^{13}C Nuclear Magnetic Resonance Studies. ^{13}C–^{14}N Spin Coupling Constants in Isocyanides

By ISAO MORISHIMA,* AKIRA MIZUNO, and TEIJIRO YONEZAWA
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*)
and KOJITSU GOTO
(*Japan Electron Optics Laboratory Co. Ltd., Akishima, Tokyo, Japan*)

Summary The ^{13}C–^{14}N nuclear spin coupling constants for isocyanides have been observed using the proton-decoupled ^{13}C n.m.r. method, and the results compared with the corresponding coupling constant for cyanides together with the theoretical values obtained by molecular orbital calculations.

AVAILABILITY of the proton-decoupled ^{13}C n.m.r. technique enables us to obtain the nuclear spin coupling constant between ^{13}C and nuclei other than protons, *e.g.* ^{19}F, ^{31}P, ^{14}N. We report ^{13}C–^{14}N spin coupling constants for isocyanides, R–^{14}N≡^{13}C. The ^{13}C–^{14}N spin coupling constant in ^{13}CH$_3$NC was measured from ^{13}C satellite lines in the ^{1}H n.m.r. spectrum using a heteronuclear double-resonance technique.[1] However, the ^{14}N–^{13}C coupling constant in R–^{14}N≡^{13}C had not previously been obtained. Comparison of the ^{13}C–^{14}N coupling constant for the isocyanide bond with that for the cyanide bond is of interest in terms of the elucidation of the nature of the N≡C bond in isocyanides. In isocyanides, the electronic symmetry about the nitrogen nucleus is expected to be sufficient to give the small electric-field gradient necessary to avoid losing the ^{13}C–^{14}N fine structure on account of quadrupolar relaxation (*cf.* H–^{14}N coupling in isocyanides[2]). We have observed ^{13}C–^{14}N spin coupling constants for methyl, ethyl, and t-butyl isocyanides from proton-decoupled ^{13}C n.m.r. spectra.†

Proton decoupling in ^{13}C spectra enables one to eliminate the effect of long-range ^{13}C–H coupling which broadens the ^{13}C signal. A ^{13}C–{H} spectrum of ethyl isocyanide, for example, shows three carbon signals, the two lower-field signals having triplet fine structure due to coupling with the ^{14}N nucleus and the highest-field one giving rise to a sharp singlet (see Figure). The resulting ^{13}C–^{14}N coupling constants and ^{13}C chemical shifts are summarized in the Table. It is of interest to compare these values with those for the corresponding nitriles and various other types of hybrid bonds. McFarlane[3] and Binsch *et al.*[4] have obtained ^{13}C–^{15}N coupling constants for molecules containing various hybrid bonds. The corresponding ^{13}C–^{14}N coupling constants are available from these data by the relation $J(^{13}\text{C–}^{14}\text{N}) = -0{\cdot}713 \times J(^{13}\text{C–}^{15}\text{N})$. These values are compared with those for isocyanide in the Table. There are substantial differences in the values of J_{CN} for isocyanide and cyanide bonds. The magnitude of J_{CN} for a bond involving *sp*^{3}-hybridized carbon is comparable with that for the N≡C bond involving *sp*-carbon, and the latter is quite small compared with that for the C≡N bond in cyanides. As has been shown by Binsch *et al.*,[4] the carbon–nitrogen spin coupling constant is proportional to the product of the *s*-character of the atoms involved in the bond. However, this relation does not appear to hold for isocyanide.

In order to interpret the difference in J_{CN} values of isocyanide and cyanide bonds, the experimental values were examined theoretically. The Table also lists the theoretical values of ^{13}C–^{14}N spin coupling constants obtained by INDO SCF–MO calculations[5] for methyl isocyanide and methyl cyanide. Fermi contact terms as well as spin-dipolar and orbital terms are included in the

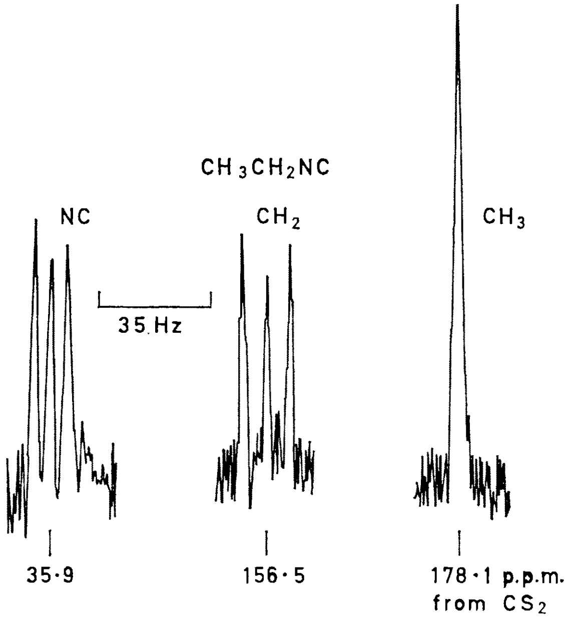

FIGURE.

TABLE

Molecule	Coupled nuclei	$J(^{13}\text{C–}^{14}\text{N})$ (Hz)	δ_c (p.p.m. from CS$_2$)
$C_aH_3C_bH_2NC_c$	^{14}N–^{13}C$_c$	±5·2 ± 0·3	35·9
	^{13}C$_b$–^{14}N	±7·3 ± 0·3	156·5
	^{13}C$_a$–^{14}N	<1	178·1
$(C_aH_3)_3C_bNC_c$	^{14}N–^{13}C$_c$	±5·1 ± 0·3	37·5
	^{13}C$_b$–^{14}N	±6·7 ± 0·3	134·5
	^{13}C$_a$–^{14}N	<1	182·7
$C_aH_3NC_b$	^{13}C$_a$–^{14}N	+7·0±1[a] (+1·55)[b]	166·0
	^{14}N–^{13}C$_b$	±6·5±0·3 (−6·02)[b]	36·2
$C_aH_3C_bN$	^{13}C$_b$–^{14}N	+12·5[c] (+0·20)[b]	—
$C_6H_5C_aH{=}N{-}CH_3$	^{13}C$_a$–^{14}N	±4·9[d]	—

[a] Ref. 1.
[b] MO theoretical values obtained by INDO calculations (ref. 5).
[c] Ref. 2.
[d] Ref. 3.

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† The ^{13}C spectra were recorded on a JEOL-4H-100 spectrometer operating at 25·15 MHz with an NSS (Nuclear Single Sideband) mode. The sample was placed in an 8 mm sample tube as neat liquid. Proton decoupling was accomplished with a JEOL IS-100 and SD-HC heterospin decoupler.

calculation. The Fermi term is dominant for the C≡N and the N≡C bonds. The calculation predicts negative values of $J_{N\equiv C}$ for isocyanide bonds, but positive values for cyanides.

The calculated J_{C-N} value in $^{13}CH_3NC$, small as compared with the experimental value, but the positive trend is in agreement with experiment. Though the sign of the $J_{N\equiv C}$ value has not been determined in the present study, a negative sign appears likely. If the trend predicted by MO calculations is accepted, one should not compare $^{13}C-^{14}N$ coupling constants for isocyanide and cyanide with relation to the hybridized nature of the bond, because signs of these coupling constants are different.

(*Received, July 14th,* 1970; *Com.* 1139.)

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