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THE STRUCTURE OF THE PROTON SKELETON IN 1,3-BUTADIENEIRON TRICARBONYL AS DETERMINED FROM THE NMR SPECTRA OF ORIENTED MOLECULES

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Summary

^{1}H NMR spectra of 1,3-butadieneiron tricarbonyl oriented in a nematic liquid crystal solvent have been analysed and used to derive the structure of the proton skeleton, which is found to be non-planar. The distance of the *anti* protons from the plane defined by the remaining four protons is 0.77 ± 0.06 Å.

Introduction

For more than fifteen years there has been a continuing interest in the structure of 1,3-butadieneiron tricarbonyl. Various physical methods such as X-ray [1,2,3] and electron diffraction [4] and ^{1}H and ^{13}C NMR spectroscopy [5—8] were used to obtain structural information. General agreement was reached on the planar *cisoid* structure of the four carbon atoms in the 1,3-butadiene moiety. The protons could not be located by the early X-ray work [1,2] and the NMR results were interpreted in terms of both a planar [7] and a non-planar [6,8] proton skeleton. However, in the latter case only an upper limit of the distortion was given [6]. The angle between the four-carbon plane and the *anti*-proton—carbon bond was estimated to be smaller than 37°. Electron diffraction data [4] provided no unique results and were analysed in terms of two models, one fully planar, the other with non planar terminal protons but with a large uncertainty for the position of the latter. The *anti*-proton—carbon and *syn*-proton—carbon bonds make angles of +12.4 ± 6.2° and —9.3 ± 6.3°, respectively, with the four-carbon plane. From an X-ray study [3] of two substituted 1,3-butadieneiron tricarbonyls an approximate model for the unsubstituted compound was derived with corresponding angles of +30 and —20°.

We have now determined the structure from the ^{1}H NMR spectrum of the molecule oriented in a nematic liquid crystal solvent. This method has been successfully applied to several organometallic species [9].

During our analysis of the spectra it turned out that some of the reported indirect couplings [7] were inprecise or had wrong signs. We have, therefore, reanalysed the isotropic phase spectrum, and present the results in Table 1.

Experimental

Commercially available 1,3-butadieneiron tricarbonyl was used without further purification.

The isotropic phase spectrum was obtained from a 0.1 g ml^{-1} solution in $CHCl_3$ at room temperature on an HA-100 spectrometer, with spectral width of 50 Hz and $CHCl_3$ as the lock substance. The average linewidth was 0.3 Hz.

The nematic phase spectra were recorded on 90 and 360 MHz Bruker Spectrometers in the FT mode with pulse widths of 4.5 and 15 μsec, delays of 1 sec, and 99, respectively, 25 transients. The accumulation and transformation of the data were performed in a 16 k computer.

The temperatures were 27 and 19°C, and the concentrations 9.87 (sample I at 90 MHz) and 9.55 (sample II at 360 MHz) weight percent in the solvent Licrystal Phase VII from Merck.

Spectral analysis

Although the ^{1}H NMR spectra of oriented 6-spin systems are usually easily analysed, the spectrum of 1,3-butadieneiron tricarbonyl at 90 MHz resisted analysis for a long time because of the missing features in the line spacings. The analysis was still difficult even at 360 MHz. A further problem arose from the wrong or inprecise indirect couplings [7], of which one sign (J_{12}, see Fig. 1) in particular had to be reversed in order to reduce the rms error of the least squares fit from 1.9 to 1.0 Hz (146 assigned transitions). In a recent communication [8] J_{12} has also been found to be negative by INDOR experiments. The isotropic phase spectrum has two possible solutions (rms error 0.06 Hz with 139 assigned lines) of which one could be ruled out because it disagreed with the oriented phase spectrum.

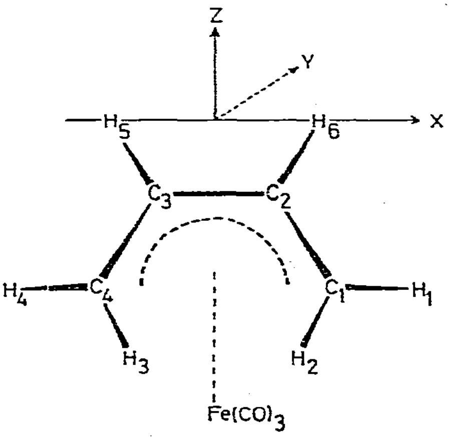

Fig. 1. The structure of 1,3-butadiene iron tricarbonyl showing numbering of nuclei and definition of axes.

TABLE 1

SPECTRAL PARAMETERS FOR 1,3-BUTADIENEIRON TRICARBONYL IN THE ISOTROPIC AND THE NEMATIC PHASE

Parameter	Isotropic phase (Hz)	Parameter	Nematic phase	
			Sample I [b] (Hz)	Sample II [c] (Hz)
J_{12}	-2.41 ± 0.02	D_{12}	-151.36 ± 0.18	-163.44 ± 0.15
J_{13}	-0.08 ± 0.02	D_{13}	-46.95 ± 0.19	-51.67 ± 0.17
J_{14}	0.03 ± 0.02	D_{14}	-23.14 ± 0.15	-25.23 ± 0.15
J_{15}	1.14 ± 0.02	D_{15}	-7.90 ± 0.12	-8.16 ± 0.12
J_{16}	6.91 ± 0.02	D_{16}	212.22 ± 0.11	239.66 ± 0.12
J_{23}	-0.33 ± 0.02	D_{23}	-326.69 ± 0.17	-360.36 ± 0.16
J_{25}	-1.08 ± 0.02	D_{25}	40.60 ± 0.15	46.50 ± 0.16
J_{26}	9.30 ± 0.02	D_{26}	160.98 ± 0.16	181.61 ± 0.16
J_{56}	4.66 ± 0.02	D_{56}	-173.06 ± 0.15	-191.01 ± 0.12
ν_1 [a]	-180.25 ± 0.01	$\nu_1 - \nu_5$	348.00 ± 0.24	1405.54 ± 0.21
ν_2 [a]	-28.98 ± 0.01	$\nu_2 - \nu_5$	458.06 ± 0.22	1830.72 ± 0.21
ν_5 [a]	-539.29 ± 0.01			

[a] At 100 MHz with respect to TMS. [b] Recorded at 90 MHz. [c] Operating frequency is 360 MHz.

On the basis of the parameters obtained from the 360 MHz spectrum, the 90 MHz spectrum could also be definitively analysed. All the data as derived with the program LEQUOR [10] on a UNIVAC 1108 computer are summarized in Table 1.

Results and discussion

The structural information on the proton skeleton was obtained iteratively from the measured direct couplings (Table 1) with the help of the computer program SHAPE [11]. A planar geometry could immediately be excluded because the rms error of the fit remained larger than 2 Hz and the direct coupling D_{13} could not be reproduced with a deviation smaller than 6 Hz. The non planar geometry was found to be consistent with the experimental data. The results are shown in Table 2.

The NMR spectra of oriented molecules provide information only on distance ratios. We have, therefore, defined the nonplanarity of the proton skeleton by the ratio d/r_{56}, with d equal to the distance between the protons 3 or 4 and the plane containing the protons 1, 4, 5 and 6. Our result ($d/r_{56} \sim 0.30$) deviates considerably from the corresponding X-ray value (~ 0.42) and also from the electron diffraction data (~ 0.19). For $r_{56} = 2.5$ Å we obtain $d = 0.77 \pm 0.06$ Å.

Unfortunately ^{1}H-measurements do not permit determination of the distance of the protons from the carbon plane without further assumptions. If we assume that protons 5 and 6 are in the plane of the four carbon atoms, that the C—C bond lengths are all 1.415 Å, and that the angle $C_1C_2C_3 = 120°$, $r(C_2H_6) = 1.08$ Å and $r(H_5H_6) = 2.50$ Å, we find that our data correspond to average angles of $+18.5°$ and $-16.3°$ between the carbon plane and the *anti* proton and *syn* proton carbon bonds, respectively. We also derive the angle $H_1C_1H_2$ as 114.8°. This value indicates some rehybridisation towards sp^3 at the terminal carbons.

TABLE 2

STRUCTURAL AND ORIENTATIONAL PARAMETERS FOR 1,3-BUTADIENEIRON TRICARBONYL AS DETERMINED FROM THE NMR SPECTRA IN THE NEMATIC PHASE. THE STRUCTURAL PARA-PARAMETERS HAVE BEEN COMPARED WITH THOSE OBTAINED FROM X-RAY [3] AND ELECTRON DIFFRACTION [4].

Parameter [a]	NMR		X-Ray	Electron-diffraction	
	Sample I	Sample II		Planar	Non-planar
r_{12}/r_{56}	0.729 ± 0.005	0.726 ± 0.004	0.784	0.741	0.740
r_{13}/r_{56}	1.454 ± 0.002	1.455 ± 0.002	1.503	1.407	1.419
r_{14}/r_{56}	1.956 ± 0.004	1.964 ± 0.004	2.002	1.999	1.988
r_{15}/r_{56}	1.723 ± 0.002	1.727 ± 0.001	1.750	1.739	1.737
r_{16}/r_{56}	1.007 ± 0.001	1.009 ± 0.001	1.029	1.013	1.015
r_{23}/r_{56}	0.8091 ± 0.0003	0.8093 ± 0.0002	0.822	0.716	0.738
r_{25}/r_{56}	1.540 ± 0.001	1.542 ± 0.001	1.568	1.518	1.521
r_{26}/r_{56}	1.250 ± 0.001	1.252 ± 0.001	1.279	1.260	1.256
d/r_{56}	0.318 ± 0.018	0.294 ± 0.016	0.415	0	0.192
S^{*}_{xx}	0.02252 ± 0.00002	0.02486 ± 0.00002			
S^{*}_{zz}	−0.04291 ± 0.00020	−0.04885 ± 0.00020			
S^{*}_{yz} [b]	−0.00505 ± 0.00095	−0.00443 ± 0.00106			

[a] For numbering of nuclei and definition of axes see Fig. 1. d is the distance between the protons 2 or 3 and the plane defined by the protons 1, 4, 5 and 6 (the x—z plane). [b] On the basis of r_{56} = 2.50 Å.

It should be pointed out that the validity of these results depends upon the assumptions made, and they should be confirmed by direct measurement. We plan to perform such measurements with ^{13}C enriched oriented species.

Acknowledgements

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