

Scalar coupling constants across the intramolecular NHN hydrogen bond of symmetrically and non-symmetrically substituted 6-aminofulvene-1-aldimines

Mariusz Pietrzak,¹ Hans-Heinrich Limbach,^{1*} Marta Pérez-Torralba,² Dionísia Sanz,² Rosa María Claramunt² and José Elguero³

¹ Institut für Chemie der Freien Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany

² Departamento de Química Orgánica y Biología, Facultad de Ciencias, UNED, Senda del Rey 9, E-28040 Madrid, Spain

³ Instituto de Química Médica, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain

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Multinuclear liquid state magnetic resonance experiments have been performed on two seven-membered ¹⁵N-labeled H-chelates of the 6-aminofulvene-1-aldimines type in order to characterize the strong intramolecular NHN hydrogen bonds as a function of the molecular symmetry. In particular, the symmetrically substituted *N,N'*-diphenyl-6-aminopentafulvene-1-aldimine-¹⁵N₂ (1) and its asymmetric analog *N*-phenyl-*N'*-(1,3,4-triazol)-6-aminopentafulvene-1-aldimine-¹⁵N₅ (2) have been studied. For 1, an NN coupling constant across the hydrogen bridge of ^{2h}*J*(¹⁵N,¹⁵N) = 10.6 Hz was determined indirectly by ¹³C NMR at two different Larmor frequencies, 125.76 and 67.93 MHz; this coupling constant is characteristically enhanced compared with the value of 8.6 Hz obtained previously for 2. Because of a fast degenerate proton tautomerism the hydrogen bond proton in 1 is coupled with both nitrogen atoms with a coupling constant of -40.8 Hz. {¹⁵N} tickling experiments were performed on 2 in order to determine the relative signs of the coupling constants of the NHN hydrogen bridge. We find that ^{2h}*J*(¹⁵N,¹⁵N) and ^{1h}*J*(¹H,¹⁵N) = +4.4 Hz exhibit the same sign, i.e. the opposite sign compared with ¹*J*(¹⁵N,¹H) = -88.6 Hz. This finding proves that ^{1h}*J*(¹H,¹⁵N) corresponds to an intrinsic coupling, which is not induced by a tautomerism absent in 2 because of the large difference in basicities of the aniline and the amino-1,3,4-triazole substituents. Therefore, these observations indicate a sign change of *J*(¹⁵N,¹H) when the proton is transferred successively from one nitrogen to the other, as observed previously for FHF hydrogen bonds. The relation between the values of the coupling constants and the hydrogen bond geometries is discussed in terms of the valence bond order model, as are the implications for obtaining equilibrium constants of tautomerism from coupling constant data. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Although scalar couplings across hydrogen bonds have been known for a very long time, especially for cases of intramolecular hydrogen bonds,¹ an increased theoretical interest in these quantities has been developed² with the recent finding of scalar couplings across intermolecular hydrogen bonds in small hydrogen-bonded clusters³ and biological molecules,⁴ when the condition of slow hydrogen bond exchange can

be realized. This range is often achieved in the case of biomolecules, whereas in the case of small hydrogen-bonded complexes special low-temperature NMR techniques need to be employed. One of the most puzzling effects observed was that ^{2h}*J*(A,B) couplings of hydrogen-bonded systems A-H...B tend to be larger than ^{1h}*J*(H,B) couplings; however, both are propagated along hydrogen bond H...B and labeled as ^h*J*.^{2,4} Some of us have attributed this phenomenon to a negative contribution to this coupling.^{2a,3a} Furthermore, it has been proposed that ^{2h}*J*(A,B) couplings should exhibit a maximum value for the shortest and symmetric hydrogen bonds.^{2a} However, in the past, potentially symmetric hydrogen-bonded systems presented two problems. Firstly, it is very difficult to distinguish intrinsic ^{1h}*J*(H,B) couplings from those arising from a proton tautomerism in a double well potential. Secondly, because of the molecular symmetry it is difficult to measure ^{2h}*J*(A,B) when A and B are chemically

*Correspondence to: H.-H. Limbach, Institut für Chemie der Freien Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany.
E-mail: limbach@chemie.fu-berlin.de
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equivalent. Inspired by a finding of Elguero *et al.*,¹⁵ some of us have recently proposed an indirect method to observe this coupling in the case of symmetrically substituted molecules exhibiting $^{15}\text{N}^{15}\text{N}$ hydrogen bonds *via* ^{13}C NMR⁵ at different magnetic fields, where the additional ^{13}C nucleus destroys the nuclear spin symmetry of the $^{15}\text{N}^{15}\text{N}$ system by producing an ABMX spin system. The principles of such desymmetrization, leading to the break of symmetry of the molecule, have been known for a while. An example is the mono- ^{13}C labeled acetylene $\text{H}-^{12}\text{C}\equiv^{13}\text{C}-\text{H}$, which exhibits an ABX spin system, and therefore the $^3J(\text{H},\text{H})$ coupling can be obtained from the analysis.⁶ The novelties of our study are the application of this method for a $^{15}\text{N}^{15}\text{N}^{13}\text{C}$ hydrogen-bonded system, and a full analysis of the couplings using only the X part of the ABX multiplet, i.e. ^{13}C spectra. Finally, Claramunt *et al.*⁷ have proposed to select and to study symmetrically and asymmetrically substituted 6-aminofulvene-1-aldimines as model systems exhibiting strong intramolecular hydrogen bonds but which present at the same time an intramolecular proton tautomerism, depicted in Fig. 1 for the symmetric *N,N'*-diphenyl-6-aminopentafulvene-1-aldimine- $^{15}\text{N}_2$ (**1**), and its asymmetric analog *N*-phenyl-*N'*-(1,3,4-triazol)-6-aminopentafulvene-1-aldimine- $^{15}\text{N}_5$ (**2**). The synthesis and the crystal structure of **1** have already been reported by Mueller-Westerhoff and coworkers, who determined the X-ray structure of **1** and the NMR properties of the unlabeled material in solution.⁸ Claramunt *et al.*⁷ reported not only the crystal structure of **2** (Fig. 1), but also a very large value of $^2hJ(^{15}\text{N},^{15}\text{N}) = 8.6$ Hz between the $^{15}\text{N}-1$ and $^{15}\text{N}-9$ of **2**. The observation of temperature-independent values of $^1J(^{15}\text{N},^1\text{H}) = -88.6$ Hz and $^1hJ(^1\text{H},^{15}\text{N}) = 4.4$ Hz were also a surprise, because this finding indicated the localization

of the hydrogen bond proton on N(1), which consequently meant that $^1J(^{15}\text{N},^1\text{H})$ and $^1hJ(^1\text{H},^{15}\text{N})$ represent intrinsic values rather than tautomerism-affected values. Unfortunately, the sign of $^1hJ(^1\text{H},^{15}\text{N})$ could not be established in our previous study. The scope of the present study was, therefore, twofold, i.e. to establish the scalar couplings across the hydrogen bonds for the symmetric compound **1** for comparison with **2**, and to establish the sign of $^1hJ(^1\text{H},^{15}\text{N})$ for **2**. In fact, we will show that the sign of $^1J(^{15}\text{N},^1\text{H})$ and $^1hJ(^1\text{H},^{15}\text{N})$ in **2** are opposite, i.e. that $^1hJ(^1\text{H},^{15}\text{N})$ is really intrinsic, and not caused by a tautomerism, implying that the NHN system also leads to a sign change of the scalar NH coupling when the NH distance is increased, at a configuration where the NN coupling is still large.

This paper is organized as follows. After an experimental section the results of our NMR experiments performed on **1** and **2** are described. Finally, the implications of the findings for the understanding of NHN hydrogen-bonded proton transfer systems are discussed in terms of the valence bond order model described previously.^{2a}

EXPERIMENTAL SECTION

The synthesis of ^{15}N -labeled compound **2** has been described recently.⁷ **1** was prepared according to the recipe of Mueller-Westerhoff using ^{15}N -labeled aniline enriched to about 98% with ^{15}N .^{8a}

For the NMR measurements we used a Bruker AMX 500 operating at 500.13 MHz for ^1H , at 125.76 MHz for ^{13}C and at 50.70 MHz for ^{15}N and a Bruker AM 270 spectrometer operating at 270.13 MHz for ^1H and at 67.93 MHz for ^{13}C . Tickling experiments were performed on the 500 MHz instrument using small power waltz16 decoupling (pulse

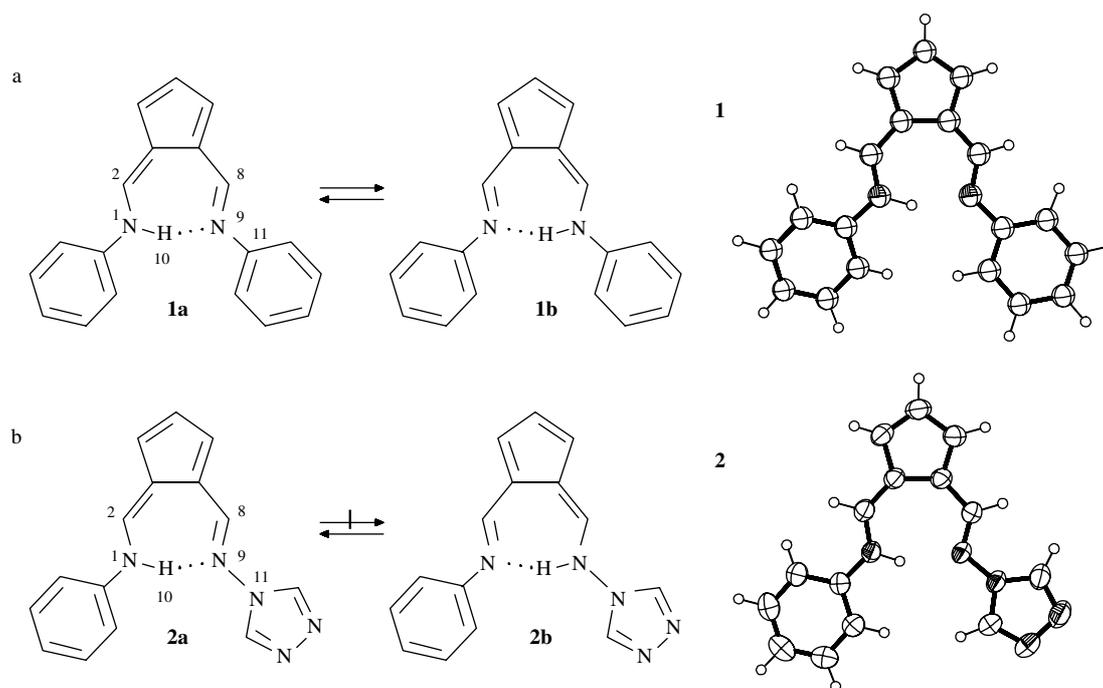


Figure 1. Tautomerism and X-ray structures of *N,N'*-diphenyl-6-aminopentafulvene-1-aldimine- $^{15}\text{N}_2$ (**1**) and *N*-phenyl-*N'*-(1,3,4-triazol)-6-aminopentafulvene-1-aldimine- $^{15}\text{N}_5$ (**2**). The X-ray structure of **1** was published by Ammon and Mueller-Westerhoff^{8b} and of **2** by Claramunt *et al.*⁷

length 3 ms, pulse power 50 dB), applied to the ^{15}N nuclei. All experiments, except the series of ^1H spectra of **2** measured at different temperatures, were done at room temperature.

The ^{15}N chemical shifts are given with respect to nitromethane, where the reference with respect to crystalline ammonium chloride is given by⁹

$$\delta(\text{CH}_3\text{NO}_2) = \delta(^{15}\text{NH}_4\text{Cl}_{\text{cryst}}) - 338.1 \text{ ppm} \quad (1)$$

The high-order NMR spectra were simulated using a home-made computer program modified for a PC, based on the program DNMR2 of Binsch and Kleier.¹⁰

RESULTS

Scalar coupling constants of the NHN hydrogen bond in **1**

The hydrogen bond proton of **1** appears at 15.6 ppm as a triplet of triplets, by tautomerism-induced coupling with N-1 and N-9, and with H-2 and H-8. Consequently, a single averaged N-1/N-9 signal is observed at -168.3 ppm. The simple NMR parameters are summarized in Table 1.

Whereas it is impossible to measure $^2J(\text{A},\text{B})$ under the conditions where the two atoms A and B are equivalent, the situation is different for the isotopomers containing a ^{13}C nucleus that is coupled to one of the ^{15}N nuclei. In this case an ABX spin system is obtained. This is because the chemical shifts of A and B are slightly different, as A is bound to ^{12}C and B to X = ^{13}C . $J(\text{A},\text{B})$ can be obtained from either the ^{13}C satellites in the AB signal part—which are difficult to observe in the case of nitrogen NMR—or by natural abundant $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy at different magnetic fields.⁵

Here, we chose the second option and measured the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** dissolved in CDCl_3 . Figure 2 contains the experimental and simulated signals of C-2/C-8 and of C-11/C-11', which are direct neighbors of ^{15}N -1/ ^{15}N -9, obtained at two magnetic fields, i.e. 6.3 and 11.7 T.

We would like to comment on the analysis as follows. A look at the NMR theory of the ABX spin system described by Dischler^{11a} (see also Ref. 11b) shows that the X part of an ABX spin system consists of three line pairs of unequal intensity separated by the line splittings:

$$\Delta\nu^{\text{A}} = 2 \left\{ \sqrt{0.25J_{\text{AB}}^2 + [0.5d + 0.25(J_{\text{AX}} - J_{\text{BX}})]^2} + \sqrt{0.25J_{\text{AB}}^2 + [0.5d - 0.25(J_{\text{AX}} - J_{\text{BX}})]^2} \right\} \quad (2)$$

$$\Delta\nu^{\text{B}} = |J_{\text{AX}} + J_{\text{BX}}| \quad (3)$$

$$\Delta\nu^{\text{C}} = \left| 2 \left\{ \sqrt{0.25J_{\text{AB}}^2 + [0.5d + 0.25(J_{\text{AX}} - J_{\text{BX}})]^2} - \sqrt{0.25J_{\text{AB}}^2 + [0.5d - 0.25(J_{\text{AX}} - J_{\text{BX}})]^2} \right\} \right| \quad (4)$$

where $J_{\text{AB}} = J(\text{A},\text{B})$, $J_{\text{AX}} = J(\text{A},\text{X})$ and $J_{\text{BX}} = J(\text{B},\text{X})$.

These splittings are illustrated in Fig. 2. They depend not only on the coupling constants, but also on the isotope shift

$$d = |\Delta|\gamma_{\text{X}}B_0/2\pi \times 10^{-6} \text{ Hz} \quad (5)$$

where γ_{X} represents the gyromagnetic ratio of X, B_0 the magnetic field and Δ the chemical shift difference between A and B. Here, $\Delta = \Delta^{15}\text{N}\{^{13}\text{C}\}$, i.e. the chemical shift difference between the ^{12}C and ^{13}C -bound ^{15}N nuclei. In Eqns (2)–(4) there are four unknowns, i.e. $J(\text{A},\text{B})$, $J(\text{A},\text{X})$, $J(\text{B},\text{X})$ and d , but only three measurable quantities. If $\Delta = 0$ we obtain the case of an AA'X spin system with $\Delta\nu^{\text{C}} = 0$; where $J(\text{A},\text{A}')$ can only be obtained from the AA', not from the X part. However, if $\Delta \neq 0$, $\Delta\nu^{\text{A}}$ and $\Delta\nu^{\text{C}}$ are field dependent. By measuring $\Delta\nu^{\text{A}}$, $\Delta\nu^{\text{B}}$ and $\Delta\nu^{\text{C}}$ at two different fields, it is then possible to obtain the field-independent parameter set $J(\text{A},\text{B})$, $J(\text{A},\text{X})$, $J(\text{B},\text{X})$ and Δ . The spectra of Fig. 2 were analyzed in this way. In a first stage, we measured the splittings and calculated the four parameters. In a second stage, the parameters were refined by a simultaneous fit of all spectra of a given carbon atom at the two fields. The results are presented in Table 2. We note that the values of $^2J(^{15}\text{N}, ^{15}\text{N})$ of **1** obtained by analysis of the two different carbon signals agree well within the margin of error.

High-order signals have also been observed for other carbon atoms not directly connected to the nitrogen atoms. However, in these cases the couplings to nitrogen were smaller, and we were not able to analyze the signals in a satisfactory way.

The sign of $^1J(^1\text{H}, ^{15}\text{N})$ in **2**

In this section we will describe the determination of the sign of $J_{9,10} = ^1J(^1\text{H}, ^{15}\text{N})$ of **2** dissolved in CDCl_3 . For this purpose, let us first briefly review some important features of the ^{15}N and ^1H spectra of **2** dissolved in CDCl_3 that have been described previously in detail,⁷ where the main parameters are already summarized in Table 1.

The signal of the hydrogen bond proton H-10 is depicted in Fig. 3a. It is split by coupling with N-1, H-2 and N-9. The ^{15}N signals of N-1 and N-9 are depicted in Fig. 3b and c, and

Table 1. The most important NMR parameters of the intramolecular NHN hydrogen bonds of **1** and **2** in CDCl_3 at room temperature

Compound	δ_{10}/ppm	δ_1/ppm [δ_9/ppm]	$J_{1,10}/\text{Hz}$ [$J_{9,10}/\text{Hz}$]	$J_{1,9}/\text{Hz}$	$J_{2,10}/\text{Hz}$
1	15.60 (15.33) ^a	-168.3	-40.8	$+10.6$	$+6.9$ (7) ^a
2	12.76 (12.77) ^b	-239.0 (-238.1) ^b [-122.3 (-121.0) ^b]	-88.6 (88.6) ^b [$+4.4$ (4.4) ^b]	$+8.7$ (8.6) ^b	$+13.9$ (13.9) ^b [~ 0]

^a In CCl_4 for non-labeled molecule, Mueller-Westerhoff.^{8a}

^b Claramunt *et al.*⁷

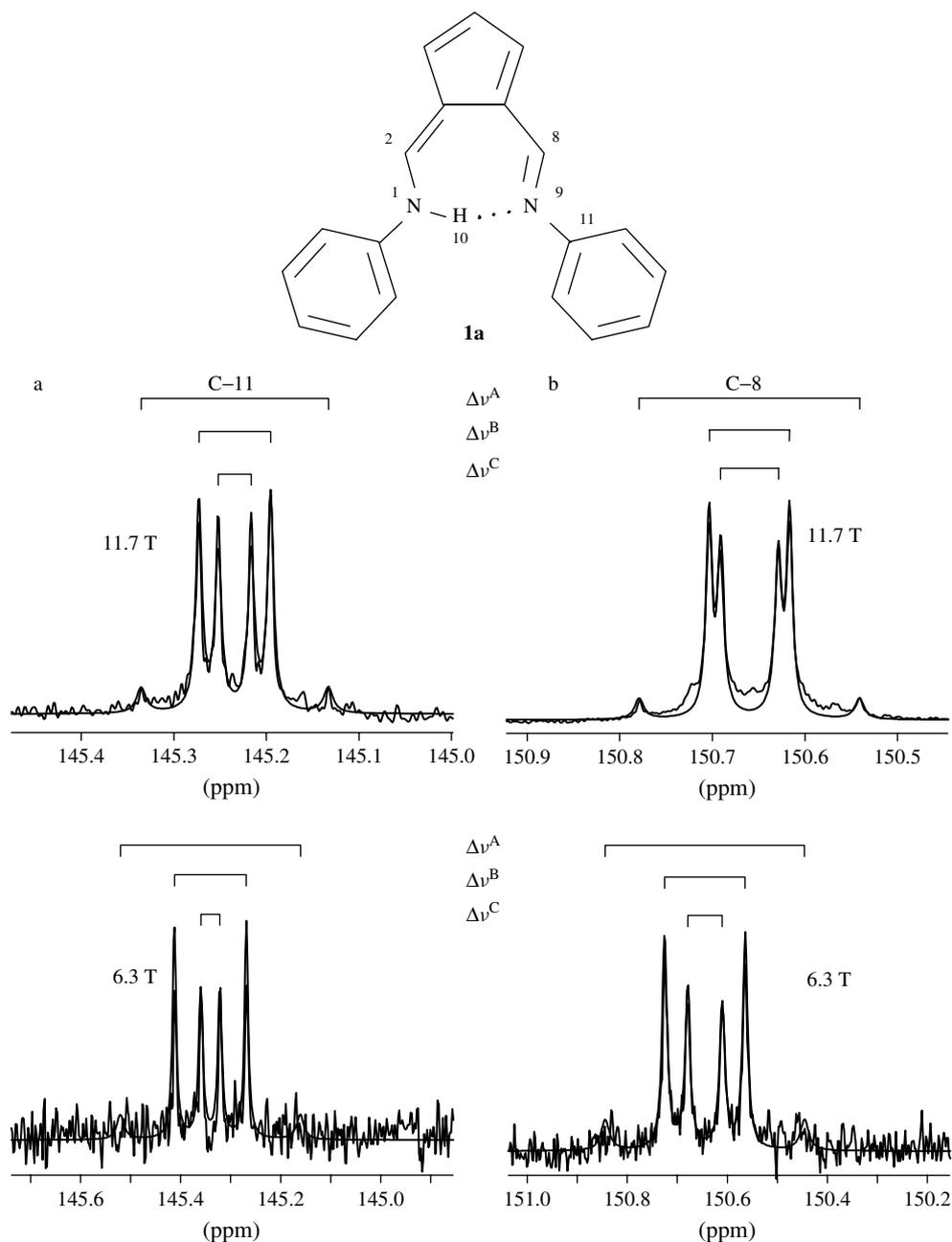


Figure 2. Superposed experimental and simulated $^{13}\text{C}\{^1\text{H}\}$ signals of **1** dissolved in CDCl_3 recorded at 11.7 and 6.3 T at room temperature: (a) signal at 145.3 ppm, (b) signal at 150.7 ppm.

the corresponding $\{^1\text{H}\}$ -decoupled signals are in Fig. 3d and e. The signal of N-1 is split by coupling with H-10 and N-9; other couplings are unresolved. With $\{^1\text{H}\}$ decoupling only the coupling with N-9 survives. The signal of N-9 exhibits a coupling with N-11, N-1, H-10 and H-8. The measurement of some temperature-dependent NMR-spectra of **2** dissolved in CD_2Cl_2 did not reveal significant changes (Table 3).

In order to determine the sign of $J_{9,10}$ we performed tickling experiments according to Freeman and Anderson^{12a} (see also Ref. 12b). The experiment relies on the observation that low-power irradiation of any transition i,j between the energy levels i and j of a nuclear spin system in a magnetic field leads to a doubling, or, under conditions of lower resolution to a broadening, of all transitions i,k and j,l with $k,l \neq i,j$ connected to i or j .¹² The results are depicted in Fig. 3f.

The NHN bridge can be considered as an AMX part of the larger fulvenaldimine spin system, where the four first-order transitions of N-1 are labeled as A_1 to A_4 . The transitions M_1 to M_4 are twofold because of the coupling with H-2. The transitions of N-9 are obscured by the couplings with N-11, H-10 and H-8 and are not considered further.

It is worth mentioning that, for the tickling experiment, it is very important to implement such a value of low-power decoupling, so that only one line of the multiplet is irradiated. In our case the width of the pulse should be smaller than the smallest coupling in the irradiated part of the multiplet, i.e. 8.6 Hz or less. Too small a decoupling power leads to no changes in the spectrum, whereas too big a decoupling power causes a larger bandwidth of excitation and, in consequence, irradiation of at least two lines of the multiplet, which leads

Table 2. NMR data of **1** in CDCl₃ at room temperature

¹³ C{ ¹ H} signal (ppm)	Observable parameters at		Results obtained from the analysis
	11.7 T	6.3 T	
145.3	$\Delta\nu^A = 25.4$ Hz $\Delta\nu^B = 9.8$ Hz $\Delta\nu^C = 4.4$ Hz	$\Delta\nu^A = 22.3$ Hz $\Delta\nu^B = 9.8$ Hz $\Delta\nu^C = 2.6$ Hz	$J_{1,9} = {}^{2h}J(^{15}\text{N}, ^{15}\text{N}) = \pm 10.4$ Hz $J_{9,11} = {}^1J(^{13}\text{C}, ^{15}\text{N}) = -10.7$ Hz $J_{1,11} = {}^3hJ(^{13}\text{C}, ^{15}\text{N}) + {}^6J(^{13}\text{C}, ^{15}\text{N})^a$ $\approx {}^3hJ(^{13}\text{C}, ^{15}\text{N}) = +0.9$ Hz ${}^1\Delta^{15}\text{N}(^{13}\text{C}) = \pm 0.04$ ppm
150.7	$\Delta\nu^A = 29.9$ Hz $\Delta\nu^B = 10.9$ Hz $\Delta\nu^C = 7.9$ Hz	$\Delta\nu^A = 25.4$ Hz $\Delta\nu^B = 10.9$ Hz $\Delta\nu^C = 4.7$ Hz	$J_{1,9} = {}^{2h}J(^{15}\text{N}, ^{15}\text{N}) = \pm 10.9$ Hz $J_{1,2} = J_{8,9} = {}^1J(^{13}\text{C}, ^{15}\text{N}) = -12.4$ Hz $J_{1,8} = J_{2,9} = {}^3hJ(^{13}\text{C}, ^{15}\text{N})$ $+ {}^4J(^{13}\text{C}, ^{15}\text{N})^a = +1.5$ Hz ${}^1\Delta^{15}\text{N}(^{13}\text{C}) = \pm 0.07$ ppm

^a Scalar coupling constant propagated along backbones.

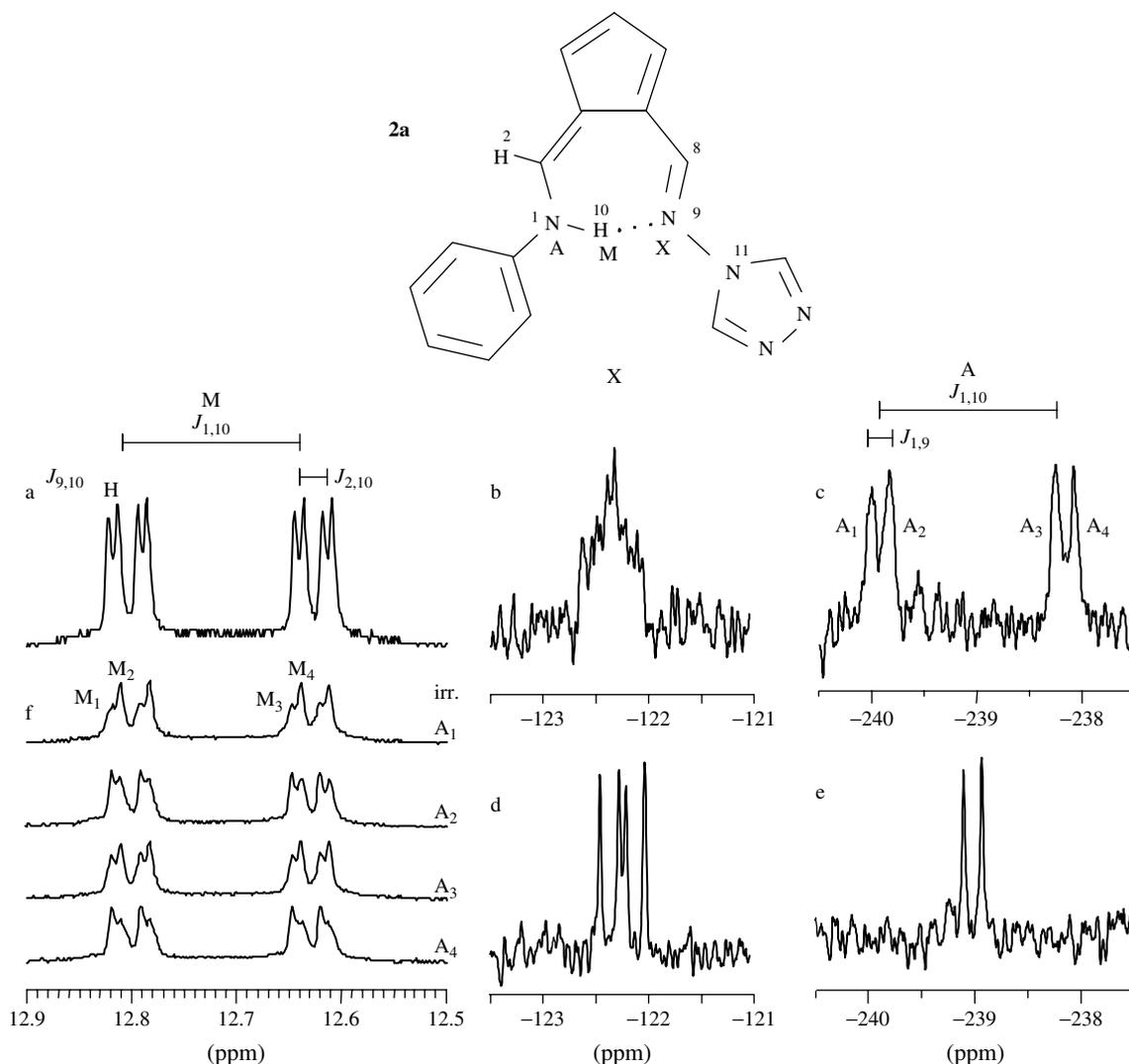


Figure 3. NMR spectroscopy (11.7 T) of **2** dissolved in CDCl₃ at 293 K under various conditions: (a) ¹H NMR signal of the hydrogen bond proton H-10; (b) and (c) ¹⁵N NMR signals of N-1 and N-9 (d) without and (e) with {¹H} decoupling; (f) signal of H-9 under successive low-power irradiation of the transitions A₁ to A₄ of N-1.

Table 3. NMR parameters of **2** in CD₂Cl₂ at different temperatures

T/K	$\delta_{\text{H-10}}$ /ppm	$-J_{1,10}$ /Hz	$J_{9,10}$ /Hz	$J_{2,10}$ /Hz
293	12.72	88.57	4.51	13.87
273	12.74	88.58	4.52	13.90
253	12.77	88.56	4.48	13.90
233	12.79	88.54	4.54	13.97
213	12.82	88.52	4.61	13.99
183	12.85	88.51	4.64	13.96

first to the broadening of all lines and for greater power to a fully decoupled spectrum. We found the correct value of decoupling power (50 dB) experimentally, varying it from 70 to 40 dB.

In the experiments that we performed, the transitions A₁ to A₄ of N-1 were consecutively irradiated and the M transitions of H-10 monitored. Under these conditions, the outcome of the experiment is invariant to the sign of the active coupling between A and M, but it is affected by the relative signs of the two passive couplings $J(A,X) = J_{1,9}$ and $J(M,X) = J_{9,10}$. If $J(A,X)$ and $J(M,X)$ exhibit the same sign, then irradiation of transition A₁ will affect transitions M₁ and M₃ but not M₂ and M₄; however, if $J(A,X)$ and $J(M,X)$ exhibit opposite signs, then irradiation of A₁ will affect M₂ and M₄ but not M₁ and M₃, etc.

The outcome of the experiment depicted in Fig. 3f clearly shows that the former is true, i.e. that $J(A,X) = J_{1,9} = {}^2J(^{15}\text{N}, ^{15}\text{N})$ and $J(M,X) = J_{9,10} = {}^1J(^1\text{H}, ^{15}\text{N})$ exhibit the same sign. As the couplings ${}^2J(^{15}\text{N}, ^{15}\text{N})$ are always positive and as large NH couplings, here $J_{1,10} = {}^1J(^{15}\text{N}, ^1\text{H})$, are negative,² because of the negative sign of the gyromagnetic ratio of ¹⁵N, this result means that ${}^1J(^{15}\text{N}, ^1\text{H})$ and ${}^1J(^1\text{H}, ^{15}\text{N})$ exhibit opposite signs.

DISCUSSION

We have used liquid-state ¹H and ¹⁵N NMR to study the scalar couplings of the nuclei involved in the intramolecular NHN hydrogen bonds of the symmetric *N,N'*-diphenyl-6-aminopentafulvene-1-alimine-¹⁵N₂ (**1**), and its asymmetric analog *N*-phenyl-*N'*-(1,3,4-triazol)-6-aminopentafulvene-1-alimine-¹⁵N₅ (**2**). In addition to our previous study,⁷ it was possible to determine the value of $J_{1,9}$ in the symmetric compound **1**. The value of 10.6 Hz is slightly larger than the value of 8.6 Hz⁷ for the asymmetric compound **2**. These values are at the upper end of those found for similar couplings (6–10 Hz) of intermolecular NHN hydrogen bonds of nucleic acid base pairs.² In principle, there are two coupling pathways between N-1 and N-9, one *via* the intramolecular hydrogen bond and another *via* the five intramolecular bonds of the molecular backbone. However, to our knowledge, ${}^5J(^{15}\text{N}, ^{15}\text{N})$ couplings have not been reported in the literature. Moreover, replacement of H-10 in **2** by a methyl group led to a disappearance of this coupling. Therefore, we assign the couplings $J_{1,9}$ in **1** and **2** to the couplings ${}^2J(^{15}\text{N}, ^{15}\text{N})$ across the intramolecular NHN hydrogen bonds.

In addition, it was possible to establish that the sign of $J_{9,10}$ in **2** is equal to the sign of ${}^2J(^{15}\text{N}, ^{15}\text{N})$. As ${}^2J(^{15}\text{N}, ^{15}\text{N})$

couplings are accepted to be positive,² this means that $J_{9,10}$ is also positive and exhibits the opposite sign compared with $J_{1,10} = {}^1J(^{15}\text{N}, ^1\text{H})$, which is negative because of the negative gyromagnetic ratio of ¹⁵N. In the case of a fast proton tautomerism between two tautomers a and b, any coupling between two nuclei *i* and *j* corresponds to the average

$$J_{ij} = x_a J_{ij}(a) + x_b J_{ij}(b) \quad (6)$$

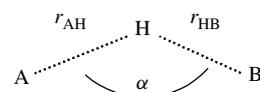
where x_a and x_b represent the mole fractions of a and b, and $J_{ij}(a)$ and $J_{ij}(b)$ are the intrinsic couplings between nuclei *i* and *j* in tautomers a and b. If the intrinsic coupling $J_{9,10}(a)$ across the hydrogen bond were zero, then the term $x_b J_{ij}(b)$ determining the observed coupling should be negative, as the $J_{9,10}(b)$ would correspond to a normal large and negative coupling of about –90 Hz. Moreover, the mole fraction x_b , and hence $J_{9,10}$, should depend strongly on temperature, which is apparently not the case. Therefore, we assign the observed value of $J_{9,10}$ to the intrinsic positive value $J_{9,10}(2a) = {}^1J(^1\text{H}, ^{15}\text{N})$, with $x_a = 1$.

Finally, we were able in the case of **1** to observe the coupling between N-1 and C-11. Here, it is more difficult to dissect the backbone pathway through six bonds *via* the molecular backbone from the pathway across the hydrogen bond (three bonds). However, we think that the hydrogen bond pathway plays a substantial role.

In the following, we will discuss the implications of these results summarized above for the properties of intramolecular NHN hydrogen bonds. For this purpose, we will make intensive use of the valence bond order model of hydrogen bonding, reviewed briefly in the next section.

Valence bond order model of hydrogen bonding

One can associate to any hydrogen-bonded system A–H···B two distances $r_1 \equiv r_{\text{AH}}$ and $r_2 \equiv r_{\text{HB}}$ (using either a bond labeling or an atom pair labeling) and a hydrogen bond angle α , as indicated in Scheme 1.

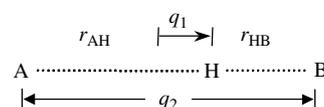


Scheme 1

It is convenient to define additionally the coordinates q_1 and q_2 according to

$$q_1 = \frac{1}{2}(r_{\text{AH}} - r_{\text{HB}}), q_2 = r_{\text{AH}} + r_{\text{HB}} \quad (7)$$

In the case of a linear hydrogen bond q_1 corresponds directly to the distance of the proton with respect to the hydrogen bond center and q_2 to the heavy atom A···B distance, as indicated in Scheme 2.



Scheme 2

According to the valence bond order concept of Pauling^{13a} and Brown,^{13b} one can define a valence p_{ij} of a diatomic molecule $ij = \text{AH}$ as

$$p_{ij} = \exp[-(r_{ij} - r_{ij}^0)/b_{ij}] \quad (8)$$

where b_{ij} is a decay parameter and r_{ij}^0 the distance where $p_{ij} = 1$. p_{ij} becomes zero at infinite distance. A hydrogen-bonded system $\text{A}-\text{H} \cdots \text{B}$ is then characterized by two bond valences, $p_1 = p_{\text{AH}}$ and $p_2 = p_{\text{HB}}$, and two distances, $r_1 = r_{\text{AH}}$ and $r_2 = r_{\text{HB}}$ (Scheme 1). In this paper A and B correspond to nitrogen atoms.

$$p_{\text{AH}} + p_{\text{HB}} = \exp[-(r_{\text{AH}} - r_{\text{AH}}^0)/b_{\text{AH}}] + \exp[-(r_{\text{HB}} - r_{\text{HB}}^0)/b_{\text{HB}}] = 1 \quad (9)$$

It follows that the two bond distances r_{AH} and r_{HB} cannot be varied independently. Using Eqn (9), it is possible to express r_{AH} as a function of r_{HB} , or q_1 as a function of q_2 . For the cases of OHO or NHN hydrogen bonds where $b_{\text{AH}} = b_{\text{HB}} = b$ and $r_{\text{AH}}^0 = r_{\text{HB}}^0 = r^0$, it follows that¹⁴

$$q_2 = r_1 + r_2 = 2r^0 + 2q_1 + 2b \ln[1 + \exp(-2q_1/b)] \quad (10)$$

The validity of Eqn (9) has been demonstrated¹⁵ on the basis of a number of neutron diffraction structures contained in the Cambridge Structural Data Base. The parameters of the correlation depend on the types of heavy atom of the hydrogen bonds. For NHN bonds Benedict *et al.*¹⁴ proposed the parameter set $r_{\text{NH}}^0 = 0.992 \text{ \AA}$ and $b_{\text{HN}} = 0.404 \text{ \AA}$, in close agreement with the values of Steiner.^{15d} Using these parameters, we calculated the solid line depicted in Fig. 4a. It indicates that when the proton is transferred from one nitrogen atom to the other, the $\text{N} \cdots \text{N}$ distance first shortens, then reaches a minimum and finally widens again.

The hydrogen bond data for **1** and **2** obtained by X-ray crystallography, listed in Table 4, are included in Fig. 4a as full squares. They indicate the presence of non-linear hydrogen bonds, with hydrogen bond angles of α around 155° (Table 4). Whereas the data of **1** are quite well located on the correlation curve, those of **2** show a significant deviation. This deviation probably arises from the well-known problems of X-ray crystallography for the localization

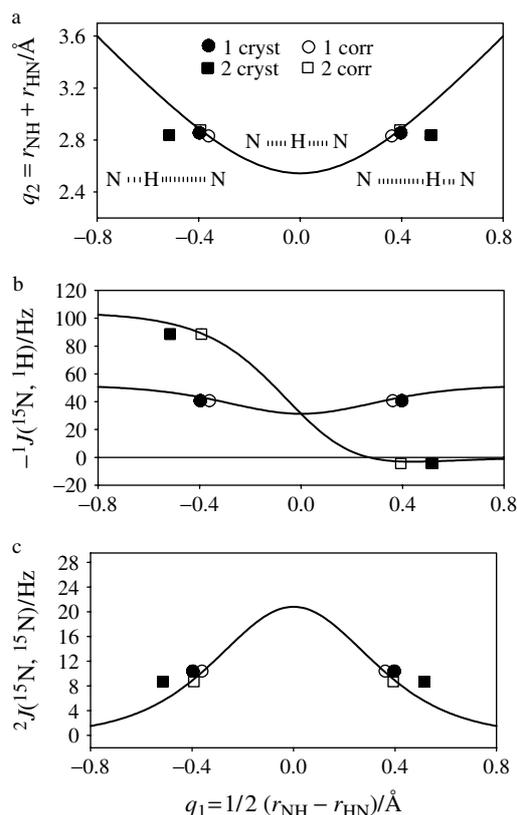


Figure 4. (a) Solid line: correlation of the geometrical parameters: $q_2 = r_{\text{NH}} + r_{\text{HN}}$ as a function of $q_1 = \frac{1}{2}(r_{\text{NH}} + r_{\text{HN}})$ for NHN hydrogen-bonded systems according to Steiner and coworkers^{15b-d} and Benedict *et al.*¹⁴ The full squares and full circles are taken from the X-ray crystallographic data of **1**^{8b} and of **2**,⁷ the other data points are corrected values for an H-bond angle of 160° according to Table 4. (b) Scalar $^1\text{H} - ^{15}\text{N}$ couplings and (c) scalar $^{15}\text{N} - ^{15}\text{N}$ couplings of **1** and **2** as a function of q_1 .

of protons. In order to locate the latter, either neutron diffraction or dipolar NMR studies are necessary, which were beyond the scope of this study. Table 4 also includes the equilibrium hydrogen-bond distances and angles of **1**, **2a** and the parent compound 6-aminopentafulvene-1-aldimine

Table 4. Geometries of the NHN hydrogen bonds of 6-aminopentafulvene-1-aldimines

	$r_{1,10}/\text{\AA}$	$r_{9,10}/\text{\AA}$	$q_1/\text{\AA}$	$q_2/\text{\AA}$	$r_{1,9}/\text{\AA}$	α		$r_{1,10}/\text{\AA}$	$r_{9,10}/\text{\AA}$	$q_1/\text{\AA}$	$q_2/\text{\AA}$	$r_{1,9}/\text{\AA}$	α
1	1.031 ^a	1.824 ^a	-0.397	2.855 ^a	2.791 ^a	154.59 ^a	2	0.937 ^b	1.968 ^b	-0.516	2.838 ^b	2.838 ^b	153.56 ^b
1	1.064	1.723	-0.330	2.787	2.791	180	2	1.054	1.783	-0.365	2.838	2.838	180
1	1.060	1.743	-0.342	2.803	2.791	170	2	1.051	1.798	-0.374	2.849	2.838	170
1	1.055	1.777	-0.361	2.832	2.791	160	2	1.046	1.892	-0.393	2.878	2.838	160
1	1.046	1.835	-0.395	2.881	2.791	150	2	1.038	1.892	-0.427	2.930	2.838	150
3	1.006 ^c	1.935 ^c	-0.465 ^c	2.941 ^c	2.849 ^c	150	2a	1.003 ^c	1.969 ^c	-0.483 ^c	2.972 ^c	2.893 ^c	152

Unless indicated otherwise the values are calculated as a function of the hydrogen bond angle α using the correlation of Eqn (10) and the NN distances of 2.791 \AA for **1** and of 2.828 \AA for **2**.

^a X-ray crystal structure from Ref. 8b.

^b X-ray crystal structure from Ref. 7.

^c Equilibrium values from *ab initio* calculations at the HF/6-31G** level partially reported in Ref. 7; values without vibrational averaging correction. **3** corresponds to the parent compound 6-aminopentafulvene-1-aldimine, where the phenyl groups in **1** were replaced by H.

(3) resulting from *ab initio* calculations at the HF/6-31G** level reported by Claramunt *et al.*⁷ These calculations predict hydrogen-bond angles of about 150°. However, in order to apply these values or improved values arising from higher-level calculations to the interpretation of experimental data it would be necessary to include a correction for the strongly anharmonic ground-state vibrations.

Therefore, we proceeded as follows. Assuming the validity of the hydrogen-bond correlation, we calculated $r_{1,10}$ and $r_{9,10}$ based on the crystallographic value of $r_{1,9}$ as a function of the hydrogen-bond angle α . The results are included in Table 4. It seems to us that a hydrogen-bond angle of about 160° for **1** and **2a** is the most realistic one, and this is used in the following discussion on the distance values corresponding to this angle.

Coupling-constant–distance correlation for NHN hydrogen bonds

Based on the NHN hydrogen bond correlation, Benedict *et al.*^{2a} have proposed the following relations for the scalar NHN hydrogen bond couplings, i.e.

$$J(^{15}\text{N}, ^{15}\text{N}) = J(^{15}\text{N}, ^{15}\text{N})^0(\alpha)(4p_{\text{N}}p_{\text{HN}}) \quad (11)$$

and

$$J(^{15}\text{N}, ^1\text{H}) = J(^{15}\text{N}, ^1\text{H})^0 p_{\text{NH}} + 8\Delta J(^{15}\text{N}, ^1\text{H}) p_{\text{NH}} p_{\text{HN}}^2 \quad (12)$$

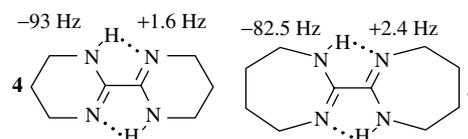
where the parameters of Eqns (11) and (12) are empirical. $J(^{15}\text{N}, ^{15}\text{N})^0(\alpha)$ corresponds to the value of the coupling at $p_{\text{NH}} = p_{\text{HN}} = 0.5$, i.e. in the symmetric case to the maximum coupling, for a given hydrogen-bond angle α . Here, we assumed that α remains constant. The coupling constant $J(^{15}\text{N}, ^1\text{H})$ corresponds to the sum of a term linear to the valence bond order p_{NH} and a non-linear second-order term. The parameter $\Delta J(^{15}\text{N}, ^1\text{H})$, which is negative, represents the deviation of $J(^{15}\text{N}, ^1\text{H})$ from $J(^{15}\text{N}, ^1\text{H})^0/2$ at the symmetric point where $p_{\text{NH}} = p_{\text{HN}} = 0.5$.

The upper solid line of Fig. 4b was calculated using Eqn (12), by adapting the values $J(^{15}\text{N}, ^1\text{H}) = 105$ Hz and $\Delta J(^{15}\text{N}, ^1\text{H}) = -22$ Hz to the experimental coupling constants $J_{1,10}$ and $J_{9,10}$ of **2**. The lower solid line in Fig. 4b, which corresponds to the average of both couplings $[J(^{15}\text{N}, ^1\text{H}) + J(^1\text{H}, ^{15}\text{N})]/2$, reproduces well the average experimental value of $(J_{1,10} + J_{9,10})/2$ of **1**. In addition, the solid line in Fig. 4c, calculated using Eqn (11) by adapting the parameter $J(^{15}\text{N}, ^1\text{H})^0$ to a value of 22 Hz, reproduced well the experimental finding that $J_{1,9}$ is larger for the **1** than for **2**.

CONCLUSIONS

The results discussed above clearly establish that the hydrogen-bond-induced sign change of the scalar coupling $J(\text{A},\text{H})$ in $\text{A}-\text{H}\cdots\text{B}$ when the $\text{A}\cdots\text{H}$ distance is increased during the transfer of H to B, observed first for FHF hydrogen-bonded systems by Shenderovich and coworkers,^{2a,3a} is a general phenomenon that is also valid for NHN hydrogen-bonded systems. In the region of the sign change the scalar coupling $J(\text{A},\text{B})$ is still quite large. As mentioned before,^{2a,3a}

this result, which is against the normal intuition of the NMR spectroscopist, is one of the main reason why heavy atom scalar couplings across hydrogen bonds have not been searched and recognized earlier. The problem with small intermolecular hydrogen-bonded systems is that they can be observed in the slow exchange region only by using novel low-temperature NMR techniques,^{3a} and the problem with the intramolecular hydrogen bonds was that proton tautomerism interferes with the determination of intrinsic couplings. The two contributions can even cancel. Moreover, our results indicate that the sign change has to be taken into account if one wants to extract equilibrium constants of tautomerism from coupling constants. The assumption that $J(\text{A},\text{H})$ is zero at larger $\text{A}\cdots\text{H}$ distances is no longer justified.



Scheme 3

In view of the present results, previous results reported by Scherer and Limbach¹⁶ for 2,2'-bis-3,4,5,6-tetrahydro-1,3-diazine-¹⁵N₄ (**4**) and 2,2'-bis-4,5,6,7-tetrahydro-1,3-diazepine-¹⁵N₄ (**5**) become clearer (Scheme 3). In those studies, the kinetics of the proton and deuteron tautomerism of both compounds was studied by dynamic NMR as a function of the ring size and the strength of the intramolecular hydrogen bonds. A curious observation was made, which could not be explained before, i.e. of $^1\text{H}(^1\text{H}, ^{15}\text{N})$ couplings across the hydrogen bonds whose sign was opposite to those of the large $^1J(^{15}\text{N}, ^1\text{H})$ couplings. The results obtained in this paper indicate that this is another example of a hydrogen-bond-induced sign change.

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