

COUPLING CONSTANTS NITROGEN-15-NITROGEN-15 AND NITROGEN-15-HYDROGEN IN PHENYLHYDRAZONES FORMING HYDROGEN BOND

Antonín LYČKA and Dobroslav ŠNOBL

Research Institute of Organic Syntheses, 532 18 Pardubice - Rybitví

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Absolute values of the coupling constants $^1J(^{15}\text{N}^{15}\text{N})$, $^1J(^{15}\text{NH})$ of six phenylhydrazones forming hydrogen bond, $^2J(^{15}\text{N}^{15}\text{NH})$ of four, and $^4J(^{15}\text{NH})$ of two phenylhydrazones have been determined. Three coupling constants $^1J(^{15}\text{N}^{15}\text{N})$ have been obtained from the nitrogen-15 monolabelled compounds by measuring the other nitrogen at natural abundance. The coupling constants $^2J(^{15}\text{N}^{15}\text{NH})$ have been measured with the nitrogen-15 doubly labelled compounds, because in the arrangement $^{15}\text{N}^{14}\text{NH}$ there exists a broadening of the proton signal due to nitrogen-14. Absolute values of the coupling constants $^1J(^{15}\text{N}^{15}\text{N})$ of the phenylhydrazones forming hydrogen bond to the ester group are smaller (~ 10.8 Hz) than those of the phenylhydrazones having hydrogen bond to carbonyl group (~ 11.1 Hz). The coupling constants $^2J(^{15}\text{N}^{15}\text{NH})$ have a value 2.4 ± 0.2 Hz. The value of $^1J(^{15}\text{N}^{15}\text{N})$ of 1-phenylazo-2-naphthanol decreases with increasing content of hydrazone form. The values of $^2J(^{15}\text{N}^{15}\text{NH})$ of this compound are within 1.2 to 1.6 Hz.

A relatively small number of the coupling constants $^nJ(^{15}\text{N}^{15}\text{N})$ are known (see refs¹⁻⁵ and those cited therein). These constants were obtained by measuring the nitrogen-15 doubly or triply labelled compounds. For easier and precise determination of the values $^nJ(^{15}\text{N}^{15}\text{N})$ it is necessary¹ to use the compounds having each of their nitrogen centres enriched with the ^{15}N isotope. These compounds are prepared by usual procedures from ^{15}N enriched intermediates (usually 95% ^{15}N and above; 50% ^{15}N in ref.³).

The coupling constants $^1J(^{15}\text{NH})$ are used for estimation of azo-hydrazone equilibria⁶.

A number of the coupling constants $^2J(^{15}\text{NH})$ were measured^{2,5,6}, but mostly for the arrangement $^2J(^{15}\text{NCH})$. Four coupling constants $^2J(^{15}\text{N}^{15}\text{NH})$ were described^{7,5}.

The aim of this work was to determine absolute values of the coupling constants $^1J(^{15}\text{N}^{15}\text{N})$, $^1J(^{15}\text{NH})$ and $^2J(^{15}\text{NNH})$ of phenylhydrazones forming hydrogen bond. The ^{13}C and ^{15}N chemical shifts and absolute values of the coupling constants $^nJ(^{15}\text{N}^{13}\text{C})$ are given in refs^{8,9}.

EXPERIMENTAL

2,3,4-Pentanetrione 3-phenylhydrazono¹⁰ (*Ia*), dimethyl 2-phenylhydrazonopropanedioate¹¹ (*Ib*), ethyl 2-phenylhydrazono-3-oxobutanoate¹¹ (*Ic,d*), 1-phenyl-3-methyl-1*H*-pyrazole-4,5-dione 4-phenylhydrazono¹² (*II*) and 1-phenylazo-2-naphthalenol¹³ (*III*) were prepared according to the literature using aniline or aniline ^{15}N (94.8% ^{15}N) and NaNO_2 or $\text{Na}^{15}\text{NO}_2$ (96.2% ^{15}N). The ^{15}N -labelled compounds were obtained from Isocommerz, Berlin. The ^1H and ^{15}N -NMR spectra were measured at 99.602 and 10.095 MHz, respectively, using a JNM-FX 100 apparatus (JEOL). The spectra were recorded for the solutions of the compounds *I*–*III* in deuteriochloroform at 300 K, if not otherwise stated. The solutions of the measured substances were placed in 10 mm (o.d.) NMR test tubes, and deuteriochloroform was used as a lock substance. For the determination of $^1J(^{15}\text{N}^{15}\text{N})$ of the compounds *Ia,b* and *II* we used the solutions with concentrations 0.5 mol l^{-1} , whereas in the other measurements the concentrations were 0.1 to 0.2 mol. l^{-1} . The apparatus parameters for the measurements of $^1J(^{15}\text{N}^{15}\text{N})$: spectral width 300 Hz, 8 K, 9 μs (30 μs $\sim 90^\circ$), pulse repetition 14 s, proton noise decoupling; for the measurements of $^1J(^{15}\text{NH})$ and $^2J(^{15}\text{N}^{15}\text{NH})$: spectral width 1500 Hz or less, 16 K, 5 μs (6 μs $\sim 90^\circ$), pulse repetition 4 s.

RESULTS AND DISCUSSION

The published coupling constants $^nJ(^{15}\text{N}^{15}\text{N})$ were obtained by measuring the ^{15}N doubly or triply labelled compounds. In the present paper the values $^1J(^{15}\text{N}^{15}\text{N})$ of the compounds *Ia,b* and *II* have been determined for the ^{15}N -monolabelled compounds ($\text{N}_\beta = ^{15}\text{N}$) by measuring the nitrogen —NH— in natural abundance. The situation is analogous to measurement of the coupling constants $^nJ(^{15}\text{NX})$

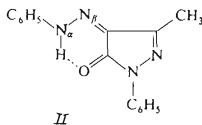
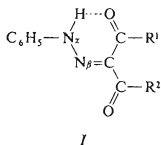
TABLE I

Absolute Values of Coupling Constants (in Hz) $^1J(^{15}\text{N}^{15}\text{N})$ (± 0.1 Hz), $^1J(^{15}\text{NH})$, and $^2J(^{15}\text{N}^{15}\text{NH})$ (± 0.2 Hz) of the Compounds *Ia*–*d* and *II* in Deuteriochloroform

Compound	$^1J(^{15}\text{N}^{15}\text{N})$	$^1J(^{15}\text{NH})$	$^2J(^{15}\text{N}^{15}\text{NH})$
<i>Ia</i>	11.04	95.2	—
<i>Ib</i>	10.70	95.8	—
<i>Ic</i>	11.10 ^a	95.0 94.7 \pm 0.3 ^b	2.34
<i>Id</i>	10.80 ^a	95.9 96.1 \pm 0.3 ^b	2.44
<i>II</i>	11.13	96.3 96.5 \pm 0.5 ^c	2.56

^a Ref. 8, ^{15}N doubly labelled compound; ^b ref. 1; ^c ref. 20.

from the ^{15}N -NMR spectra in natural abundance, X being a nucleus with $1/2$ spin, which is currently used for $X = \text{H}$, and the coupling constants ${}^nJ(^{31}\text{P}^{15}\text{N})$ measured in this way are published¹⁴⁻¹⁶. The nitrogen carrying hydrogen was chosen for the measurement in natural abundance due to shorter relaxation times and the favourable signal enhancement caused by the nuclear Overhauser effect. We used a narrow spectral width to attain sufficient digital resolution and to have the absorption of the signal $-\text{N}=\text{O}$ outside this range. A typical spectrum is given in Fig. 1 where inversion of signals occurred due to large negative value of the nuclear Overhauser effect. Measurement of the coupling constants ${}^nJ(^{15}\text{N}^{15}\text{N})$ from the ^{15}N -monolabelled compounds can be useful for the substances whose ^{15}N doubly labelling is synthetically difficult. Absolute values of the coupling constants ${}^1J(^{15}\text{N}^{15}\text{N})$ (Table I) of the phenylhydrazones forming hydrogen bond to the ester group (*Ib* and *Id*) are smaller than those of *Ia*, *Ic* and *II*. The values of ${}^1J(^{15}\text{N}^{15}\text{N})$



Compound	R ₁	R ₂
<i>Ia</i>	CH ₃	CH ₃
<i>Ib</i>	OCH ₃	OCH ₃
<i>Ic</i>	CH ₃	OC ₂ H ₅
<i>Id</i>	OC ₂ H ₅	CH ₃

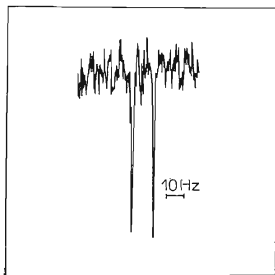


FIG. 1
Splitting of the ^{15}N -NMR Signal of N_αH Nitrogen (measured at the natural abundance) by N_β Nitrogen (96.2% ^{15}N) for Compound *Ia* (0.5 mol l^{-1} in deuteriochloroform, spectral width 300 Hz, 8 K, pulse width $9 \mu\text{s}$, $30 \mu\text{s} \sim 90^\circ$, pulse repetition 14 s, proton noise decoupling, 3 600-pulses)

of the phenylhydrazones forming hydrogen bond are comparable with $^1J(^{15}\text{N}^{15}\text{N}) = 10.7$ Hz of 4-nitrobenzaldehyde phenylhydrazone¹ but markedly greater than those of phenylhydrazine itself (6.7 Hz, ref.¹) and two configuration isomers of 2-acetyl-1-phenylhydrazine (3.0 and 3.6 Hz, ref.⁷). The azo coupling product of benzenediazonium chloride and 2-naphthalenol represents a mixture of azo and hydrazone forms *IIIa* and *IIIb*, their equilibrium being influenced by both solvent and tempera-



ture. Values of the coupling constants $^1J(^{15}\text{N}^{15}\text{N})$ of compound *III* depending on temperature (and, hence, also on the azo-hydrazone equilibrium) are given in Table II. Increasing content of the azo form increases the value of the coupling constant $^1J(^{15}\text{N}^{15}\text{N})$. Approximate extrapolation to 100% content of azo form gives the value $^1J(^{15}\text{N}^{15}\text{N}) \sim 14$ Hz which agrees quite well with the value $^1J(^{15}\text{N}^{15}\text{N})$ obtained for 4-hydroxyazobenzene¹⁸ (15.0 ± 0.5 Hz; hexadeuteriodimethyl sulphoxide).

Absolute values of the coupling constants $^1J(^{15}\text{NH})$ of the compounds *Ia-d* and *II* are given in Table I. They were obtained from $^1\text{H-NMR}$ spectra of the compounds

TABLE II

Temperature Dependence of Absolute Values of Coupling Constants (in Hz) $^1J(^{15}\text{N}^{15}\text{N})$ (± 0.2 Hz), $^1J(^{15}\text{NH})$ (± 0.5 Hz), Content of Hydrazone Form $^2J(^{15}\text{N}^{15}\text{NH})$ (± 0.2 Hz), Chemical Shift of Bridge Hydrogen and Half-Height-Width Bridge Hydrogen (for the non-labelled compound) of the Compound *III* in Deuteriochloroform

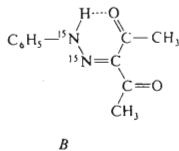
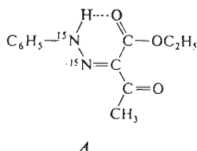
Temperature, K	$^1J(^{15}\text{N}^{15}\text{N})$	$^1J(^{15}\text{NH})$	% Hydrazone	$^2J(^{15}\text{N}^{15}\text{NH})$	(NH)	$w_{1/2}(^{14}\text{NH})$
230	11.6	81.5	84.9	1.5	16.40	2.3
250	11.7	76.6	79.8	1.5	16.32	3.0
270	11.9	72.0	75.0	1.6	16.21	3.5
290	11.9	68.0	70.8	1.5	16.14	5.0
310	12.0	64.3	67.0	1.2	16.05	6.2
330	12.2	61.2	63.8	1.2	15.95	7.2

labelled with ^{15}N isotope ($N_\alpha = ^{15}\text{N}$ or $N_\alpha = N_\beta = ^{15}\text{N}$). The absolute values of $^1J(^{15}\text{NH})$ of the phenylhydrazones forming hydrogen bond to the ester group (*Ib* and *Id*) are greater than those of *Ia*, *Ic* and *II*, the trend being thus opposite to that of the constants $^1J(^{15}\text{N}^{15}\text{N})$. The coupling constants $^1J(^{15}\text{NH})$ of the substance *III* (Table II) were used for assessment of the hydrazone form content^{17,18} according to Eq. (1) (For $^1J(^{15}\text{NH})$ of 1,2-naphthalenedione 1-phenylhydrazone we used the value 96 Hz which corresponds better to $^1J(^{15}\text{NH})$ of phenylhydrazones with hydrogen bond (Table I)).

$$\% \text{ hydrazone} = [{}^1J(^{15}\text{NH})/96] \cdot 100 \quad (1)$$

Absolute values of the coupling constants $^2J(^{15}\text{NH})$ of the compounds *Ic*, *d* and *II* are given in Table I, that of *III* in Table II. The measurement was carried out with the ^{15}N doubly labelled substances, *i.e.* for the arrangement $^{15}\text{NH}-^{15}\text{N}=\text{}$. Attempts to measure $^2J(^{15}\text{NNH})$ from the proton spectra of the substances *Ia*, *b* which were only prepared with one ^{15}N -labelled centre ($N_\beta = ^{15}\text{N}$), (*i.e.* in the arrangement $-\text{}^{14}\text{NH}-^{15}\text{N}=\text{}$) failed due to broadening of the proton signal by action of ^{14}N isotope. Well-resolved ^1H -NMR signals of the group ^{15}NH of the compound *II* are obtained at temperatures below 280 K when the relaxation of the ^{15}NH nitrogen decreases, and the proton signals narrow down.

With the derivative *Id* ($N_\alpha = N_\beta = ^{15}\text{N}$) we observed splitting of the ^1H -NMR signal of COCH_3 group into a doublet ($J = 0.78$ Hz). Similarly with the compound *Ia* ($N_\beta = ^{15}\text{N}$) the upfield shifted signal of COCH_3 ($\Delta\nu(\text{COCH}_3) = 11.3$ Hz) was split into a doublet with $J = 0.76$ Hz. From comparison it follows that the effect is due to the coupling constants $^4J(^{15}\text{NCCCH})$. The $^4J(^{15}\text{NH})$ was not observed with the compound *Ic* and for the second COCH_3 group of *Ia* ($^4J < 0.3$ Hz). The observed difference in $^4J(^{15}\text{NCCCH})$ is connected obviously with different conformation of the groups COCH_3 caused by strong repulsion of negative atoms carrying free electron pairs ($-\text{N}=\text{}$ and CO). On the basis of this consideration we suggest conformations *A* and *B* for the compounds *Id* and *Ia*, respectively. The ^{15}N -labelling also affects the appearance of ^1H -NMR signals of the aromatic protons, but the values $^nJ(^{15}\text{NH})$ were not determined due to coincidence of the signals.



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