The strain energy in 1,3-dehydroadamantanes is not especially great however; scanning calorimetric measurements on 5-cyanodehydroadamantane show endotherms at 69–71° (2.08 ± 0.05 kcal/mol), 99–102° (1.41 ± 0.02 kcal/mol), and a relatively large exotherm (28.6 ± 1.2 kcal/mol) at *ca.* 120–145° (heating rate 10°/min under nitrogen). These correspond respectively to a phase transition into a mesomorphic plastic-crystal,[19] then melting at 99–102°, and finally 1,3 polymerization to a hard clear solid (mp > 300°, the ir cyano band at 2250 cm^{-1} is retained in the polymer). Heats of polymerization have been directly related to strain energies,[20] and assuming that the polyadamantane is relatively free from conformational strain, the strain of near 28.6 kcal/mol in **1** (X = CN) is close to that of cyclopropane (28 kcal/mol,[21] calculated heat of polymerization 27 kcal/mol at 25° [22]). Special stability in p–σ bonding of two inverted carbon atoms such as in 1,3-dehydroadamantanes has been described theoretically.[23] Even if the unusual bonding in **1** and related compounds results in no great increase in energies, the reactivities of these propellane compounds are much greater than that of any simple cyclopropane. This is shown by the reactions at low temperatures with oxygen or iodine, the ring opening reactions of **1** (X = OH or OCH_3), and the polymerization of **1** (X = CN). The ring openings of **1** (X = OH or OCH_3), which are apparently made possible by the electron donor capabilities of the oxygen atom, may be aided by the predicted polar ("zwitterionic"[23]) character of this type of cyclopropane carbon–carbon bond.

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Conformation of Angiotensin II in Aqueous Solution. Evidence for the γ-Turn Model

Sir:

We wish to report nmr data supporting the proposed γ-turn model[1] for the conformation of Asn_1Val_5 angiotensin II in aqueous solution. Two possible models were suggested based on the finding of two abnormally slowly exchanging hydrogens[2] and dialysis data.[3] The β-turn model had two intramolecular hydrogen bonds involving the amide protons of Val_3 and His_6, while the previously undescribed γ turn involved the Val_3 and Val_5 amide protons in hydrogen bonds. Energy minimization calculations indicate that the γ turn has a potential energy minimum equal to or less than that expected for the β turn.[4] A γ turn was recently identified in thermolysin based on X-ray diffraction analysis.[5]

In the experiments reported here we simultaneously followed the spectral changes in the α region as the disappearance of the amide resonances was observed in deuterium oxide. This technique allows simultaneous measurement of the rates of exchange of the amide protons and the identification of their corresponding α protons since the coupling between α and amide protons disappears as deuterium replaces amide hydrogen. The subsequent assignment of the α-proton resonances is then achieved by conventional spin decoupling in deuterium oxide.

The Asn_1Val_5 angiotensin II was synthesized by the solid phase method[6] and was homogeneous by high voltage electrophoresis at pH 1.7, paper chromatography in three systems, and amino acid analysis. It was digested down to proline by aminopeptidase M. Nmr spectra were recorded at a probe temperature of 17 ± 1° on a Varian HR 220 spectrometer operated by a consortium at Rockefeller University. The deuterium exchange experiments were done at pH 2.5 adjusted with trifluoroacetic acid.

The half-lives for the exchange of the amide resonances in angiotensin II are listed in Table I. The rates

Table I. Exchange Data and Resonance Assignments for Angiotensin II

Resonance line	Half-life, min (pH 2.3, 17°)	Residue	Evidence
A	Fast[a]	Arg_2	Exchange rate
B	5.3 ± 0.5	His_6	pH profile
C	15.9 ± 0.6	Tyr_4	
D	5.8 ± 0.8	Phe_8	pH profile
E	28.7 ± 1.2		
F	30.2 ± 0.9	Val_3, Val_5	Decoupling

[a] Not observed after 4.5 min.

were obtained from a least-squares fit of a semilogarithmic plot of the resonance amplitudes *vs.* time. After 20 min of exchange only the amides associated with resonances E and F are still protonated to a significant extent. From Figure 1, the collapse of the α resonances at 4.04 and 4.13 ppm to two doublets after 23 min of exchange is therefore entirely due to the two slowly exchanging amide protons, E and F. The spin-decoupling experiments gave the results shown in Figure 2. In each case the β-proton resonances were irradiated while the α and γ resonances were recorded. Since the resonance near 0.8 ppm can be uniquely assigned to the γ protons of valine, the slowly exchanging amide protons must also be assigned to the two valine residues.

The pH and temperature dependences of the amide region have also been studied and will be reported elsewhere in greater detail. The results of these studies permit the assignment of the remaining amide resonances of angiotensin II. Resonance A shows an en-

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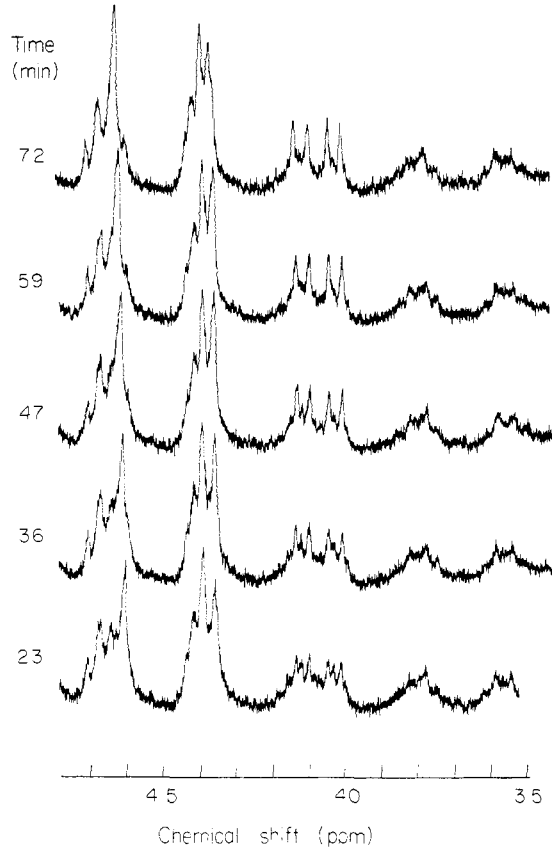

Figure 1. The α-proton region of the 220-MHz spectrum of angiotensin II during deuterium exchange. As a function of time the two resonances at 4.04 and 4.13 ppm simplify as they are no longer coupled to pronated amides.

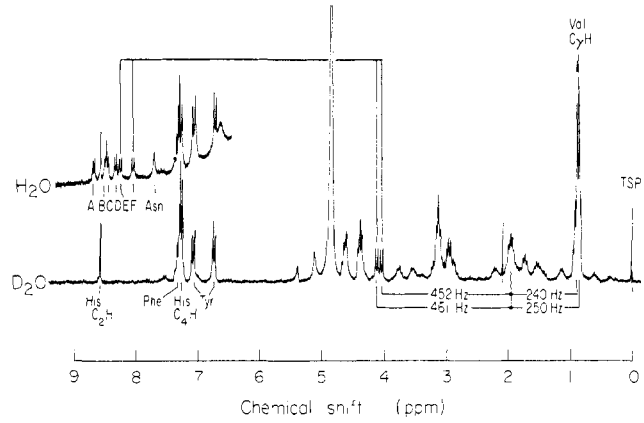

Figure 2. The 220-MHz spectrum of angiotensin II in D_2O and H_2O at pH 2.5 and 17°.

hanced rate of base-catalyzed proton exchange as it was not observed 4.5 min after initiating the deuterium exchange experiment in Table I. In addition, it begins to broaden earlier than any other amide resonance as either the pH or the temperature is increased. It can therefore be assigned as the N-terminal amide of Arg_2 by the known exchange characteristics of N-terminal peptide amides.[7] A partial pH profile of the chemical shift of resonance B assigns it to the amide of His_6. The pH profile of resonance D identifies it as the amide proton of Phe_8. By elimination, resonance C can be assigned to the amide proton of Tyr_4 as is summarized in Table I.

The observation of the two slowly exchanging amide protons in Asn_1Val_5 angiotensin II is in agreement with tritium–hydrogen exchange results.[2] Assignment of these protons to the valines rules out the β-turn model, at least in water since it requires a slowly exchanging histidine amide. The observed half-life of 16 min for the exchange of the amide of Tyr_4 is longer than the value of 6–8 min that can be predicted from published data.[7] A shielding of the amide of Tyr_4 could occur from a folding of the C-terminal end of the peptide chain in a conformation similar to the model proposed by Fermandjian, *et al.*,[8] on the basis of circular dichroism, infrared, and Raman studies. The assignment of the slowly exchanging amides to Val_3 and Val_5 is in disagreement with the nmr findings of Weinkam and Jorgensen[9] and Fermandjian, *et al.*,[10] unless a different conformation results from Me_2SO. The data strongly support the proposed γ-turn conformation of angiotensin II in aqueous solution. This folding pattern has been proposed as the most stable conformation in solution as well as the most interesting one pharmacologically.[1,2] Comparative studies in this laboratory with the C-terminal hexapeptide fragment of angiotensin II and with angiotensin I provide evidence for similar conformations, with varying degrees of stability, of all three peptides in aqueous solution.[11]

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trans-Hydridodinitrogenbis-[1,2-bis(diphenylphosphino)ethane]rhenium(I)

Sir:

Although a substantial number of dinitrogen complexes have been characterized, only a few of these also contain hydrogen bonded to the metal atom. The known hydridodinitrogen complexes are so far restricted to group VIII metals (Fe, Co, Ru, and Os) and tungsten. In the present communication we report *trans*-$ReH(N_2)(dppe)_2$ (dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), the second hydridodinitrogen complex outside of group VIII. Interest in this compound is enhanced by its ability to undergo a variety of reactions. We report examples of protonation at the metal, oxidative addition with loss of N_2, reaction of the Re–H bond with halocarbons, and simple replacement of dinitrogen. Taken together these represent a novel chemistry for a rhenium complex. Similar reactions have not