3440 (shoulder), 3421, and 3346 cm^{-1}. Samples were prepared and spectra obtained as described in ref 14.

Our observations with the Pro-Ala dipeptide indicate that an intramolecularly hydrogen-bonded β-turn (**1a**) is enthalpically preferable to all other available folding patterns under these conditions. In contrast, the internally hydrogen-bonded state (γ-turn) of Ac-Pro-NHMe has little or no enthalpic advantage over the non-hydrogen-bonded state in CH_2Cl_2.[12] For the Pro-Ala



1a **1b**

dipeptide, the energetic balance between folding patterns **1a** and **1b** in methylene chloride is apparently sufficiently delicate that the entropic advantage of the 7-membered hydrogen-bonded ring allows this γ-turn to become increasingly competitive with the β-turn at higher temperatures. The enthalpic disparity presumably results from differences in the strengths of the hydrogen bonds (arising from variations in geometry) and in other steric and/or dipolar interactions that develop as the peptide backbone folds back upon itself.[13]

We have previously shown that $\Delta\delta NH/\Delta T$ data can provide thermodynamic information on folding processes in small molecules.[14] Such an analysis is possible for **1**, based on the C-terminal $\Delta\delta NH/\Delta T$ data, if we use the $\Delta\delta NH/\Delta T$ data for **2** to represent the β-turn state and $\Delta\delta NH/\Delta T$ data for **3** to represent the non-β-turn state. (The "non-β-turn state" operationally defined here involves multiple conformations, including the γ-turn across Pro and conformations lacking any C=O···H—N hydrogen bonds). A van't Hoff plot (210–305 K) indicates that the β-turn is enthalpically favored by 1.4 kcal/mol relative to the non-β-turn state.[10,15] Similar analyses of Ac-Pro-Gly-NHMe and the Pro-Val analogue indicate that β-turn formation is enthalpically favored by 1.7 and 0.6 kcal/mol, respectively in methylene chloride.[10,15,16] The differences in these derived thermodynamic values are significant in terms of the reproducibility of the NMR measurements, but systematic error arising from the choice of limiting $\Delta\delta NH/\Delta T$ values is more difficult to account for and may be as high as 30%.[14] Since, however, such errors should have similar impacts on the

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(8) We use the term "non-hydrogen-bonded" to signify the absence of a strong N—H···O=C interaction. Such protons are presumably engaged in weak interactions with the solvent.

(9) ^1H NMR data indicate minor populations of the cis-proline rotameric forms of **1** (ca. 8%) and **2** (ca. 2%) at 298 K in CD_2Cl_2; these populations do not change significantly at 193 K. The *cis*-proline forms of **1** and **2** cannot adopt β-turn-like folding patterns.

(10) Data available in the supplementary material.

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(15) For all three dipeptides, our analysis indicates the β-turn folding pattern to be entropically disfavored by ca. 4–5 eu. Because these entropies are obtained from the intercept of a van't Hoff plot, they are subject to greater uncertainty than the enthalpies, which are obtained from a slope.

(16) Previous studies, including those involving dipeptides similar to **1** (ref 11a), have shown that Pro-Ala and Pro-Val sequences favor type I turns while Pro-Gly favors type II turns (refs 1 and 2).

three analyses, the enthalpic differences among the Pro-Ala, Pro-Gly, and Pro-Val systems are significant. Statistical analyses of protein crystal structures indicate a decreasing tendency for β-turn formation across Pro-Gly, Pro-Ala, and Pro-Val sequences.[2,16,17]

The conformational behavior of these model peptides in a solvent of low dielectric constant is relevant to the protein folding problem because the interior of a folded protein is thought to be characterized by a relatively low dielectric constant[18] and because many proteins adopt their native conformations is nonpolar locales (e.g., the interior of a biomembrane). The thermodynamic data we have provided should also be useful for evaluating the accuracy with which computational methods reproduce the balance of noncovalent forces that controls peptide conformation.[5]

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Supplementary Material Available: Figures pertaining to the van't Hoff analyses of β-turn formation in the Pro-Ala, Pro-Gly, and Pro-Val dipeptides (7 pages). Ordering information is given on any current masthead page.

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Evidence from Photoinduced EPR for a Radical Intermediate during Photolysis of Cyclobutane Thymine Dimer by DNA Photolyase

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Ultraviolet light (200–300 nm) induces adjacent pyrimidines in DNA to undergo a symmetry-allowed [2 + 2] cycloaddition reaction, which produces pyrimidine dimers (Pyr⟨⟩Pyr).[1] DNA photolyases repair the Pyr⟨⟩Pyr by utilizing photonic energy of near-UV and visible light (300–500 nm).[2] All photolyases characterized to date contain $FADH_2$ as the catalytic cofactor in addition to a second chromophore of high extinction coefficient which functions as a photoantenna, absorbing 300–500 nm photons and transferring the excitation energy to $FADH_2$.[3-7] On the basis of model reactions with a variety of photosensitizers,[8] it has been proposed that enzymatic Pyr⟨⟩Pyr splitting is initiated by electron transfer between $FADH_2$ and the photodimer.[2a,7a] A recent picosecond flash photolysis study revealed the build-up of a new absorption band ($\lambda \approx 400$ nm) following the quenching of the excited singlet state of $FADH_2$ by Pyr⟨⟩Pyr.[9] The 400-nm species was not identified, but it was attributed to a reaction intermediate produced during catalysis. In this communication, we use time-resolved EPR to show that a radical intermediate is generated during flash-induced dimer repair by DNA photolyase.

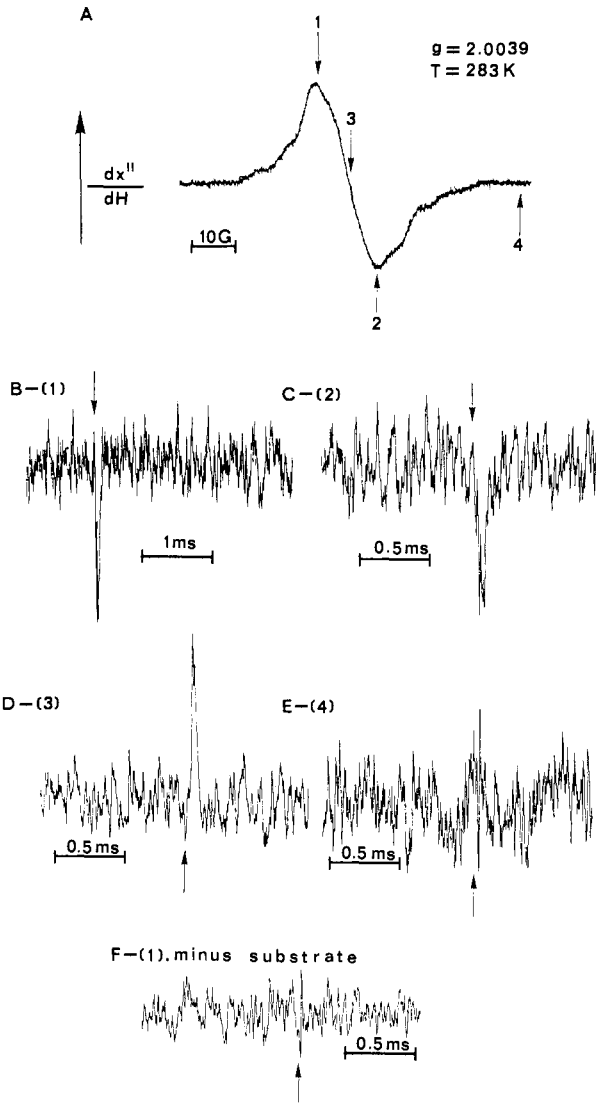

Figure 1. EPR detection of radical transients in *E. coli* DNA photolyase catalyzed pyrimidine dimer splitting reaction. A is the dark-stable EPR spectrum of E–$FADH^*$, and B–E are the kinetic transients of E–$FADH_2$ + T⟨⟩T at field positions 1–4, respectively. F is the kinetic transient of E–$FADH_2$ at field position 1 in the absence of T⟨⟩T. At each field position, 1200 flashes (positions indicated by arrows in B–F) were averaged. The spectrometer gain was 1.6×10^6 for all kinetic traces. For each measurement, fresh sample was used.

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