

## THE CONFORMATION OF ( $\mu$ -BUTATRIENE)HEXACARBONYLDIIRON COMPLEX FROM PROTON NMR STUDIES IN THREE NEMATIC PHASES

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### Summary

Proton NMR spectroscopy in three different liquid crystals has been used to determine two conformational angles of ( $\mu$ -butatriene)hexacarbonyldiiron complex, namely the angle between the two  $\text{CH}_2$  planes and the dihedral angle between the two planes containing four carbon atoms of the butatriene moiety. The values are 44 and 46°, respectively. The direct and the indirect geminal HH couplings are shown to be of the same sign in the liquid crystals with positive diamagnetic anisotropy.

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### Introduction

For deriving structural parameters from the NMR spectra of oriented molecules, the number of independent dipolar couplings ( $D_{ij}$ 's between interacting nuclei  $i$  and  $j$ ) must exceed that of independent parameters ( $S_{ij}$ 's) required to specify the molecular order at least by the number of independent geometrical informations to be determined [1]. In cases where this is not so, certain plausible assumptions on the molecular structure can be made and/or the studies can be undertaken under different orientation conditions (such as in different liquid crystals) in order to derive information which is otherwise difficult to obtain. Such a situation occurs in the proton NMR spectrum of ( $\mu$ -butatriene)hexacarbonyldiiron (Fig. 1) oriented in a single liquid crystal. A study in 3 different solvents permits the evaluation of the elements of the order matrix and the conformational angles  $\theta$  and  $\phi$  between the two  $\text{CH}_2$  planes and the dihedral angle between the four carbons of the ( $\mu$ -butatriene) moiety, respectively under the assumption of reasonable bond lengths and bond angles. The results are described below.

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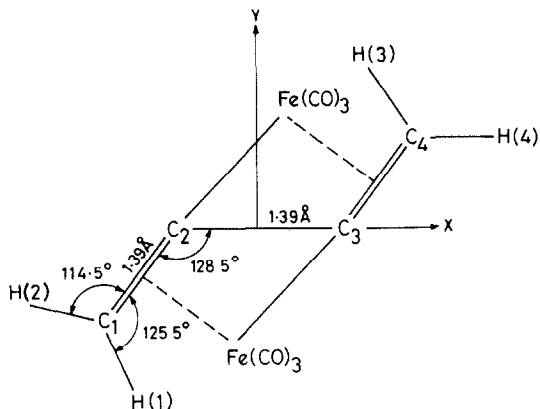


Fig. 1. The structure of ( $\mu$ -butatriene)hexacarbonyldiiron complex.

## Experimental

The sample of ( $\mu$ -butatriene)hexacarbonyldiiron was studied in three nematic liquid crystals namely: (i) *N*-(*p*'-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA), (ii) *p*-*n*-butyl-*p*'-methoxyazoxybenzene (Merck Phase IV) and (iii) ZL1-1167 (a ternary eutectic mixture of propyl-, pentyl- and heptyl-bicyclohexyl carbonitrile). The solute concentrations were 3.67 and 3.5 mol%, respectively, in EBBA and phase IV, and 7.9 weight-% in ZL1-1167. The proton NMR spectra were recorded at 27 and 32°C on

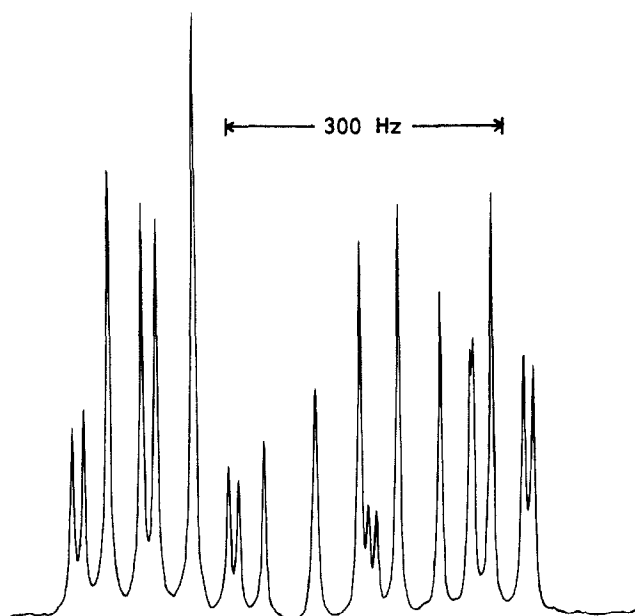


Fig. 2. Proton NMR spectrum of ( $\mu$ -butatriene)hexacarbonyldiiron complex in ZL1-1167. Spectrometer frequency: 270 MHz. Solute concentration: 7.9 weight per cent. Temperature 32°C.

Bruker WS-90 and WH-270 spectrometers. A typical spectrum with an average line-width of 3 Hz is shown in Fig. 2 along with the experimental details.

## Results and discussion

The spectra were analysed using the NMRX Programme [2] which takes into account the  $C_2$ -symmetry of molecules. The calculations were carried out on a DEC-1090 computer. The long range HH indirect couplings are negligible, whereas the geminal coupling is 1.7 Hz as derived from the spectrum in the isotropic medium [3]. Keeping the value of this coupling constant constant, iterations were carried out on the 4 direct dipolar couplings and the chemical shift ( $\nu_1-\nu_2$ ) (Fig. 1). The root-mean-square error was minimum (around 0.49 Hz) for the sign combination of the parameters as given in Table 1. The relative signs of the direct and the indirect couplings are given in Table 1.

Assuming the geminal indirect HH coupling to be negative [4], the signs of the dipolar couplings are as shown.

Each of the three spectra gives four different dipolar couplings (Table 1). Of these, three are needed to characterise the molecular orientation in each case, and hence only one item of geometrical information can be obtained from each spectrum. Even a combination of 3 spectra does not provide sufficient dipolar couplings to determine the entire structural and conformational information.

The complex is unstable to X-rays [5] and hence no structural information is available from this technique. However, X-ray data on substituted derivatives of the complex are available. Since the bond lengths and the bond angles are not likely to change very much as a result of substitution, the values (Fig. 1) were assumed for the present case and the conformational angles  $\theta$  and  $\phi$  were derived from the 12 dipolar couplings along with the 9 order parameters. A suitable modification of the SHAPE programme [6] was used for such a purpose. The root-mean-square error between the observed and the best fit calculated dipolar couplings was 1.0 Hz, which is reasonable in view of the various assumptions made.

The best-fit  $\theta$  and  $\phi$  angles and the  $S$  values are given in Table 2. An error of about  $5^\circ$  is estimated for the conformational angles taking into the consideration variations of the various bond lengths and the bond angles as well as the errors of the dipolar couplings.

TABLE 1  
SPECTRAL PARAMETERS FOR ( $\mu$ -BUTATRIENE)HEXACARBONYLDIIRON IN THREE DIFFERENT LIQUID CRYSTALS

Parameter <sup>a</sup>	Value (Hz)		
	EBBA	Phase IV	ZL1-1167
$J_{12} = J_{34}$	-1.7	-1.7	-1.7
$D_{12} = D_{34}$	$-116.22 \pm 0.10$	$-252.59 \pm 0.09$	$55.11 \pm 0.14$
$D_{13}$	$71.13 \pm 0.14$	$62.16 \pm 0.36$	$-2.89 \pm 0.14$
$D_{14} = D_{23}$	$67.54 \pm 0.11$	$65.39 \pm 0.11$	$-29.85 \pm 0.14$
$D_{24}$	$8.36 \pm 0.14$	$23.57 \pm 0.35$	$-31.72 \pm 0.15$
$(\nu_1-\nu_2)$	$5.74 \pm 0.19$	$-12.56 \pm 0.47$	$265.97 \pm 0.17$

<sup>a</sup> The numbering of nuclei corresponds to that given in Fig. 1.

TABLE 2  
THE BEST FIT  $\theta$  AND  $\phi$  ANGLES AND THE S-VALUES

Parameter	In EBBA	In Phase IV	In ZLI-1167
$S_{xx}^a$	0.1135	0.0637	0.0065
$S_{yy}^a$	0.0771	0.0549	-0.0821
$S_{xy}^a$	0.1641	-0.1243	-0.0539
$\theta$		44°	
$\phi$		46°	

<sup>a</sup> With respect to a right handed Cartesian coordinate system where the X and Y axes are in the hypothetical plane containing the atoms C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> when  $\phi = 0$  and the x-axis is the C<sub>2</sub>C<sub>3</sub> axis (Fig. 1).

The corresponding angles in [bis(biphenylidene)butatriene]hexacarbonyldiiron as determined from X-ray studies are 80 and 34°, respectively [5].

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