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Published in:
Journal of Magnetic Resonance

DOI:
10.1016/0022-2364(75)90025-6

Published: 01/01/1975

Citation for published version (APA):
\textbf{\textsuperscript{1}H and \textsuperscript{13}C NMR Spectral Data for Spiro[2.4]heptadiene-4,6 and Spiro[4.4]nonadiene-1,3}

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Received September 30, 1974

\textsuperscript{1}H and \textsuperscript{13}C NMR spectral data have been obtained for spiro[2.4]heptadiene-4,6 and spiro[4.4]nonadiene-1,3, using selective decoupling of proton lines and matching of calculated and experimentally observed spectra. The high-field olefinic proton signals in spiro[4.4]nonadiene-1,3 are assigned to the "inner" olefinic protons. The results indicate that comparable \textsuperscript{1}H-\textsuperscript{1}H and \textsuperscript{1}H-\textsuperscript{13}C coupling constants in the cyclopentadiene parts of both molecules are similar. This indicates similar bond localizations as well.

Recently a number of publications appeared concerning the analysis of high-resolution, coupled \textsuperscript{13}C NMR spectra of 5- and 6-membered heteronuclear aromatic rings (1). Of the corresponding hydrocarbons only benzene (2) and naphthalene (3) have been analyzed in detail. No complete analyses of cyclopentadiene systems have as yet been published.

Here we present \textsuperscript{1}H and \textsuperscript{13}C NMR analyses of spiro[2.4]heptadiene-4,6 (I) and spiro[4.4]nonadiene-1,3 (II). Apart from being 5,5-disubstituted cyclopentadiene derivatives, these compounds are of special interest because some controversial remarks have been made concerning the supposed spiro-aromaticity of I. In 1970, Clark and Fiato (4) decided that a combination of the cyclopentadienyl anion and the ethenyl cation will contribute to the extent of ca 15\%. These arguments have been used in a later stage to...
explain similar phenomena in related systems (5, 6). However, the original conclusions of Clark and Fiato have since then been questioned, based on electron diffraction (7) and MO calculations (7, 8). No conjugative effects are to be expected for compound II (9). Since the original arguments (4) were based entirely on chemical shift considerations of the cyclopropyl protons in I and 13C NMR chemical shifts yield no clear evidence for special effects in I, detailed 1H and 13C NMR results of compounds I and II could be valuable to clarify the situation.

1H NMR spectra of I and II were obtained of neat compounds on a Varian HA-100 spectrometer. Assignments of olefinic signals of I to protons H4, H7 and H6, H6 were based on long-range couplings with the cyclopropyl protons of H4, H7. Accordingly, the high-field part was assigned to H4, H7, in agreement with previous publications (4). The olefinic spectrum of II, however, is completely symmetric. Only after the 13C nuclei had been involved in the analysis (both via the 13C NMR spectra and via the 13C sidebands in the 1H NMR spectra) did it become clear that the low-field multiplet is to be assigned to H1, H4, the high-field part to H2, H3; see also the discussion of the 13C NMR spectra. This latter assignment stands in contrast to the commonly observed fact that “inner” protons of a conjugated hydrocarbon diene absorb at lower fields than the corresponding “outer” protons (10).

Spectral parameters were calculated from the spectra using LAOCOON-3 and modified NMRIT and NMREN programs. The olefinic protons were treated as AA'BB' systems with additional long-range coupling (1st order) caused by the cyclopropyl protons on H4, H7 in I. Vicinal proton couplings in the cyclopropyl system of I were determined from the 13C sidebands (vide infra). The cyclopentyl system of II was not analyzed in detail. Results are presented in Table 1.

<table>
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<th>TABLE 1</th>
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<tr>
<td><strong>1H NMR Spectral Data of I and II</strong></td>
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* Diagonal elements: chemical shifts in ppm downfield from TMS; off-diagonal elements: coupling constants in cps.
In the iterative calculations it was shown that all couplings between protons at the unsaturated rings in I and II have the same sign. Since vicinal olefinic couplings are positive, it follows that all other couplings are positive as well. Finally, long-range couplings were observed in I between $H_1$, $H_2$ and $H_4$, $H_7$ and also between $H_1$, $H_2$ and $H_5$, $H_6$. In each of these cases, there are two different types of coupling. Only the absolute value of the sum was determined:

$$|J_{H_1H_4} + J_{H_1H_5}| \approx 0.15 \text{ cps}$$

The $^{13}$C NMR results were obtained in the Fourier transform mode on a Varian HA-100 spectrometer interfaced with a Digilab FTS-NMR-3 pulsing and data system. High-resolution spectra were made using 5-mm sample tubes, 16 or 32 K transform sizes combined with a spectral width of approximately 1000 cps. C$_2$Br$_2$F$_4$ served as an external $^{19}$F lock. The preliminary results for the olefinic parts of I and II were obtained with selective decoupling of the saturated protons. Vice versa, unsaturated protons were irradiated while the saturated carbons were observed. Again, no full analysis of the cyclopentyl system of II was performed. The olefinic carbon signals were analyzed as X-parts of ABCDX spectra, the symmetry in the proton spectra being distorted by $^{13}$C isotope effects on the $^1$H shifts. As has been noted before (Id), ambiguities may arise concerning the distinction between different sets of coupling constants obtained by permutation. A similar uncertainty arises concerning different relative signs of the couplings. In order to enable a decision, both the $^{13}$C spectra (coupled) and the outer $^{13}$C sidebands in the $^1$H NMR spectra were analyzed. For each olefinic carbon in I and II, 16 different sets of coupling constants with olefinic protons may exist. In the literature several ways of distinguishing between those sets have been reported separately, like selective irradiation of proton lines and minimum standard deviations between calculated and observed $^{13}$C lines. The procedure used in this work will be outlined for C$_5$ in compound I. The absolute values of the couplings with $H_5$ and $H_6$ were obtained from simple inspection of the spectra. This is also true for the absolute values of the sum of the couplings with $H_4$ and $H_7$. The individual absolute values of these last two interactions were deduced by preliminary trial and error calculations (at this stage, these couplings are still interchangeable).

Assuming that one-bond $^{13}$C-$^1$H couplings are positive, $^{13}$C spectra and $^{13}$C outer sidebands in $^1$H spectra were computed for all 16 possible sets. Eight of these, with different signs for $J_{C=CH_2}$ and $J_{C=CH_3}$, yield spectra considerably different from the experimental ones, both for $^{13}$C and $^1$H. Of the remaining eight sets, four yield $^{13}$C spectra, for which each half is the mirror image of the experimental spectrum, or, alternatively, the two halves should be interchanged. Two other sets yield mirror images of the experimentally observed outer $^{13}$C sidebands in the $^1$H spectra. Finally, two possible sets remained: set I ($J_{C=CH_4} = +4.23 \text{ cps}$, $J_{C=CH_6} = +5.91 \text{ cps}$, $J_{C=CH_7} = +10.45 \text{ cps}$). And set II ($J_{C=CH_4} = -10.45 \text{ cps}$, $J_{C=CH_6} = +5.91 \text{ cps}$, $J_{C=CH_7} = -4.23 \text{ cps}$).

Selective irradiation of the lowest field outer $^{13}$C sideband line of $H_5$ (or $H_3$) yielded a decreased intensity (with more decoupling power negative intensities) of the lowest field line in the low field part of the spectrum of C$_5$ (or C$_3$). In contrast, the intensity of the lowest field line in the high field part of the C$_5$ (or C$_3$) spectrum increased markedly. These results are only compatible with set I. Couplings according to set II would have yielded changing intensities of other lines in the $^{13}$C spectrum. The use of selective...
irradiation as the only means of distinction (1e) could have left some ambiguities because for instance the combination:

\[ J_{C_5H_6} = +10.45 \text{ cps}, \quad J_{C_5H_7} = +5.91 \text{ cps}, \quad J_{C_5H_7} = +4.23 \text{ cps} \]

(set III) would have yielded decoupling results similar (not identical) to those of set I. When used in conjunction with arguments put forward in the previous paragraph, however, the experimental results are quite clear.

Recently, the \(^{13}\text{C}\) spectrum of furan was reanalyzed using the root mean square (rms) errors between calculated and experimental \(^{13}\text{C}\) lines as the only criterion. Quite interestingly this criterion would have led to a smaller rms error for set III than for set I. Obviously, the exclusive use of rms errors is useful only in a limited number of examples. In the present case, the rms error for set I (0.059 cps) is considerably larger than that for furan in (1d). This is presumably caused by small couplings between H\(_1\), H\(_2\) and C\(_5\), C\(_6\) in I and by overlap of 2 x 2 lines in the C\(_5\) spectrum, introducing some uncertainty in the assigned line positions for these transitions. Including the \(^1\text{H}\) lines in the iteration yielded a rms error for the \(^{13}\text{C}\) lines of 0.074 cps with \(^{13}\text{C}\) isotope effects as indicated in Table 2.

### Table 2

| \(^{13}\text{C}\) NMR Spectral Data of I and II* |
|-------------------------------|-------------|-------------|-------------|-------------|
| I C\(_1\) C\(_3\) C\(_4\) C\(_5\) |
| Shift | 12.67 | 38.32 | 139.75 | 129.69 |
| H\(_1\) | +164.90 | 2.42 | 3.12 | 0.10 |
| H\(_4\) | 0.75 | 6.53 | +168.91 | 4.19 |
| H\(_5\) | 0.43 | 11.93 | +3.22 | +164.51 |
| H\(_6\) | 0.43 | 11.93 | +6.97 | +5.90 |
| H\(_7\) | 0.75 | 6.53 | +4.69 | +10.50 |
| \(\delta \delta_{25}\) | — | — | +0.01 | — |
| \(\delta \delta_{47}\) | — | — | — | — |
| \(\tau\) | 0.022 | 0.023 | 0.154 | 0.074 |

| II C\(_6\) C\(_7\) C\(_5\) C\(_1\) C\(_2\) |
|-------------------------------|-------------|-------------|-------------|-------------|
| Shift | 32.95 | 26.66 | 64.64 | 143.89 | 128.64 |
| H\(_6\), H\(_9\) | — | — | — | 3.10 | 0.10 |
| H\(_7\), H\(_8\) | — | — | — | — | 0.10 |
| H\(_1\) | — | 0.10 | 7.20 | +165.70 | +4.63 |
| H\(_2\) | — | 0.10 | 8.70 | +2.81 | +163.97 |
| H\(_3\) | — | 0.10 | 8.70 | +6.84 | +6.42 |
| H\(_4\) | — | 0.10 | 7.20 | +4.89 | +10.77 |
| \(\delta \delta_{23}\) | — | — | — | +0.02 | — |
| \(\delta \delta_{14}\) | — | — | — | — | — |
| \(\tau\) | — | — | — | 0.193 | 0.112 |

* Shifts in ppm downfield from TMS, all other parameters in cps.

b Only the absolute value was determined.

c Absolute value of the sum of two different couplings

e.g. \(|J_{C_4H_14} + J_{C_4H_16}|\), etc.
Selective irradiation of $^{13}$C sidebands of H$_4$ and H$_7$ in I yielded changing intensities in the $^{13}$C spectrum, compatible only with the results depicted in Table 2. These changes could be observed in spite of the still existing long-range couplings between the cyclopropyl protons and C$_4$ (and C$_7$). It only meant that a quintuplet instead of a single line was affected. In each case at least three lines of a "submultiplet" were observed independently.

Couplings involving the spiro C atom were obtained from first-order analysis of the multiplet (X-part of AA'BB'X spectrum with additional splitting caused by the cyclopropyl protons). Relative signs of these couplings were not determined. Couplings within the cyclopropyl system of I were obtained from coupled spectra; the couplings with olefinic protons were treated as first-order perturbations. In general, for compound II similar techniques and considerations were applied as for I. Again, the cyclopentyl system was not analyzed in detail because of the complexity already noted.

In contrast with the C$_5$ spectrum of compound I, the C$_2$ spectrum of II was not symmetric with respect to the resonance frequency of C$_2$. Two pairs of weak lines on either side showed markedly different intensities. No satisfactory agreement between calculated and observed patterns could be obtained unless the low-field olefinic proton signals were assigned to H$_1$, H$_4$ and the high-field signals to H$_2$, H$_3$ (vide supra). Final results for I and II are summarized in Table 2.

The $^{13}$C chemical shifts of I have been reported earlier (8). While Table 2 in this reference reports the chemical shifts correctly, the text of one of the footnotes rests on a reversed assignment of C$_4$ and C$_5$. Also, these authors wrongly quote Clark and Fiato (4) for having assigned the low-field olefinic proton lines to H$_4$ and H$_7$. This, again, could point to a reversed assignment of C$_3$ and C$_6$. Comparison of the results presented here with those reported previously for heteroaromatic 5-membered rings is somewhat difficult because the spectrum of furan has recently been reassigned, independently, by two groups (1d, ii). For thiophene and selenophene the original analyses (1a) still stand. Furan seems to be the only system in which two bond $^{13}$C–$^1$H couplings are consistently larger than 3- and 4-bond couplings. Our results for the "inner" olefinic carbons correspond closely to those of thiophene and selenophene, the "outer" carbons are quite dissimilar. More importantly, however, the mutual differences between compounds I and II are only minor. This indicates that bond localizations in these compounds should also be very similar.

ACKNOWLEDGMENT

This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES