${}^{13}C$ NMR Spectra of Trimethylene Oxide and Sulphide

Jukka Jokisaari and Juha Kuonanoja
Department of Physics, University of Oulu, 90100 Oulu 10, Finland
and
Anna-Maija Häkkinen
Department of Medical Physics, University of Helsinki, 00170 Helsinki 17, Finland

Z. Naturforsch. **33a**, 7—10 (1978); received October 25, 1977

The ${}^{13}C$ NMR spectra of trimethylene oxide and trimethylene sulphide have been recorded and analysed as second-order spectra. The values of all the C—H coupling constants with their signs are reported. The signs of the C—H coupling constants in trimethylene oxide were determined by selective irradiation experiments and theoretical calculations, while in trimethylene sulphide the signs were obtained directly from the analysis. The one-bond C—H coupling constants are approximately 3 Hz greater in trimethylene oxide than in trimethylene sulphide, while the absolute values of the two-bond and three-bond coupling constants, ${}^2J_{C_\beta H}$ and ${}^3J_{C_\alpha H}$, are about 1 Hz greater in the latter molecule.

Experimental

The samples used were 70 ± 1 mole per cent solutions in $CDCl_3$. They were degassed with the freeze-pump-thaw method. All the spectra were recorded with a JNM-FX-100 FT NMR instrument operating at the DQD (Digital Quadrature Detection) mode using a frequency range of either 500 Hz or 400 Hz and collecting 16 k data points. The spectra were Fourier-transformed without apodizing. The single resonance spectra were analysed with the program LAOCN 3, while in the calculations of theoretical double resonance spectra the program HETERO [1] was used.

The power used in selective double resonance experiments was adjusted by measuring the residual coupling, ${}^1J^r_{CH}$, and by comparing it with the value obtained from the calculated spectrum.

Introduction

Trimethylene oxide as well as trimethylene sulphide have been objects of several nuclear magnetic resonance, infrared and microwave studies. Lozach and Braillon [2] and Ferretti [3] have measured the ${}^1H$ NMR spectra and reported the H—H spin-spin coupling constants. Unfortunately, however, the spectra do not yield very easily all the coupling constants because of the symmetry of the spin systems and the deceptive simplicity of the spectra. This is why the error limits, especially in the geminal coupling constants, are relatively large. Furthermore, these inaccuracies lead to difficulties in analysing the ${}^{13}C$ NMR spectra, particularly in the case of trimethylene sulphide, where the ${}^{13}C$ spectrum shows marked second-order features.

Lippert and Prigge [4] reported the values for the one-bond C—H coupling constants in both the molecules in question, but as far as we know, this is the first time when the complete analyses, which also give the long-range C—H coupling constants, have been carried out.

Infrared and microwave studies have focussed on the ring-puckering vibrations of the molecules [5—7]. These studies show that in gaseous phase the rings are planar, although the potential functions are double minimum functions. In trimethylene sulphide the potential barrier is much higher than in trimethylene oxide. Ring-puckering vibrations of the present molecules have also been studied with ${}^1H$ NMR spectroscopy in liquid crystalline media [8—10].

Results and Discussion

Both the ${}^{13}C_\alpha$ and the ${}^{13}C_\beta$ spectra of trimethylene oxide and sulphide consist of a triplet. The components of these triplets show second-order features, which is why iterative analyses were applied using LAOCN 3. The ${}^{13}C$ spectra of trimethylene sulphide are presented in Figures 1 and 2. The C—H coupling constants with their error limits obtained from the LAOCN 3 output are shown compiled in Table 1.

In order to find out whether the absolute value of ${}^2J_{C_\alpha H}$ or that of ${}^3J_{C_\alpha H}$ is greater, we performed ${}^{13}C$-$\{{}^1H\}$ double resonance experiments, irradiating the α-CH_2 and β-CH_2 protons and observing the ${}^{13}C_\alpha$ resonances. The results of these experiments are shown for trimethylene oxide in Figure 3. These

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Reprint requests to J. Jokisaari, Institut für Physik der Universität Basel, Klingelbergstr. 82, CH-4056 Basel, Schweiz.

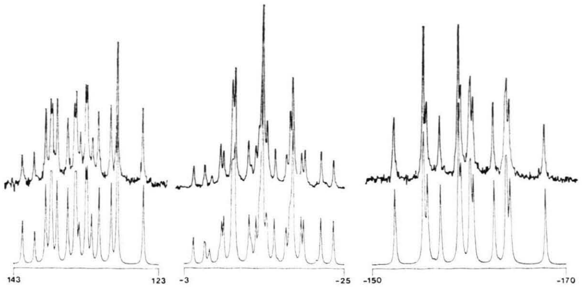

Fig. 1. The $^{13}C_\alpha$ NMR spectrum of trimethylene sulphide. The upper traces are experimental and the lower ones simulated. The intensity of the central part is reduced by a factor of 2. The frequency numbers on the abscissa are in Hz relative to an arbitrary origin.

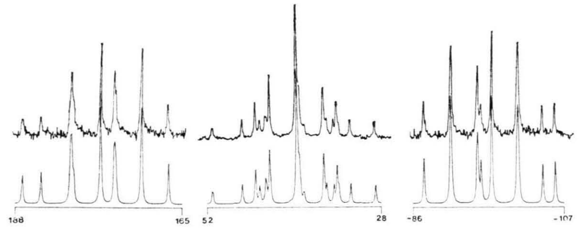

Fig. 2. The $^{13}C_\beta$ NMR spectrum of trimethylene sulphide. The upper traces are experimental and the lower ones simulated. The intensity of the central part is reduced by a factor of 2. The frequency numbers on the abscissa are in Hz relative to the same arbitrary origin as in the $^{13}C_\alpha$ spectrum.

Table 1. ^{13}C-^{1}H spin-spin coupling constants in trimethylene oxide and sulphide. The error limits are those given by LAOCN3. All the values are in Hz.

Coupling constant	Trimethylene oxide[a]	Trimethylene sulphide[b]
${}^1J_{C_\alpha H}$	149.48 ± 0.01	146.51 ± 0.01
${}^1J_{C_\beta H}$	137.36 ± 0.01	134.57 ± 0.01
${}^2J_{C_\alpha H}$	-4.41 ± 0.01	-4.14 ± 0.01
${}^2J_{C_\beta H}$	-2.92 ± 0.01	-3.69 ± 0.01
${}^3J_{C_\alpha H}$	2.90 ± 0.01	4.20 ± 0.01
$\nu_{C\alpha} - \nu_{C\beta}$		-53.38 ± 0.02

[a] The proton-proton coupling constants used were ${}^3J^{\mathrm{trans}}_{\mathrm{HH}} = 6.60$ Hz, ${}^3J^{\mathrm{cis}}_{\mathrm{HH}} = 8.70$ Hz, ${}^2J^{\mathrm{gem}}_{\mathrm{HH}(\alpha)} = -5.80$ Hz, ${}^2J^{\mathrm{gem}}_{\mathrm{HH}(\beta)} = -11.00$ Hz, ${}^4J^{\mathrm{trans}}_{\mathrm{HH}} = 0.20$ Hz and ${}^4J^{\mathrm{cis}}_{\mathrm{HH}} = 0.14$ Hz.

[b] The proton-proton coupling constants used were ${}^3J^{\mathrm{trans}}_{\mathrm{HH}} = 6.27$ Hz, ${}^3J^{\mathrm{cis}}_{\mathrm{HH}} = 8.93$ Hz, ${}^2J^{\mathrm{gem}}_{\mathrm{HH}(\alpha)} = -8.70$ Hz, ${}^2J^{\mathrm{gem}}_{\mathrm{HH}(\beta)} = -11.73$ Hz, ${}^4J^{\mathrm{trans}}_{\mathrm{HH}} = 1.20$ Hz, and ${}^4J^{\mathrm{cis}}_{\mathrm{HH}} = -0.20$ Hz.

give $|{}^2J_{C_\alpha H}| > |{}^3J_{C_\alpha H}|$. It is more difficult to perform experiments of this kind for trimethylene sulphide, because the chemical shift difference of the α-CH$_2$ and β-CH$_2$ protons is only about 28.0 Hz. However, the spectral analysis gives $|{}^2J_{C_\alpha H}| \lesssim |{}^3J_{C_\alpha H}|$ (see Table 1).

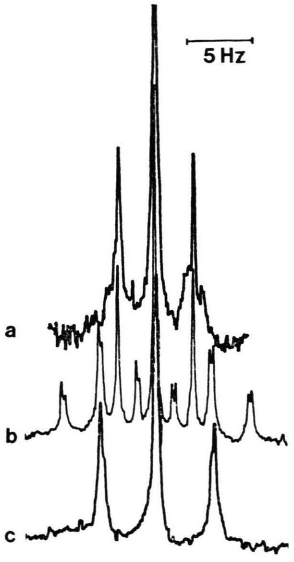

Fig. 3. Selective ^{13}C-{^{1}H} double resonance experiments, which show that $|{}^2J_{C_\alpha H}| > |{}^3J_{C_\alpha H}|$. The central component of the $^{13}C_\alpha$ triplet. a) β-CH$_2$ protons irradiated at the chemical shift, b) single resonance spectrum, c) α-CH$_2$ protons irradiated at the chemical shift.

The analysis of the ^{13}C spectrum of trimethylene sulphide also yields the signs of the long-range C—H coupling constants with respect to the other coupling constants. The proton-proton coupling constants are given in the footnote b) of Table 1. The rms errors obtained in the iterations with different sign combinations were significantly greater with the signs different form the ones given in Table 1. The ^{13}C spectrum of trimethylene oxide, however, is not sensitive to the relative signs of the coupling constants. Still, it might be expected that the two-bond C—H coupling constants are negative and the three-bond coupling constants positive. To verify these assumptions, we carried out some selective $^{13}C_\alpha$-{^{1}H} and $^{13}C_\beta$-{^{1}H} double resonance experiments and calculated the corresponding theoretical spectra. The experimental central component of the $^{13}C_\alpha$ triplet of trimethylene oxide and the corresponding parts simulated by different sign combinations of ${}^2J_{C_\alpha H}$ and ${}^3J_{C_\alpha H}$ are given in Figure 4. The one-bond ${}^1J_{CH}$ coupling constants were kept positive, and the proton-proton coupling constants were those given in the footnote a) of Table 1. The irradiation frequency in this case was the resonance frequency of the β-CH$_2$ protons, and the power $(\gamma_H B_2/2\pi)$ was approximately 100 Hz. The possibility that ${}^2J_{C_\alpha H}$ and ${}^3J_{C_\alpha H}$ could possess

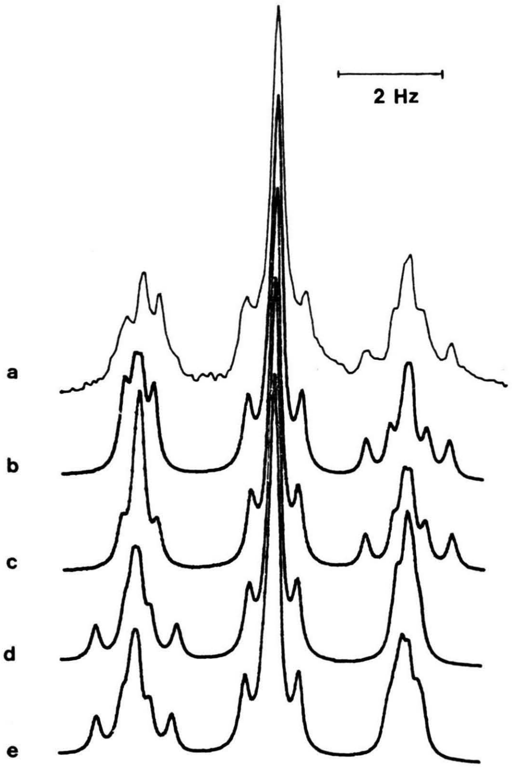

Fig. 4. The central component of the $^{13}C_\alpha$ triplet when β-CH_2 protons are irradiated at the chemical shift. Irradiation power $\gamma_H B_2/2\pi \cong 100$ Hz, a) Experimental, b) Simulated with $^2J_{C_\alpha H} < 0$, $^3J_{C_\alpha H} > 0$, c) Simulated with $^2J_{C_\alpha H} > 0$, $^3J_{C_\alpha H} < 0$, d) Simulated with $^2J_{C_\alpha H} > 0$, $^3J_{C_\alpha H} > 0$, e) Simulated with $^2J_{C_\alpha H} < 0$, $^3J_{C_\alpha H} < 0$.

the same signs can be excluded immediately by comparing the different band shapes. The best agreement seems to be achieved in case b), where $^2J_{C_\alpha H}$ is negative and $^3J_{C_\alpha H}$ positive. This choice is confirmed by a study of the higher-frequency component of the $^{13}C_\alpha$ triplet in Figure 5. It appears that the better agreement between the experimental and the simulated spectra is achieved also in this case when $^2J_{C_\alpha H} < 0$ and $^3J_{C_\alpha H} > 0$.

The sign of $^2J_{C_\beta H}$ was determined according to the principle described above, but the irradiation frequency was set ± 8 Hz off-resonance from the chemical shift of the α-CH_2 protons, for the irradiation at the chemical shift does not yield the sign. The results are given in Figure 6. It may be concluded that $^2J_{C_\beta H}$ is negative, as $^2J_{C_\alpha H}$, but the absolute value of the latter is about 50% greater than that of the former in trimethylene oxide. The same order of magnitudes is also observed in

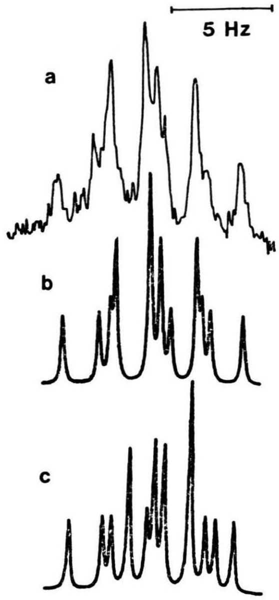

Fig. 5. The higher-frequency component of the $^{13}C_\alpha$ triplet when β-CH_2 protons are irradiated at the chemical shift. Irradaiton power $\gamma_H B_2/2\pi \cong 100$ Hz. a) Experimental. b) Simulated with $^2J_{C_\alpha H} < 0$, $^3J_{C_\alpha H} > 0$. c) Simulatedwith $^2J_{C_\alpha H} > 0$, $^3J_{C_\alpha H} < 0$.

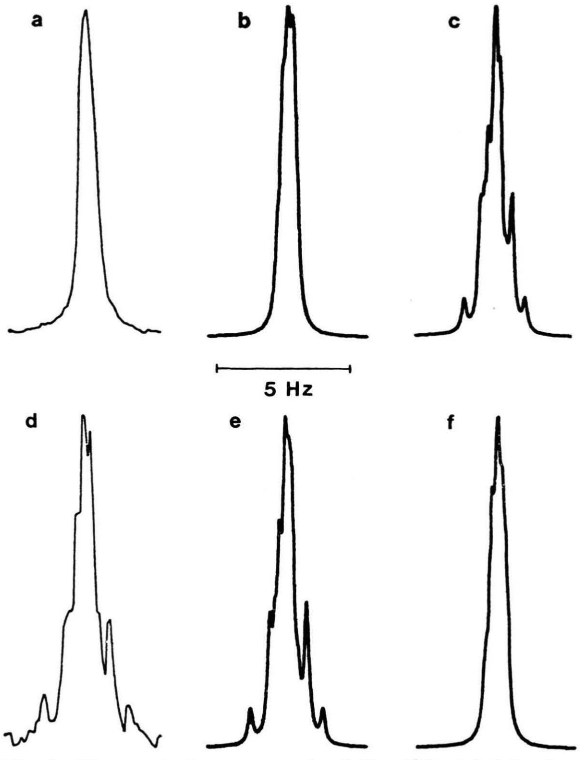

Fig. 6. The central component of the $^{13}C_\beta$ triplet when α-CH_2 protons are irradiated. Irradiation power $\gamma_H B_2/2\pi \cong 100$ Hz. a) Experimental. α-CH_2 protons irradiated 8 Hz off-resonance to higher frequency. b) Simulated with $^2J_{H_\beta C} < 0$. c) Simulated with $^2J_{C_\beta H} > 0$. d) Experimental. α-CH_2 protons irradiated -8 Hz off-resonance to lower frequency. e) Simulated with $^2J_{C_\beta H} < 0$. f) Simulated with $^2J_{C_\beta H} > 0$.

trimethylene sulphide, but now $|^2J_{\mathrm{C}_\alpha\mathrm{H}}|$ is only 12% greater than $|^2J_{\mathrm{C}_\beta\mathrm{H}}|$. The substitution of sulphur for oxygen causes a decrease of $|^2J_{\mathrm{C}_\alpha\mathrm{H}}|$ by about 0.4 Hz and an increase of $|^2J_{\mathrm{C}_\beta\mathrm{H}}|$ by about 0.8 Hz. The value of $^3J_{\mathrm{C}_\alpha\mathrm{H}}$ also increases by about 1.3 Hz (45%). The one-bond C—H couplings are about 3 Hz weaker in trimethylene sulphide than in trimethylene oxide.

[1] The HETERO program was supplied by Dr. T. Bundgaard, University of Aarhus, Denmark, who is greatly acknowledged.

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