

cyclopentenylcarbinol tosylate, 25125-22-8; Δ^3 -cyclopentenylacetonitrile, 21860-24-2; 2-(Δ^3 -cyclopentenyl)-ethanol, 766-01-8; **1**, 25125-25-1; **2**, 3742-38-9; **3**, 279-23-2; tri-*n*-butyltin hydride, 688-73-3.

Notes

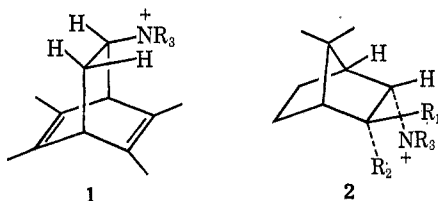
Nitrogen-15 Magnetic Resonance Spectroscopy. X. Angular Dependence of Vicinal $^{15}\text{N-H}$ Coupling Constants in Amino Acids^{1,2}

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Received February 10, 1970

In contrast to the extensive investigations of the dependence of vicinal proton-proton and proton-fluorine coupling constants on dihedral angle, relatively little is known about the angular dependence of vicinal proton-nitrogen couplings in saturated systems. The principal reasons for this are experimental difficulties associated with the quadrupole-induced relaxation of ^{14}N and the relatively small magnitudes of $^{14}\text{N-H}$ coupling constants. However, Terui, Aono, and Tori³ have recently demonstrated a geometrical dependence of the vicinal $^{14}\text{N-H}$ coupling in compounds of types **1** and **2** for dihedral angles of 0, 60, and 120°. More

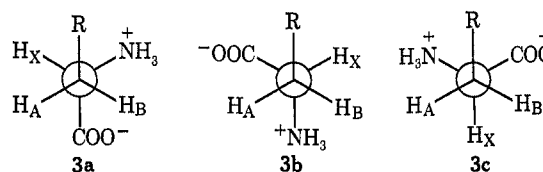


recently, Bothner-By and Cox⁴ have reported values of *gauche* and *trans* $^{14}\text{N-H}$ coupling constants derived from aliphatic isocyanides, which agree well with those determined by Terui and coworkers.

In connection with other studies, we have determined the proton magnetic resonance (pmr) chemical shifts and coupling constants for a series of ^{15}N -enriched amino acids. The H-C-C-H couplings in these spectra have been used to estimate the populations of the staggered rotational isomers **3a-3c**⁵⁻⁹ and these,

Acknowledgment.—We thank the staffs of the micro-analytical and spectral laboratories of the Universal Oil Products Co. for their cooperation and technical assistance.

in conjunction with the N-C-C-H couplings, have been used to estimate the geometrical dependence of the vicinal N-H couplings. These couplings are much easier to measure with ^{15}N because ^{15}N ($I = 1/2$) has no quadrupole moment and a slightly larger magnetogyric ratio than ^{14}N (see Figure 1).



If we denote the fractional populations of **3a-c** by p_a , p_b , and p_c , respectively, and *trans* and *gauche* proton-proton coupling constants by J_t^{H} , J_g^{H} , respectively, the observed coupling constants are given by eq 1 and 2. With the knowledge that $p_a + p_b + p_c$

$$J_{\text{BX}} = p_a J_t^{\text{H}} + (p_b + p_c) J_g^{\text{H}} \quad (1)$$

$$J_{\text{AX}} = (p_a + p_c) J_g^{\text{H}} + p_b J_t^{\text{H}} \quad (2)$$

= 1, the populations are given by

$$p_a = \frac{J_{\text{BX}} - J_g^{\text{H}}}{J_t^{\text{H}} - J_g^{\text{H}}} \quad (3)$$

$$p_b = \frac{J_{\text{AX}} - J_g^{\text{H}}}{J_t^{\text{H}} - J_g^{\text{H}}} \quad (4)$$

$$p_c = 1 - p_a - p_b \quad (5)$$

From eq 6 and 7, the *trans* and *gauche* vicinal $^{15}\text{N-H}$

$$J_{\text{NB}} = (p_a + p_b) J_g^{\text{N}} + p_c J_t^{\text{N}} \quad (6)$$

$$J_{\text{NA}} = p_a J_t^{\text{N}} + p_c J_g^{\text{N}} \quad (7)$$

$$J_g^{\text{N}} = \frac{p_c J_{\text{NA}} - p_a J_{\text{NB}}}{p_c - p_a} \quad (8)$$

$$J_t^{\text{N}} = \frac{J_{\text{NB}}(1 - p_a) - J_{\text{NA}}(p_a + p_b)}{p_c - p_a} \quad (9)$$

coupling constants are then given by eq 8 and 9. Evaluation of these expressions requires a knowledge of J_t^{H} and J_g^{H} . Pachler⁵ has suggested 13.6 and 2.6 Hz, respectively, on the basis of a variety of experiments. These values have been discussed and supported by Cavanaugh⁷ and will be used in the subsequent discussion.

The experimental data on which the calculations are based are given in Table I. Chemical shifts and coupling constants were assigned on the assumption that

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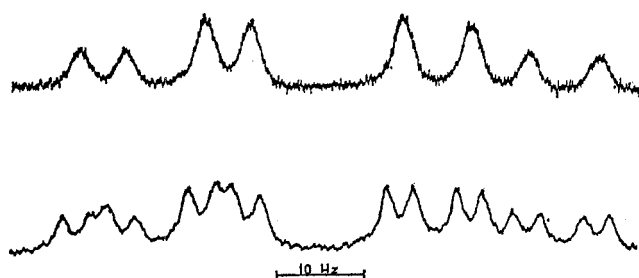


Figure 1.—Methylene region of phenylalanine. Upper trace is from the ordinary ^{14}N material, while the lower trace corresponds to the ^{15}N -labeled material. The spectra were measured at or near the isoelectric points and at different power and gain settings.

TABLE I
PROTON-PROTON AND PROTON-NITROGEN
COUPLING CONSTANTS OF AMINO ACIDS^a

Amino acid	Concn, <i>M</i>	J_{AX}^b	J_{BX}^b	J_{NA}^b	J_{NB}^b
Alanine (3, R = H)	0.43	7.0 ^c		3.1 ^d	
Phenylalanine (3, R = C ₆ H ₅)	0.08	4.7 ^c	7.9 ^c	3.4 ^d	2.9 ^d
Aspartic acid (3, R = COOH)	0.05	3.1 ^d	8.1 ^d	3.0 ^c	3.0 ^c

^a Measured at ambient probe temperatures, $\sim 35^\circ$ for alanine, $\sim 19^\circ$ for phenylalanine and aspartic acid. ^b In hertz. ^c ± 0.1 . ^d ± 0.2 . ^e ± 0.3

rotamer **3a**, with the *trans* arrangement of the large R and COO⁻ groups, is predominant.^{5,7} In accord with the above equations, the rotational isomer populations for phenylalanine are $p_a = 0.48$, $p_b = 0.19$, and $p_c = 0.33$ from which we can derive the *gauche* and *trans* ^{15}N -H couplings as $J_g^{\text{N}} = 1.8 \pm 0.8$ Hz and $J_t^{\text{N}} = 5.1 \pm 1.2$ Hz. The large probable errors are a consequence of the small difference between p_a and p_c .

Support for the derived values of J_g^{N} and J_t^{N} can be obtained in two ways. (1) Because alanine (**3**, R = H) has no preferred staggered conformation, the measured vicinal ^{15}N -H coupling constant must be a weighted average of the *trans* and *gauche* coupling constants, namely

$$J_{\text{NH, vic}} = \frac{1}{3}(2J_g^{\text{N}} + J_t^{\text{N}}) \quad (10)$$

Substitution of the above values gives $J_{\text{NH, vic}} = 2.9$ Hz, in excellent agreement with the experimental value of 3.1 Hz.¹⁰ (2) Using eq 3-5, the relative conformational populations of aspartic acid are $p_a = 0.50$, $p_b = 0.05$, and $p_c = 0.45$. These, in conjunction with equations 6-7, give calculated values of J_{NA} and J_{NB} as 3.5 ± 0.7 and 3.3 ± 1.5 Hz, which are in satisfactory agreement with the measured values.

The above treatment assumes that **3a** is the dominant conformation. If this is not assumed, and the assignments are reversed, then the alternative values of $J_g^{\text{N}} = 2.2$ Hz and $J_t^{\text{N}} = 5.8$ Hz result, which are within the probable error of the values derived above. Using these, a reasonable N-H coupling constant is derived for alanine, and values within the error limits of those given above are obtained for aspartic acid. Similarly, reversal of the aspartic acid assignments allows calculation of values for J_{NA} and J_{NB} whose

(10) The corresponding relationship should hold for the vicinal proton-proton coupling constant, but substitution for J_t^{N} and J_g^{N} gives 6.27 Hz,⁴ compared with the experimental value of 7.0 Hz (Table I).

TABLE II
ANGULAR DEPENDENCE OF VICINAL
NITROGEN-PROTON COUPLING CONSTANTS

Angle, deg	J_{NH}^a , Hz	J_{NH}^b , Hz	J_{NH}^c , Hz
0	1.9, 3.8	4.3	
60	<0.4	0.3, 1.0	1.8
120	<0.4, 1.1		
180		6.9, 8.7, 9.7	5.1

^a Reference 3. ^b Reference 4. ^c This work.

error limits span the experimental value. Thus, the particular assignment of the amino acid chemical shifts is not critical to the derivation of J_t^{N} and J_g^{N} .

In Table II, J_t^{N} and J_g^{N} are compared with those already reported.¹¹ Although the numerical agreement is far from perfect, it is perhaps better than one might expect, given the large differences in the structures of the compounds from which the values are derived. In any case, the trends are such that, if we assume all of the J_{NH} values have the same sign, the couplings define a fairly shallow and somewhat skewed Karplus-type correlation between dihedral angle and coupling constant. The minimum in the curve is uncertain but appears to be between 80 and 120° .

Experimental Section

Enriched alanine and phenylalanine were obtained from Bio-Rad Laboratories, while the aspartic acid was a product of Merck Sharpe and Dohme of Canada. Spectra were taken at ambient probe temperatures on Varian HA-60, A56/60, and HR-220¹² spectrometers. Chemical shifts were measured by direct counting of the sweep oscillator frequency (for the HA-60) or by the usual audio side-band calibration method (for the A56/60 and HR-220 spectrometers).

Registry No.—**3** (R = H), 56-41-7; **3** (R = Ph), 63-91-2; **3** (R = CO₂H), 56-84-8.

(11) The reported values for ^{14}N were corrected by $\gamma^{14}\text{N}/\gamma^{15}\text{N} = 0.713$ for this purpose.

(12) The HR-220 was purchased with the aid of National Science Foundation Grant No. GP 8450.

Charge-Transfer Energies of Benzylic Compounds with Tetracyanoethylene. A Convenient Method to Estimate the σ^* Values

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Received December 29, 1969

Much literature on the charge-transfer complex has arisen in the past decade both from experimental and theoretical point of view.² A simple molecular orbital treatment based on the perturbation theory has been applied successfully to the charge-transfer spectra of alternant and nonalternant hydrocarbons,³ where the

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