Carbon-Nitrogen Spin-Spin Coupling in Diazomethane

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(2. Naturforsch. 31 b, 1515–1518 [1976]; received August 4, 1976)
Carbon-nitrogen Coupling, Coupling Mechanism

The one-bond carbon-nitrogen coupling constant of diazomethane is reported. Analogies with carbon-carbon coupling constants in allenes are emphasized. CNDO/S-calculations are used as a support of the suggestions the C-N coupling in diazomethane to be dominated by the Fermi contact mechanism and the sign of the carbon-nitrogen-15 coupling constant to be negative.

1. Introduction

Carbon-nitrogen coupling constants have become a matter of interest concerning their signs and the question of the relative contributions of the Fermi contact term (FC), the orbital term (OB), and the spin-dipolar term (SD)\(^1\) to the total coupling\(^2\)-\(^4\). With special emphasis to these problems we wish to report the \(^{13}\)C-\(^{14}\)N coupling constant of diazomethane (1) (Fig. 1).

The qualitative discussion of the experimental result is mainly based upon comparisons of the \(^{13}\)C-\(^{15}\)N coupling in 1

\[(1J(^{13}\text{C} - ^{15}\text{N})) = -1.402 \text{ Hz}\]

with the \(^{13}\)C-\(^{13}\)C coupling in allene (2) (Fig. 1; \(1J(^{13}\text{C} - ^{13}\text{C}) = 98.7 \text{ Hz}\)\(^5\)) and 1,1-dimethylallene (3) (Fig. 1; \(1J(^{13}\text{C} - ^{13}\text{C}) = 99.5 \text{ Hz}\)\(^6\)). More quantitative interpretations of the couplings are based upon the independent-electron MO treatment of nuclear spin-spin coupling constants\(^7\) and the use of CNDO/S wave functions for 1\(^8\) and, in order to avoid problems associated with the degeneracy of the allene orbitals\(^9\), for 3\(^9\).

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2. Result and Discussion

Measuring the proton-noise decoupled \(^{13}\)C-spectrum of diazomethane in deuterochloroform\(^10\) a 1:1:1 splitting of the carbon resonance owing to \(^{13}\)C-\(^{14}\)N coupling has been observed. The coupling constant amounts to \((14.4 \pm 1.3) \text{ Hz}, \text{ i.e.} \)

\[
|1J(^{13}\text{C} - ^{14}\text{N})| = (20.2 \pm 1.8) \text{ Hz (Fig. 2).}
\]

Usually, spin coupling between \(^{14}\)N and spin-1/2-nuclei (\(^1\)H, \(^{13}\)C) is not observable because of the rapid quadrupolar relaxation of the \(^{14}\)N nucleus. However, in several instances, such as isocyanides, tetraalkylammonium salts, and nitrates, where the electric field gradient at the \(^{14}\)N nucleus is highly symmetrical, quadrupole-induced relaxation is evidently quite slow, since in these cases \(^{14}\)N-H spin coupling is preserved\(^11\). On the other hand, Roberts et al.\(^12\)

Fig. 2. 22.63 MHz proton-noise decoupled \(^{13}\)C-spectrum of diazomethane in CDC\(_3\) at 0 °C (TMS internal standard).
could observe $^{13}$C-$^{14}$N splitting in the proton-noise decoupled $^{13}$C spectrum of 2,4,6-trimethyl-benzonitrile-oxide (4) (Fig. 1). 4 has the same $C_3v$-symmetry as diazomethane$^{12}$. Diazocompounds of lower $n$-orbitals (lone-pairs), such as imines, oximes, etc., whereas in molecules with no such lone-pairs (iminium ion$^{2}$, pyridinium and quinolinium ion$^{3-4}$) $^{1}J$(C-$^{14}$N) seems to be negative$^{2-4}$. This suggests the carbon-nitrogen-15 coupling constant in diazomethane to be negative, considering the dominant resonance forms for the description of the ground state of 1$^{10}$. Our assumption is further supported by the following arguments. In one-bond carbon-carbon coupling the FC term is generally dominant$^{2,6,14,15}$. Though the OB term is nonnegligible in multiply bonded systems$^{2,14}$, it represents only a correction. Especially, Pople's "finite perturbation"$^{14}$ computational result for the FC term in allene (2) ($^{1}J$(C-$^{15}$C) = +108.5 Hz$^{15}$) in relation to the experimental value$^{5}$ suggests the OB term to be rather small in this cumulene. Therefore, on the basis of the isoelectronic principle$^{17}$, a role of dominant importance of the FC mechanism may be expected for diazomethane. This leads automatically to a positive reduced coupling constant $^{1}K$(C-$^{15}$N)$^{7,11}$. As a consequence the carbon-nitrogen-15 coupling constant in 1 should be negative, considering the negative sign of $\gamma$($^{15}$N). The isoelectronic principle states that within a series of isoelectronic molecules with the same heavy atom grouping the main electronic features are widely retained and all the electronic states of the isoelectronic systems are of comparable spectroscopic significance$^{17}$.

The strongest support for our conclusions, however, stems from the comparison of the reduced carbon-nitrogen-15 and carbon-carbon coupling constants in the structurally related systems given in Fig. 3. These systems include isosteric$^{15}$ molecules or compounds with at least comparable neighborhood topology for the atoms involved in the spin-spin coupling. If we include 1 and 2, the linear correlation (1) (linear correlation coefficient $r = 0.972$) is obtained by a least-squares fit.

$$^{1}K$(C-$^{15}$N) = 0.51 $^{1}K$(C-$^{13}$C) - 3.19 (10$^{20}$ cm$^{-3}$)

(1)

Equation (1) suggests the $^{15}$C-$^{15}$N and the $^{13}$C-$^{13}$C coupling mechanisms to be similar, at least for the systems under consideration. On the other hand, the OB term and the FC term are often of opposite sign in $^{13}$C-$^{15}$C and $^{15}$C-$^{15}$C couplings$^{2,14}$. The negative intercept of Equation (1) may be a partial simulation of the OB contribution to $^{15}$C-$^{15}$N coupling. Significant contributions of the OB term have been suggested by Brunsch et al.$^{19}$ for molecules with large downfield nitrogen-15 chemical shifts, i.e. for compounds with low-energy excited states resulting from magnetically allowed transitions. These last conditions are met with the cumulenes. They have low-energy magnetically allowed $^{1}A_{2}$ excited states resulting from $\pi \rightarrow \sigma^{*}$, $\pi \rightarrow \pi^{*}$ transitions$^{9,17,20}$ and large downfield chemical shifts for their central atoms$^{21,22}$.

For a decisive conclusion about the relative contribution of the different mechanisms to the spin coupling in the cumulenes order of magnitude calculations for the FC, OB, and SD terms in 1 and 3 have been carried out on the basis of the independent-electron MO method$^{2,7,23}$ using a "sum-over-states"

Fig. 3. Reduced carbon-nitrogen-15 and carbon-carbon coupling constants (10$^{20}$ cm$^{-3}$) in structurally related systems. a) Value for CH$_{3}$CH(NH$_{3}^{+}$)COO$^{-}$.$^{11}$
The excellent numerical agreement between calculated and observed values for 1 seems to be fortuitous, especially if the results for 3 are also considered. The computational results for the relative contributions of the different coupling mechanisms, however, support our suggestions the carbon-nitrogen-15 coupling constant in diazomethane to be negative, the OB term to be small, and the coupling to be dominated by the FC mechanism as is the case for the carbon-carbon coupling in allene (2) and 1,1-dimethylallene (3). Furthermore, in both the cases the OB term is nearly cancelled by the SD term. It seems that the OB term becomes a significant contribution only for C-N systems where the large downfield nitrogen-15 shifts are associated with $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions (amines, oximes, pyridine, etc.\textsuperscript{2,4}) and not with $\pi \rightarrow \sigma^*$ transitions as in 1. Therefore, the nitrogen lone-pair is important for the C-N coupling mechanism. Indeed, its orientation has been shown to be important for the magnitude and sign of the $^{13}\mathrm{C}^{15}\mathrm{N}$ coupling constant\textsuperscript{3,24}.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Table I. Calculated\textsuperscript{a} and observed reduced coupling constants ($10^{20}$ cm$^{-3}$) of diazomethane and 1,1-dimethylallene.

<table>
<thead>
<tr>
<th>Compound</th>
<th>FC ($1\kappa(13\mathrm{C}^{15}\mathrm{N})$)</th>
<th>OB</th>
<th>SD</th>
<th>Total</th>
<th>Exptl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+68.25</td>
<td>−5.44</td>
<td>+2.64</td>
<td>+65.45</td>
<td>+66.0\textsuperscript{b,c}</td>
</tr>
<tr>
<td>3</td>
<td>+83.58</td>
<td>−4.55</td>
<td>+3.93</td>
<td>+82.96</td>
<td>+131.1\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculation carried out by means of a "sum-over-states" independent-electron MO-method\textsuperscript{2,7,23} with CNDO/S wave functions.

\textsuperscript{b} This work.

\textsuperscript{c} $1\kappa(13\mathrm{C}^{15}\mathrm{N}) = -3.268 \cdot 10^{20} 1\kappa(13\mathrm{C}^{15}\mathrm{N})^{24}$. 

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