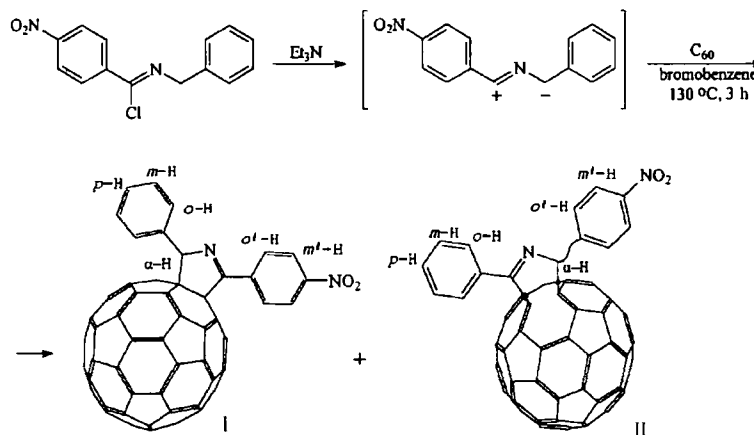# DETERMINATION OF THE ULTRA LONG RANGE SPIN-SPIN COUPLING CONSTANTS USING OVERALL LINE SHAPE ANALYSIS IN THE ^{1}H NMR SPECTRA OF FULLERENE-C_{60} CYCLOADDUCTS WITH 1-(4-NITROPHENYL)-3-PHENYLNITRILE YLIDE

V. A. Chertkov, S. V. Zubkov, A. A. Ovcharenko, A. V. Karchava, and M. A. Yurovskaya

On the basis of the overall signal line shape in the ^{1}H NMR spectra of [6,6]-closed and [5,6]-open fullerene-C_{60} cycloadducts with 1-(4-nitrophenyl)-3-phenylnitrile ylide we determined the values of the long range spin-spin coupling for the aliphatic proton of the heterocyclic fragment with the aromatic protons..

Previously [1] we have shown that cycloaddition of 1-(4-nitrophenyl)-3-phenylnitrile ylide (generated *in situ* from N-benzyl-4-nitrophenylimidoyl chloride) to fullerene-C_{60} leads to the formation of the [6,6]-closed cycloadduct 1,2-[3,4-dihydro-2-phenyl-5-(4-nitrophenyl)-2H-pyrrolo]-[60]-fullerene (I) and a diastereomeric mixture of [5,6]-open isomers II. Further, analysis of the ^{1}H NMR spectra based on the values of the long range spin-spin couplings between the α-proton and the phenyl ring protons has shown that, in the adducts II, the double bond is localized in the α-position relative to the unsubstituted phenyl nucleus.

The present report is concerned with a method of revealing and quantitatively measuring the long range spin-spin coupling values for the aliphatic α-proton with the aromatic protons in the ^{1}H NMR spectra of the cycloadducts I and II.

As might have been expected in this case, the values of all spin-spin interaction constants for the α-proton with the aromatic ring protons are less than 1 Hz and do not lead to a signal splitting for this proton at a practical level of resolution. However, its presence makes a contribution to the pattern of the α-H signal, increasing its broadness and introducing a deviation from an ideal Lorentz shape. Hence analysis of the overall shape in the ^{1}H NMR spectrum proves to have a unique potential for the resolution of this problem.
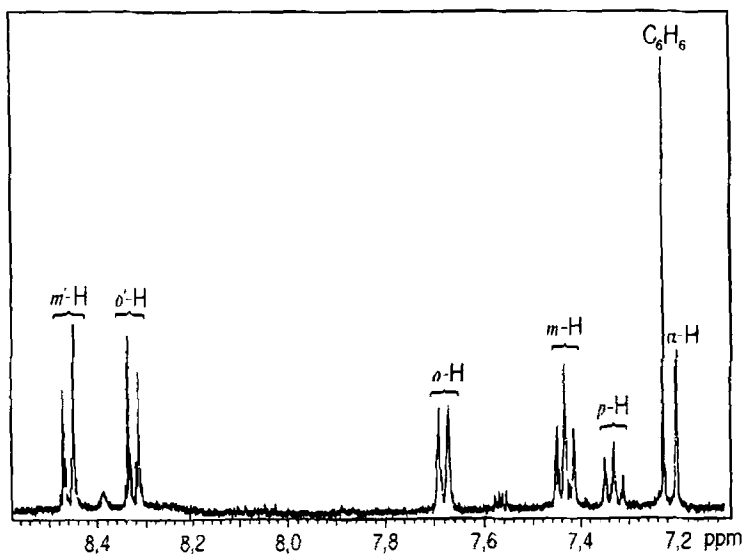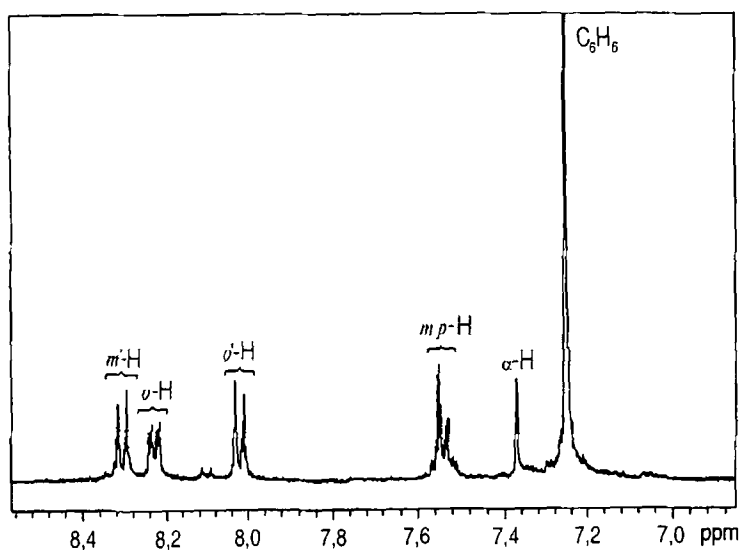
Fig. 1. ¹H NMR spectrum of compound I.

Fig. 2. ¹H NMR spectrum of compound II.

The ¹H NMR spectra of compounds I (Fig. 1) and II (Fig. 2) were recorded in the presence of benzene which was used to determine the intrinsic line width under the given conditions. There were then obtained double resonance spectra with decoupling from each group of aromatic protons (in the case of compound II the signals for the m-H and p-H protons fell together and decoupling was carried out for these two protons simultaneously). It was anticipitated that, with decoupling from the aromatic ring protons, the proton line width for the methylene group line signal would be decreased in agreement with the decrease in broadening due to spin-spin coupling.

In order to determine the contribution to the line width of the intrinsic broadening due to spin-lattice relaxation there was set up an inversion-recovery experiment for the aliphatic proton and the benzene signal. This experiment is derived from a simple sequence of π-impulse inverting the magnetization vector, delay time allowing it to relax, and π/2 impulse converting it to the xy plane for recording. The hold time for which the signal intensity proves to be zero is $t_0 = T_1 \ln 2$, where T_1 is the spin-spin relaxation time (for more detail see, e.g. [2]).

1309

TABLE 1. Inversion-Recovery Experiment Results

Delay time, s	Intensity of α-H signal	Intensity of benzene signal	Delay time, s	Intensity of α-H signal	Intensity of benzene signal
0.1	-30	-28	2.0	-3	-20
0.2	-23	-21	3.0	6	-15
0.3	-28	-30	4.0	15	-9
0.5	-27	-30	5.0	23	-2
1.0	-18	-26	6.0	28	3
1.5	-12	-25	8.0	35	14
1.8	-8	-23	10.0	39	19

t_0: 2.6 s; 5.5 s.
T_1: 3.2 s 8.0 s.

Hence, assuming that in this case T_2 is approximately equal to T_1 it is found that the contribution of the intrinsic broadening to the line shape ($1/\pi T_2$) must be approximately 0.04 Hz for benzene and 0.1 Hz for the aliphatic proton.

In Tables 2 and 3 there are given the line width for the aliphatic α-proton in spectra with decoupling from each of the aromatic protons, the broadening relative to the width of the line for benzene in each case with consideration of the contribution from the intrinsic broadening, and finally the same broadening relative to the α-proton signal in the spectra without decoupling (expressed as a percentage). From the data in Table 2 it is evident that in compound I the aliphatic α-proton has a non-zero spin-spin coupling constant with the o-H, m-H, and p-H protons and almost no interaction with the o'-H and m'-H protons, i.e the formula for compound I is as shown in the scheme.

TABLE 2. α-H and Benzene Proton Line Widths in the Spectra of Compound I with Decoupling from the Aromatic Ring Protons

Decoupling from	Line width, Hz		Broadening of the α-H line, Hz	Relative broadening, %
	α-H	C₆H₆		
m'-H	1.488	0.454	0.974	-5
o'-H	1.413	0.322	1.031	0
o-H	0.992	0.345	0.587	-43
m-H	1.115	0.355	0.700	-32
p-H	1.253	0.453	0.740	-28
Without decoupling	1.400	0.373	1.027	0

TABLE 3. α-H and Benzene Proton Line Widths in the Spectra of Compound II with Decoupling from the Aromatic Ring Protons

Decoupling from	Line width, Hz		Broadening of the α-H line, Hz	Relative broadening, %
	α-H	C₆H₆		
m'-H	1.334	0.304	0.970	-3
d'-H	1.462	0.270	1.132	13
o-H	1.009	0.310	0.639	-36
p-H+p-H*	1.368	0.413	0.895	-11
Without decoupling	1.522	0.460	1.002	-0

* In the spectrum of compound II the m-H and p-H protons fall together.

1310

It can be seen from Table 3 that the α-proton in compound II has a spin-spin coupling with the o'-H and m'-H protons, however this case also graphically demonstrates that a simple measurement of line width cannot serve as a strict criterion for analysis of the structure since a significantly larger number of factors exert control over it than included within intrinsic broadening and broadening due to weak spin-spin interaction. Specifically, upon decoupling from the m-H and p-H protons the line width of the α-proton is noticeably decreased but this can arise both from the presence of non-zero spin-spin coupling with one of them but also because the suppressed signals are situated too close to that being discussed and its intensity can also be decreased. Hence the data in Table 3 allows us to make a preliminary hypothesis that the α-proton is situated in the α-position to the p-nitrophenyl fragment as in the scheme. However, a definitive conclusion could only be made by analysis of the overall line shape of the α-H signal via the acquisition of numerical values of the spin-sin coupling parameters with the aromatic protons.

The analysis was carried out in the following way. The spectra of compounds I and II were used for accurately defining the chemical shifts of all the protons and the spin-spin coupling among the aromatic protons. The resolution of the spectrum was sufficient for this task and additional broadening was not recorded. Then for each of the spectra, double resonance was carried out in the following manner.

1. The benzene signal line width was determined, computing the trivial inverse problem using NMRCON [3] for a single spin system and defining only the line width and scaling factor.

2. The obtained line width was modified in accord with the presence of the intrinsic broadening contribution in the benzene signal and the α-proton, as determined from the inversion-recovery experiment.

3. Strict analysis of the spectrum: determination of the spin-spin coupling between the α-proton and the aromatic protons, the scaling factor and the chemical shift of the α-proton (four parameters for compound I and three for compound II). For a first approximation there were used the corresponding constants for toluene [4] and from all of the spectrum studied there was taken only the small section which contained the essential signal as shown in Fig. 3.
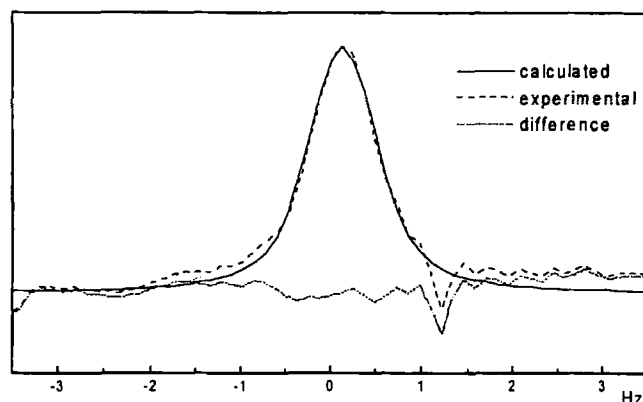

Fig. 3. Line shape for the α-proton signal in compound I
with decoupling from the p-H proton.

TABLE 4. Spin-Spin Coupling Values between the α-H Proton and the Aromatic Protons in Compound I

J, Hz	Decoupling from p-H	Decoupling from m-H	Decoupling from o-H	Mean	Analogous J for toluene
α-H, o-H	-0.68 ± 0.06	-0.38 ± 0.03	—	-0.47 ± 0.2	-0.75
α-H, m-H	0.45 ± 0.05	—	-0.23 ± 0.19	0.40 ± 0.2	-0.36
α-H, p-H	—	-0.61 ± 0.03	-0.23 ± 0.19	-0.56 ± 0.3	-0.62

TABLE 5. Spin-Spin Coupling Values between the α-H Proton and the Aromatic Protons in Compound II

J, Hz	Decoupling from o'-H	Decoupling from m'-H	Without decoupling	Mean
α-H, o'-H	—	0.19 ± 0.04	0.33 ± 0.05	0.25 ± 0.1
α-H, m-H	0.18 ± 0.05	—	0.43 ± 0.03	0.33 ± 0.18

Safeguards connected with the reduced number of variable parameters were linked to the relatively high noise level and the low degree of spectral resolution (the line shape was actually built up irregularly from 30-50 points).

In these conditions the NMRCON procedure [3] came successfully to a solution in all cases with a small number of iterations. Tables 4 and 5 show the values for the obtained α-proton spin-spin couplings. For compound I, in which this proton is found near to the unsubstituted phenyl fragment there is a close similarity for these values and those of the analogous spin-spin couplings in toluene [4], thus confirming the reliability of our results.

EXPERIMENTAL

^{1}H NMR Spectra were recorded on a Varian VXR-400 spectrometer for solutions of the compounds studied in CS_2 with the addition of 10% $(CD_3)_2CO$ and a small amount of benzene.

REFERENCES

1. A. A. Ovcharenko, V. A. Chertkov, A. V. Karchava, and M. A. Yurovskaya, Tetrahedron Lett., 38, 6933 (1997).
2. A. Derome, Modern NMR Techniques for Chemical Research [Russian translation], Mir, Moscow (1992), p. 132.
3. J. Heinzer, J. Magn. Resonance, 26, 505 (1977).
4. M. Hansen and H. J. Jakobsen, J. Magn. Resonance, 20, 520 (1975).