exhibits only a weak version of the trough at 236 mμ ([m'] −4800°).

Circular dichroism data in TFE (Figure 3) show a broad unsymmetrical negative band with a trough at 223 mμ (Δε −10.0). In dioxane and methylene chloride once again we observe that the trough undergoes a red shift to 226 mμ. A second circular dichroism band appears in TFE at 192 mμ (Δε +8.5), with a much smaller area under the curve. We believe that this peak has its origin in a 190-mμ amide $\pi \rightarrow \pi^*$ transition, while the higher wavelength trough is composed of the overlapping of $\pi \rightarrow \pi^*$ and large $n_1 \rightarrow \pi^*$ transitions for the amide group.[14-16] It appears as if a positive band represents the low-wavelength part of a split $\pi \rightarrow \pi^*$ transition. The higher wavelength negative portion falls under the large $n-\pi^*$ band. The circular dichroism of the model compound (Figure 3) shows only the trough at 223 mμ (Δε +1.5), and there does not appear to be a positive $\pi \rightarrow \pi^*$ absorption in the 192-mμ region.

The helical structure of poly-L-proline II as noted above was clearly established by X-ray diffraction analysis.[9] In spite of the fact that it is a left-handed helix, this polymer exhibits negative optical rotatory dispersion and circular dichroism peaks.[6,7] We obtained similar spectral results for poly-N-methyl-L-alanine; our results do differ somewhat from those obtained with poly-L-proline in that no *cis* form has been detected.

The α-amino acid N-carboxyanhydride (NCA) of N-methyl-L-alanine was prepared from alanine by the method of Quitt, Hellerbach, and Vogel.[17] The NCA was then polymerized by benzylamine initiation in anhydrous dioxane over a period of 2–3 weeks to obtain high molecular weight poly-N-methyl-L-alanine (mp 280–290°) in high yield.

Acknowledgment. We wish to acknowledge the generous support of this research by National Science Foundation Grant No. GB 2896.

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Murray Goodman, Maria Fried
Department of Chemistry, Polytechnic Institute of Brooklyn
Brooklyn, New York

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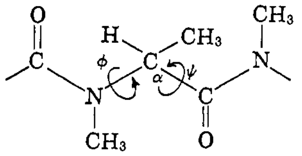
Conformational Aspects of Polypeptide Structure. XXI. Helical Poly-N-methyl-L-alanine. Theoretical Results

Sir:

In the preceding paper[1] compelling evidence in support of a helical conformation for poly-N-methyl-L-alanine was presented. In the present study stable helical forms of this peptide chain are determined by calculations of conformational energies using well-established methods.[2-5] Since it has been amply demonstrated that steric interactions are of predominant importance in the determination of allowed conformations of chain molecules,[5,6] the preliminary calculations described here include only this type of nonbonded interaction.[7] Additionally, it is assumed that all of the amide bonds in the poly-N-methyl-L-alanine chain are *trans*, and that rotational angles about N–CH_3 and C_α–CH_3 bonds are fixed and thus do not enter as variables in the conformational energy calculation. The torsional energy contribution for rotations about N–C_α and C_α–CO skeletal bonds was calculated assuming potential minima at 0 and ±120° with barrier heights of 1.5 and 1.0 kcal mole^{-1}, respectively, at ±60 and 180°.[8] van der Waals interactions between all pairs of nonbonded atoms in the dipeptide sequence were estimated using standard bond angles and bond lengths[4] and Lennard-Jones "6–12" potential functions.[4] The sum of the torsional and van der Waals interaction energies, taken to be the conformational energy E, was plotted as a function of the rotation angles φ about N–C_α and ψ about C_α–CO bonds in the customary manner.[9] Both angles were varied from 0 to 360° in 10° increments.



The most striking feature of the resulting contour map[10] of the conformational energy is that regions representing 5 kcal mole^{-1} or less of energy make up only approximately 2.5% of the total topographical area. Since only these regions are accessible to the chain at normal temperatures, the poly-N-methyl-L-alanine chain is seen to be extremely restricted in the number of conformations it can assume. Four minima in the energy were found, and are described in Table I.

Table I. Low-Energy Conformations of the Poly-N-methyl-L-alanine Chain

Helix	φ, deg	ψ, deg	E, kcal mole^{-1}
I	30	250	−0.85
II	210	250	−0.33
III	80	345	2.54
IV	240	345	1.50

Of immediate interest is the fact that the right-handed α-helix (φ = 132°, ψ = 123°),[9,11] a stable conformation for poly-L-alanine,[4,8] does *not* represent a low-energy form for poly-N-methyl-L-alanine. This is a result of severe steric repulsion between α-methyl and N-methyl groups in this conformation of the N-substituted chain.

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(7) This is certainly a good approximation in the case of the poly-N-methyl-L-alanine chain because of the severity and multitude of steric interactions compared to those occurring in polypeptide chains unsubstituted at the nitrogen atom.

(8) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.*, **23**, 47 (1967).

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It should be pointed out that one or more of the conformations listed in Table I may be excluded due to steric overlap between atoms separated by *several* peptide units.[4,8] We therefore inspected space-filling models of these forms for possible conflicts of this type.

Conformation I represents a right-handed helix that is approximately threefold; its energy, -0.85 kcal mole^{-1}, is the lowest of the four observed minima. Conformation II is very similar to the left-handed α-helix, for which $\varphi = 228°$ and $\psi = 237°$.[11] It is impossible to build a model of this conformation, however, because of extremely strong steric repulsions between oxygen atoms and N-methyl hydrogen atoms separated from them by three peptide units. The third conformation represents a left-handed helix strikingly similar to the poly-L-proline II helix.[12] Conformation IV represents a right-handed helix with approximately five peptide units per turn.

This analysis and published spectral data[1] strongly suggest that poly-N-methyl-L-alanine is helical, even though it cannot form intramolecular hydrogen bonds and does not contain pyrrolidine rings. On the basis of the relative conformational energies, the right-handed helix I seems to represent the most stable conformation for this acyclic polypeptide.

Through additional experiments and calculations we hope to extend our knowledge of some of the forces leading to helicity in polypeptides in general.[13]

Acknowledgment. We wish to acknowledge the generous support of this research by National Science Foundation Grant No. GB 2896.

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[13] NOTE ADDED IN PROOF. After submission of our paper, A. M. Liquori and P. De Santis (University of Rome) kindly placed at our disposal their calculations of conformational energies of longer sequences of N-methyl-L-alanine residues. Their results confirm in essentials the conclusions presented here.

J. E. Mark, Murray Goodman
Department of Chemistry, Polytechnic Institute of Brooklyn
Brooklyn, New York

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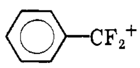
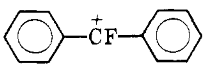
Stable Carbonium Ions. XXXVII.[1]
Alkyl- and Arylalkylfluorocarbonium Ions. The Dimethyl- and Phenylmethylfluorocarbonium Ion

Sir:

Recently we have reported[2] the observation of the first fluorocarbonium ions: the phenyl- and diphenylfluorocarbonium ions (I and II).



I



II

We wish to report now the first examples of stable alkyl- and arylalkylfluorocarbonium ions.

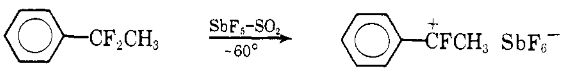
Dimethylfluorocarbonium ion (III) was obtained when 2,2-difluoropropane (prepared from acetone and sulfur tetrafluoride[3]) was dissolved in SbF_5–SO_2 solution at $-60°$. Ion III was also obtained by protonation of 2-fluoropropene with FSO_3H-SbF_5.

$$CH_3CF_2CH_3 \xrightarrow[-60°]{SbF_5-SO_2} CH_3\overset{+}{C}FCH_3\ SbF_6^- \quad \text{III}$$

$$CH_3CF{=}CH_2 \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} CH_3\overset{+}{C}FCH_3\ SbF_5FSO_3^-$$

The pmr spectrum of III (Figure 1) shows the methyl protons as a doublet at -3.93 ppm ($J_{HF} = 26$ Hz) substantially deshielded from their position in the covalent starting material at -1.36 ppm ($J_{HF} = 19$ Hz). The ^{19}F nmr spectrum of III (Figure 2) shows the fluorine atom of III as an extremely deshielded septuplet at -182.0 ppm as compared with the position of the fluorine resonance in the covalent 2,2-difluoropropane ($+81.5$ ppm). The deshielding in ion III thus is -263.5 ppm, clearly indicating the presence of the dimethylfluorocarbonium ion. The coupling constant (J_{HF}) increases from 19 to 26 Hz upon ionization.

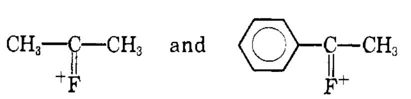
Phenylmethylfluorocarbonium ion (α-fluorostyryl cation) (IV) was obtained when α,α-difluoroethylbenzene was dissolved[4] in SbF_5–SO_2 at $-60°$.



IV

The ^1H and ^{19}F resonance spectra of ion IV were obtained (Figures 3 and 4). The pmr spectrum shows the methyl doublet at -3.70 ppm ($J_{HF} = 23$ Hz), compared with -1.65 ppm ($J_{HF} = 17.6$ Hz) in the covalent starting material. The ring protons are also highly deshielded and show a characteristic phenylcarbonium ion pattern. The ^{19}F resonance of ion IV shows the fluorine atom as a highly deshielded quadruplet at -51.3 ppm, as compared with the fluorine resonance of the covalent α,α-difluoroethylbenzene ($+89.2$ ppm).

The phenylmethylcarbonium ion (styryl cation) is extremely difficult to observe in acidic solution as a stable species. It loses a proton easily (at least in equilibrium), and the styrene formed undergoes extremely rapid secondary reaction (alkylation, polymerization, etc.). In contrast, the α-fluorostyryl cation IV is quite stable, despite the fact that proton elimination still could yield α-fluorostyrene and subsequent side reactions. Ion IV as well ion III are tertiary carbonium ions, where the α-fluorine atoms through backdonation of its unshared electron pairs into the vacant sp^2-carbon orbital help stabilize the carbonium ions. Resonance forms like



must contribute to stabilization. The considerable fluorine deshielding effects directly substantiate this suggestion.

Attempts to prepare CH_3CHF^+ (V) or $CH_3CF_2^+$ (VII) either by protonation of vinyl or vinylidene fluoride with FSO_3H-SbF_5 or from CH_3CHFCl or CH_3-CF_2Cl with SbF_5 were unsuccessful.

Protonation of vinyl fluoride gave a product whose pmr spectrum shows a low-field doublet of quartets at -6.5 ppm ($J_{HH} = 5$ Hz; $J_{HF\,gem} = 5.65$ Hz) and an up-

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[1] Part XXXVI: G. A. Olah and D. H. O'Brien, *J. Am. Chem. Soc.*, in press.

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