

One- and Two-bond ^{13}C - ^{15}N Coupling Constants in Saturated Amides. Absence of Three-bond Coupling on Rotational Averaging

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Summary One-bond carbon-nitrogen coupling constants in amides vary over a narrow range, while two-bond couplings show a much more pronounced structural dependence; no three-bond values are observed.

CURRENT experimental¹ and theoretical² interest in coupling constants to nuclei other than protons, and the possibility that these may be applicable in elucidating peptide conformations,³ prompt us to report our preliminary results on a series of compounds chosen as precursors to structurally rigid models.

The Table summarizes the results† $^1J_{\text{CN}}$ remains essentially in the range expected for amides,⁴ and agrees reasonably well with values expected on the basis of the simple equation proposed by Binsch and his co-workers⁵ relating $^1J_{\text{CN}}$ to s character. The slight increase with apparent strain at the carbonyl substituent may reflect an associated increase in the $\text{C}_1\text{-C}_\alpha$ orbital electronegativity, which would be expected

to increase $^1J_{\text{CN}}$ analogous to increases in $^1J_{\text{CH}}$ in similar bonding situations.⁶ Values in cyclopropanecarboxamide (6) and acrylamide (7) support this.

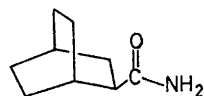
TABLE. ^{13}C - ^{15}N Coupling constants in amides

Compound	$^1J_{\text{CN}}/\text{Hz}$	$^2J_{\text{CN}}/\text{Hz}$
(1)	13.4	7.4
(2)	13.4	6.9
(3)	14.0	7.8
(4)	14.3	8.2
(5)	14.5	8.0
(6)	15.1	10.3
(7)	15.0	9.0

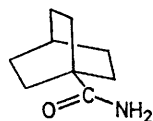
Values of $^2J_{\text{CN}}$ agree with those of acetamide (9.5 Hz)⁴ and propionamide (6.5 Hz)⁴, and with that (8.5 Hz) estimated from $^2J_{\text{CC}}$ of acetone (16.1 Hz)⁷ when corrected for differences in magnetogyric ratios ($\gamma_{\text{N}}/\gamma_{\text{C}}$ ca. 0.4) and hybridization ($S_{\text{N}}/S_{\text{C}} = 1.32$) in the two types of compounds. It thus appears that common factors are likely to

† ^{13}C spectra were determined in $(\text{CD}_3)_2\text{SO}$ on a Varian XL-100 spectrometer modified for Fourier-transform operation; estimated error ± 0.2 Hz. The ^{15}N -enriched compounds were synthesized by standard methods.

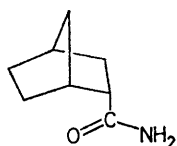
influence both ${}^2J_{\text{CC}}$ and ${}^2J_{\text{CN}}$ in these types of compounds, and on this basis a negative sign for ${}^2J_{\text{CN}}$ (hence a positive reduced coupling) is predicted. The decrease with increasing substitution at the α -carbon parallels the trend observed in ${}^2J_{\text{CCH}}$ in a series of aldehydes,⁸ which was attributed to presumed electron-donating effects of the alkyl groups. This seems unlikely, however, since the effect of the alkyl groups on ${}^{13}\text{C}$ chemical shifts are interpretable in terms of



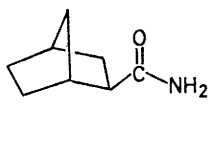
(1)



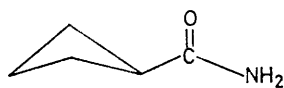
(2)



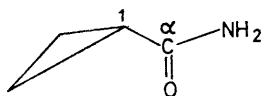
(3)



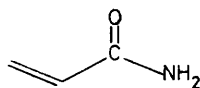
(4)



(5)



(6)



(7)

electron withdrawal. Very recently, Maciel and his co-workers⁹ noted that steric effects may well influence values

of J_{CC} , and this factor is likely to operate in the rigid bicyclic systems. Moreover, the change from (6) to (7) suggests the effect of the substituent cannot be associated entirely with changes in the σ bond, and only a rough correlation exists between ${}^1J_{\text{CN}}$ and ${}^2J_{\text{CN}}$. In considering ${}^2J_{\text{CN}}$ in (7), decreased amide nitrogen lone-pair delocalization into the carbonyl group because of cross-conjugation of the latter with the vinyl group might be expected to raise the ΔE value within the framework of the average energy approximation to calculation of coupling constants, and lead to a smaller absolute value. No appropriate data are available for comparison.

That no three-bond couplings were observed might have been expected on the basis of the small (1.2 Hz) value of ${}^3J_{\text{NH}}$ in acetamide.⁴ On the other hand, the calculations of Bystron and Solkan³ predict average values of ${}^3J_{\text{NH}}$ and ${}^3J_{\text{CH}}$ of -1.7 and -1.3 Hz, respectively. The former value agrees reasonably well with the acetamide value, so it is surprising that corresponding values for ${}^3J_{\text{CH}}$, which are outside experimental resolution, were not observed. Models indicate no conformational preferences which might be expected to give rise to near-vanishing values. The calculations assume only the Fermi contact mechanism, and conceivably other spin-spin coupling mechanisms may be important, *e.g.*, spin-orbit and dipole-dipole interactions. Alternatively, the parameters used may not be optimum because of insufficient experimental data. Finally because the compounds reported here are conformationally mobile about the amide linkage, the possibility exists that in appropriate rigid compounds measurable and geometrically dependent values can be determined. Studies are in progress to elucidate this point further.

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