the heteronuclear complex containing the lanthanide atom is stabilized to a greater extent than the homotrinulcear zinc(II) complex. As a result, only the central zinc ion of the homo complex formed initially is replaced quantitatively by the lanthanide(III) ion.

We believe that this facile and effective strategy to synthesize helical or cyclic heteronuclear complexes will open a new way to construct various functionalized coordination systems

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The Structure of Neutral Proline**

Alberto Lesarri, Santiago Mata, Emilio J. Cocinero, Susana Blanco, Juan C. López, and José L. Alonso*

The conformational behavior of amino acids is of critical importance to understand the dynamic role of these molecules in protein or polypeptide formation.[1] Consequently, extensive structural research has been conducted on amino acids in their natural solid-state phase. This point is worth noting because solid amino acids present a zwitterionic structure in the solid state (i.e. a bipolar, ionized form of the type $^+H_3N{-}CH(R){-}COO^-$), which does not occur in the polypeptide chain.[2] To obtain the structure of the neutral form of amino acids, research should be conducted in the gas phase, in an atmosphere that is essentially free of intermolecular interactions with other partners. In particular, the collisionless environment of a supersonic jet[3] seems particularly well adapted for such studies. The obvious difficulties of experimental studies in the gas phase are caused by the high melting points and associated low vapor pressures of amino acids. Classical heating methods were employed for the analysis of the only two amino acids that have been studied to date in the gas phase, glycine[4] and alanine[5]. As an alternative, laser ablation offers an advantageous way of vaporizing solid organic compounds,[6] in which the fast desorption produced by the energy of a laser pulse prevents the thermal decomposition caused by the heating methods. Despite the extensive use of laser ablation with mass-spectrometry techniques,[7] few groups have explored the possibility of combining laser ablation with the high resolution of rotational spectroscopy. Suenram et al.[8] and Walker and Gerry[9] independently developed two laser-ablation devices, mostly devoted to investigate the rotational spectra of metal oxides and halides. The first was also applied in the structural study of glycine in the gas phase, but it was reported that the classical heating method was more reliable.[10]

In this context we have configured a new experiment in which a laser-ablation system especially constructed for solid organic compounds is combined with Fourier-transform (FT) microwave spectroscopy in a supersonic jet, to allow the structural characterization of the vaporized species in the gas phase. The ablation nozzle is accommodated at the back side of one mirror of the Fabry–Pérot resonator, close to the resonator axis (Figure 1). An oil diffusion pump, backed by a roots blower, evacuates the chamber. Laser ablation is produced by the second harmonic ($\lambda = 532$ nm) of a pulsed

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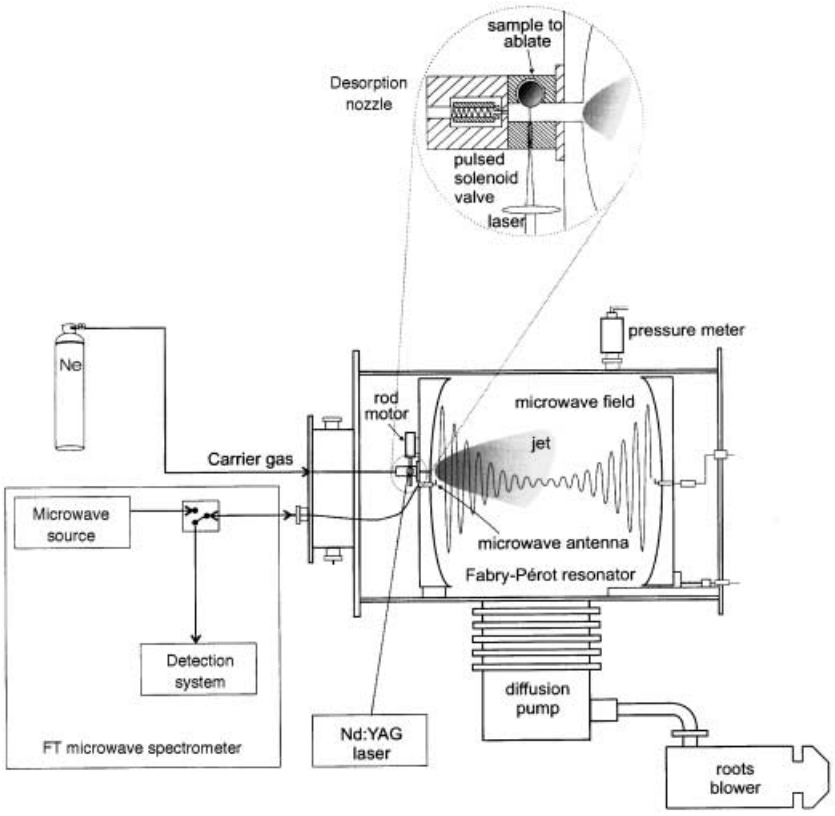

Figure 1. A general block diagram of the experimental setup.

Q-switching Nd:YAG laser, focused on the target rod trough a small lateral orifice of the desorption nozzle. The sample rod is held vertically at the nozzle exit channel and is rotated and translated, so the laser beam reaches a different fresh surface position for each pulse. The experimental sequence starts with a gas pulse of a light inert gas, followed by a laser hit on the solid sample, which generates the ablation products. These desorbed species are seeded in the carrier gas and expanded supersonically between the mirrors of the evacuated Fabry–Pérot microwave resonator, to create a supersonic expansion. A very short microwave pulse from the FT microwave spectrometer follows, which induces a polarization in the vaporized molecules. Once the microwave excitation ceases, the molecular emission signal containing the resonance frequencies that correspond to the rotational transitions is captured in the time domain by the detection system of the spectrometer. Finally, the usual frequency-domain spectrum is obtained from the Fourier transformation of the time-domain signal. Several thousand cycles can be phase-coherently coadded to detect very weak transitions. The species present in the supersonic expansion are thus probed by their rotational spectrum. Initial tests carried out with the known rotational spectrum of glycine[4,10] and alanine[5] confirmed the excellent performance of the experiment.

Proline (m.p. 228 °C) is unique among natural amino acids because of its special role in the formation of polypeptides.[11] This amino acid is the only natural amino acid which contains a secondary amino group as part of a flexible five-membered ring. Structural studies conducted in the condensed phase,[12–17] which include an X-ray crystal-diffraction analysis of the zwitterion,[12] yield different interpretations concerning the ring conformation. A recent infrared spectroscopic study of matrix-isolated neutral proline[18] has been interpreted with the help of ab initio calculations in terms of the existence of two bent conformers. However, to date no experimental structure of neutral proline has been reported.

The conformational behavior of isolated proline will be conditioned by the potential formation of three different types of intramolecular hydrogen bonds. Type **1** involves hydrogen bonding between the lone pair of the nitrogen atom and the hydroxy group hydrogen atom (N···H–O). Types **2** and **3** have an interaction that links the hydrogen atom on the imino group to the the oxygen atom of the carbonyl (N–H···O=C) and hydroxy (N–H···O–H) groups, respectively. Furthermore, and assuming a bent configuration of the pyrrolidine ring, *endo*-like (a) and *exo*-like (b) conformations with respect to the carboxy moiety can also be expected. Hence, a total of six plausible conformers, shown in Figure 2, can be initially considered. All of them can be independently detected in the supersonic expansion by their rotational spectra, just as in the case of a mixture of stable species, their individual structures can be determined.

The analysis of the rotational spectrum was started with the aid of the estimated values of rotational constants for each of the conformers in Figure 2. After completing a wide frequency scan, it was possible to assign a set of transitions to an asymmetrical, nearly prolate rotor. All measured lines exhibit ^{14}N nuclear quadrupole hyperfine structure,[19] which helped

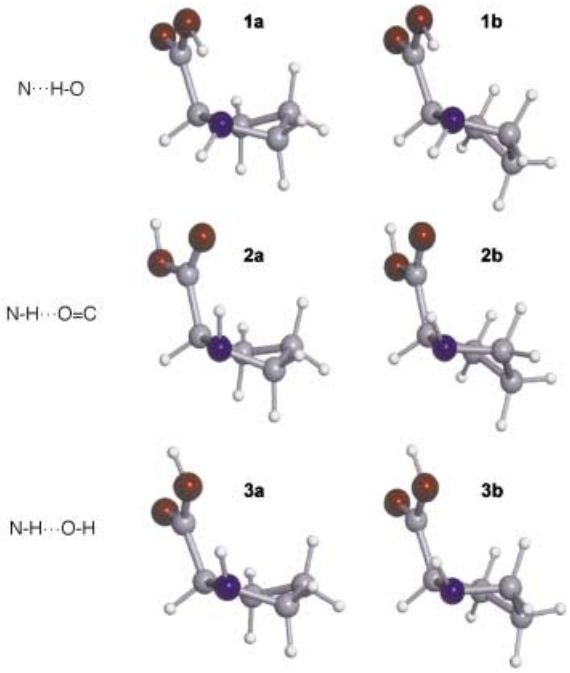

Figure 2. Plausible conformers of proline.

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us to confirm that they belonged to one of the proline conformers. By comparison of preliminary rotational constants with those predicted for all the plausible conformers of Figure 2, the good agreement with the *endo*-like conformer **1a** soon became apparent. To confirm unambiguously the presence of this conformer, the rotational assignment was extended to the minor ^{13}C-monosubstituted species, which are present in a natural abundance of 1.1%. After a careful search, the very weak spectra of all these species were observed. This clearly shows the high sensitivity reached in our experiment. The analysis was completed with the assignment of the spectrum of the *N*-deuterated and *O*-deuterated proline species (ND-proline and OD-proline, respectively) and a commercially enriched ^{15}N-proline sample. The final values of the spectroscopic parameters for all species were derived from an iterative least-squares analysis of the transition frequencies (110 were fitted for the parent) to a semirigid A-reduced Watson Hamiltonian ($\mathscr{H}_R^{(A)}$) supplemented with a nuclear quadrupole coupling interaction term [Eq. (1) $\mathscr{H}_Q$]:

$$\mathscr{H} = \mathscr{H}_R^{(A)} + \mathscr{H}_Q \quad (1)$$

The semirigid Watson Hamiltonian[20] is given by Equation (2)

$$\begin{aligned}\mathscr{H}_R^{(A)} = {} & A\,\mathbf{P}_a^2 + B\,\mathbf{P}_b^2 + C\,\mathbf{P}_c^2 \\ & -\Delta_J\,\mathbf{P}^4 - \Delta_{JK}\,\mathbf{P}^2\,\mathbf{P}_a^2 - \Delta_K\,\mathbf{P}_a^4 - 2\,\delta_J\,\mathbf{P}^2\,(\mathbf{P}_b^2 - \mathbf{P}_c^2) - \delta_K\,[\mathbf{P}_a^2(\mathbf{P}_b^2 - \mathbf{P}_c^2) \\ & + (\mathbf{P}_b^2 - \mathbf{P}_c^2)\,\mathbf{P}_a^2]\end{aligned} \quad (2)$$

where A, B, and C represent the rotational constants and Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are the quartic centrifugal distortion constants. The nuclear-quadrupole coupling term $\mathscr{H}_Q$[19] accounts for the interaction of the ^{14}N nuclear electric quadrupole moment with the molecular electric field gradient at the ^{14}N nucleus. The associated determinable spectroscopic parameters are the elements of the nuclear quadrupole coupling tensor $\chi_{\alpha\beta}$ ($\alpha, \beta = a, b,$ and c). The final rotational parameters are presented in Table 1.

In the hope of observing the spectrum of the other conformers, a further search was performed. Once the lines belonging to the conformer **1a** were discarded, it was possible to identify the weak transitions of a second conformer. The values of the rotational constants given in Table 2 were very similar to those predicted for the *exo*-like conformer **1b**. However, the definitive identification was done once the ^{15}N isotopic species was analyzed from a commercially enriched sample. Rough calculations of the dipole moment gave similar values for both conformers, so the large differences observed in the intensities of the rotational transitions between conformers are conclusive evidence that the *endo*-like form is the most stable in the gas phase. No lines which could be attributed to other conformers with N–H···O=C or N–H···O–H intramolecular hydrogen bonds remained in the rotational spectrum of the jet-cooled laser-ablated proline. All the observed transitions of the conformers **1a** and **1b** are available as Supporting Information.

Table 2. Rotational parameters for the proline conformer **1b**.

	Parent[a]	^{15}N-Proline
A [MHz]	3923.5648(53)	3880.3957(236)
B [MHz]	1605.87630(62)	1602.37833(163)
C [MHz]	1279.79761(46)	1274.91634(119)
Δ_J [kHz]	1.0198(105)	1.0128(136)
Δ_{JK} [kHz]	−4.645(85)	−4.621(89)
Δ_K [kHz]	−0.0119(49)	[−0.0119]
δ_J [kHz]	0.2512(63)	0.2552(133)
δ_K [kHz]	[0.0]	[0.0]
χ_{aa} [MHz]	0.0427(89)	–
χ_{bb}-χ_{cc} [MHz]	−2.1216(144)	–
σ [kHz]	2.1	1.0
N	51	14

[a] Parameter definition as in Table 1.

The 27 rotational constants of the conformer **1a** were used in an iterative fit procedure[19,21] to determine the effective structure shown in Figure 3 and Table 3. The only assumed constrains of the fit were the planarity of the carboxy group and a local C_{2v} symmetry for the hydrogen atoms of the three methylene groups. The derived structure reproduces the observed rotational constants of all isotopomers to within 1 MHz. The pyrrolidine ring in the conformer **1a** is bent, with atoms C_3-C_2-N-C_5 in a plane and an *endo*-like puckering of 138(2)°. The atoms involved in the intramolecular N···H–O hydrogen bond complete a five-membered planar ring, with an hydrogen-bond length of r(N···H) = 1.915(6) Å calculated

Table 1. Rotational parameters for the proline conformer **1a**.

	Parent	$^{13}C_2$-Proline	$^{13}C_3$-Proline	$^{13}C_4$-Proline	$^{13}C_5$-Proline	$^{13}C_6$-Proline	^{15}N-Proline	ND-Proline	OD-Proline
A [MHz][a]	3673.90038(148)[d]	3656.9342(271)	3624.1035(273)	3643.635(33)	3664.5317(278)	3674.0579(294)	3638.06914(265)	3562.988(108)	3598.566(99)
B [MHz]	1688.42056(56)	1685.16963(312)	1685.18403(316)	1669.39682(268)	1664.63186(252)	1678.16956(261)	1682.55372(85)	1670.7719(32)	1685.02037(275)
C [MHz]	1407.37716(55)	1407.38153(102)	1398.09116(104)	1395.07345 (103)	1389.55374(89)	1400.26855(90)	1400.75783(74)	1394.2992(33)	1394.70467(302)
Δ_J [kHz]	0.6341(89)	[0.6341][e]	[0.6341]	[0.6341]	[0.6341]	[0.6341]	0.6204(152)	0.594(64)	0.601(50)
Δ_{JK} [kHz]	−2.402(47)	[−2.402]	[−2.402]	[−2.402]	[−2.402]	[−2.402]	−2.342(58)	−2.24(72)	2.05(69)
Δ_K [kHz]	5.118(311)	[5.118]	[5.118]	[5.118]	[5.118]	[5.118]	5.14(54)	[5.118]	[5.118]
δ_J [kHz]	0.1210(48)	[0.1210]	[0.1210]	[0.1210]	[0.1210]	[0.1210]	0.1129(109)	[0.1210]	[0.1210]
δ_K [kHz]	0.581(214)	[0.581]	[0.581]	[0.581]	[0.581]	[0.581]	[0.581]	[0.581]	[0.581]
χ_{aa} [MHz]	0.8820(30)	[0.8820]	[0.8820]	[0.8820]	[0.8820]	[0.8820]	–	0.844(153)	0.863(139)
χ_{bb}-χ_{cc} [MHz]	-0.2166(58)	[−0.2166]	[−0.2166]	[−0.2166]	[−0.2166]	[−0.2166]	–	[−0.2166]	[−0.2166]
σ [kHz][b]	1.9	2.6	2.3	2.4	2.3	2.0	1.3	4.7	3.6
N[c]	110	11	10	9	12	11	24	30	32

[a] A, B, and C represent the rotational constants; Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K are the quartic centrifugal distortion constants and χ_{aa}, χ_{bb} and χ_{cc} are elements of the ^{14}N nuclear quadrupole coupling tensor. [b] rms deviation of the fit. [c] Number of transitions. [d] Standard error in parenthesis in the units of the last digit. [e] Parameters in square brackets were fixed in the fit.

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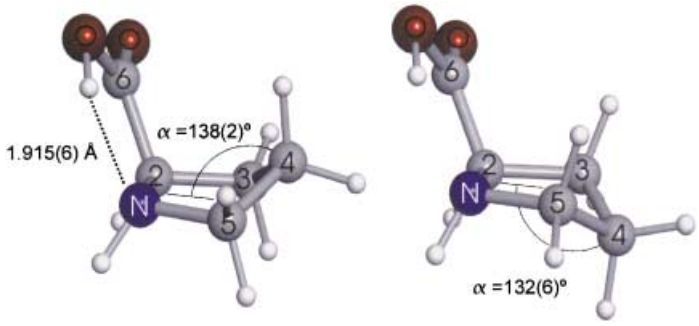

Figure 3. Calculated structure for the observed conformers of proline.

Table 3. Structure of proline.

	1a-*endo*-like	**1b**-*exo*-like[a]
$r(C_5\text{-}N)$ [Å]	1.451(6)	
r(C-C) [Å]	1.544(16)	
$r(C_6\text{-}O)$ [Å]	1.340(10)	
$r(C_6{=}O)$ [Å]	1.210(10)	
$\measuredangle(O{=}C_6\text{-}O)$ [°]	124.9(9)	
$\measuredangle(C_2\text{-}C_6\text{-}O)$ [°]	116.2(8)	
$\measuredangle(N\text{-}C_2\text{-}C_6)$ [°]	111.0(9)	
$\measuredangle(C_5\text{-}N\text{-}C_2)$ [°]	108.3(9)	
$\measuredangle(C_4\text{-}C_5\text{-}N)$ [°]	103.7(1)	
$\measuredangle(C_3\text{-}C_4\text{-}C_5)$ [°]	101.9(9)	
τ $(C_5\text{-}N\text{-}C_2\text{-}C_6)$ [°]	121(1)	
τ $(N\text{-}C_2\text{-}C_6\text{-}O)$ [°]	0(2)	
τ $(C_3\text{-}C_2\text{-}N\text{-}C_5)$ [°]	2(2)	
α [°]	138(2)	132(6)

[a] Structural parameters constrained to those of the **1a** conformer, except for the angle α, (see text).

from the Kraitchman equations.[22] With the two isotopic species available for the conformer **1b**, it was only possible to determine the ring-puckering angle α (see Figure 3 and Table 3), constraining the other structural parameters to those of **1a**.

Unlike the lowest energy conformers in glycine[4,10] and alanine[5] (stabilized by an intramolecular hydrogen bond NH···O=C), the observed conformers of proline exhibit an hydrogen bond between the hydroxy group and the nitrogen atom of the imino group (N···H–O). This result could be regarded as a consequence of the torsional restrictions imposed by the five-membered ring. The bent ring configuration observed in neutral proline contrasts with the twistlike configuration proposed by some authors[14–16] in peptide chains.

This study confirms that laser ablation combined with rotational spectroscopy in a supersonic jet may constitute a new technique (namely, laser-ablation molecular-beam Fourier-transform microwave spectroscopy or LA–MB–FTMW) which can be broadly applied to low volatility organic compounds. It makes possible the structural determination of solids in gas phase, which is particularly valuable for the neutral forms of amino acids. The results on proline and other amino acids which are presently being investigated are opening up new horizons in structural research.

Experimental Section

A new laser-ablation molecular-beam Fourier-transform microwave spectrometer working in the frequency region 8–18 GHz was used in this study. Commercial samples of proline (Aldrich) and ^{15}N-proline (Cambridge Isotope Laboratories) were used without further purification. ND- and OD-proline species were obtained by treating normal proline with D_2O. Laser pulses with energies of about 50 mJ pulse^{-1} (8 ns) were satisfactory to vaporize the samples. Argon or neon at stagnation pressures of 3–6 bar were used as carrier gases (gas pulses of 0.5–0.7 ms), with polarization pulses of 0.2–0.4 μs (0–10 dBm). Delays between the gas, laser-ablation, and microwave pulses were adjusted for maximum signal-to-noise ratio. The time-domain signal was recorded with 40-ns sampling intervals, up to 8 k data points. Frequency accuracy is better than 5 kHz.

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