

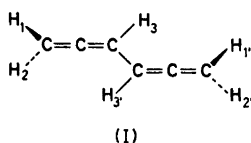
The Interpretation of the ^1H NMR Spectrum of 1,2,4,5-Hexatetraene Oriented in a Nematic Solvent

BJÖRN PEDERSEN,^{a*} JAN SCHAUG^a and HENNING HOPF^b

^a Kjemisk institutt, Universitetet i Oslo, Oslo 3, Norway and ^b Institut für Organische Chemie der Universität Karlsruhe, Postfach 6380, 7500 Karlsruhe 1, German Federal Republic

The proton magnetic resonance spectrum of 1,2,4,5-hexatriene (biallynyl) dissolved in a nematic solvent at room temperature has been recorded and interpreted in detail. The interpretation is based on a planar *trans* structure of biallynyl with symmetry C_{2h} with the terminal CH_2 groups orthogonal to the plane formed by the other atoms. Six different dipolar coupling constants are obtained from the spectral analysis. This is not sufficient to determine the relative positions completely, but some structural information, supporting the assumed structure, is obtained.

From the vibrational spectra Powel *et al.*¹ conclude that 1,2,4,5-hexatetraene (biallynyl) has the planar *trans* structure (I).



The symmetry of (I) is C_{2h} and the terminal CH_2 groups are twisted out of the molecular plane by 90° .

The geometry of the carbon skeleton in (I) has been determined quantitatively in the vapour phase by means of electron diffraction by Trættemberg *et al.*² The C—C double bond distances are found to be equal to the C—C distance in allene,^{3,4} 1.31 Å. The central C—C bond is found to be 1.47 Å as also found in 1,3-butadiene.⁵ The hydrogen atoms were not located very precisely. In the terminal CH_2

groups the C—C—H angles were assumed to be 120° and for the inner H atoms the C—C—H angle was assumed to be 118° . The C—H distances were assumed to be equal and found to be 1.10 Å.

Information on the position of the hydrogen atoms can be obtained from the ^1H NMR spectrum of biallynyl dissolved in a nematic solvent.⁶ We have recorded such a spectrum and we will give the detailed interpretation of the spectrum below. It turns out that it is not possible from the ^1H NMR spectrum alone to get sufficient information to determine completely the five parameters needed to specify the position of the hydrogen atoms in (I), but partial information is obtained supporting the proposed structure (I).

EXPERIMENTAL

Biallynyl was synthesized as described earlier.⁷ After degassing, 45 mg biallynyl was distilled into 595 mg of the liquid crystal *N*-(*p*-ethoxybenzylidene)-*p*-*N*-butylaniline contained in an NMR-tube supplied with a capillary with trifluoroacetic acid (TFA), and sealed under vacuum.

The spectrum was run on a Varian HA-100 spectrometer operating at 98 MHz in the frequency mode locked on the TFA line. The total spectral width was 7400 Hz and close to 90 lines were resolved with a width at half-height of approximately 5 Hz in the center of the spectrum. A complete spectrum is shown in Fig. 1. The analysis was carried out on the basis of an expanded spectrum recorded under slightly different experimental conditions. The calculated spectrum, also given in Fig. 1, is therefore based on slightly different coupling constants than those obtained below.

* Also at the Central Institute for Industrial Research, Oslo 3, Norway.

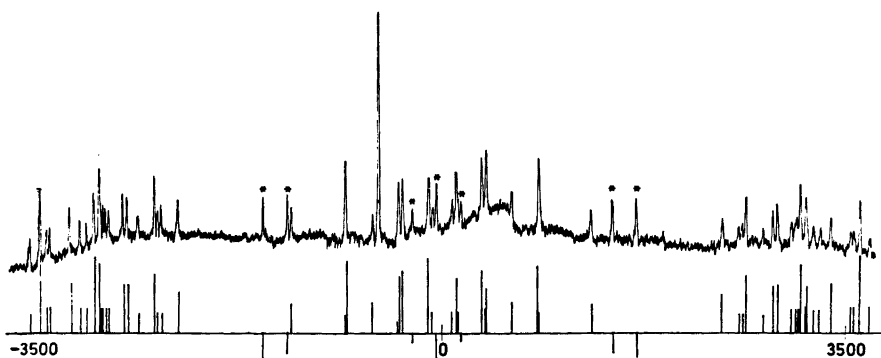


Fig. 1. The 98 MHz NMR spectrum of 1,2,4,5-hexatriene dissolved in *N*-(*p*-ethoxybenzylidene)-*p*-*N*-butylaniline (22 mol %). The calculated spectrum is given as a stick plot below. The lines marked with a star are from an impurity. The lines can be matched to the calculated lines from a A_2B system given below as an inverted stick plot.

INTERPRETATION

The six protons in (I) form a $AA'A''BB'$ spin system. The direct magnetic dipole-dipole coupling D_{ij} is the dominating coupling in the spectrum of an anisotropically reorienting molecule.⁸ In this case there are six different D coupling constants to determine. As a first approximation we can ignore the chemical shift and the indirect spin-spin coupling and regard the spin system as A_4X_2 . The four terminal protons constitute a weakly coupled two pair system. The spectrum of such a system is well known.^{8,9} It consists of two multiplets split by the dominating pair coupling D^{12} . The low field half of the spectrum is shown in Fig. 2. The only effect of the indirect spin-spin coupling is to split the strongest line into a narrow doublet also shown in Fig. 2. This last spectrum is exactly the spectrum observed for allene.⁹

In biallenyl the coupling to the X_2 protons gives rise to a more complex multiplet. But as seen in Fig. 1 the high and low field part of the spectrum consists of a superposition of four simple A_4 multiplets as expected from the X-approximation. On the other hand, each line in the doublet from the X_2 protons is split to a pentet due to the coupling to the four A-protons. This accounts for ten lines in the central part of the spectrum shown in Fig. 1.

We see that the main features of the spectrum in Fig. 1 can be understood on the basis of this simple A_4X_2 approximation. From this

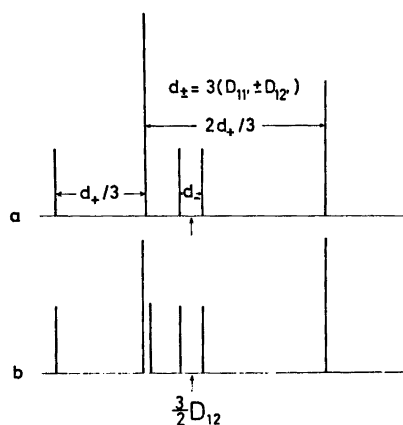


Fig. 2. The low-field half of the calculated spectrum of an oriented A_4 spin system (two weakly coupled proton pairs). (a) Dipole-dipole coupling only, (b) dipole-dipole coupling + indirect spin-spin coupling.

analysis we derive approximate values for D_{12} , $D_{11'}$, $D_{12'}$, $D_{33'}$, and $(D_{13} + D_{13'})$. D_{13} and $D_{13'}$ were assumed to be equal as a first approximation. The thus derived values for the direct coupling constants were then used as input parameters in the LAOCOONOR program.¹⁰ The indirect spin-spin coupling constants and the chemical shift were taken from the analysis of the isotropic 1H NMR spectrum.¹¹ During the iteration only the chemical shift and the D 's were varied simultaneously. The

Table 1. 98 MHz NMR parameters of 1,2,4,5-hexatetraene partially oriented in *N*-(*p*-ethoxybenzylidene)-*p*-*N*-butylaniline. (Coordinates in Å).

Observed (Hz)	Calculated (Hz)	Observed ^a (Hz)	
$D_{12} = 2021.17 \pm 0.12$	2021.17	$J_{12} = -10.0$	
$D_{11'} = -63.73 \pm 0.12$	-64.70	$J_{12'} = 3.5$	
$D_{12'} = -53.74 \pm 0.12$	-52.60	$J_{11'} = 3.5$	
$D_{13} = -235.6 \pm 1.2$	-235.62	$J_{13} = -6.7$	
$D_{13'} = -242.0 \pm 1.2$	-242.03	$J_{13'} = 1.2$	
$D_{33'} = 254.6 \pm 0.11$	254.67	$J_{33'} = 10.5$	
$D_{13} + D_{13'} = 477.65 \pm 0.15$ Hz		$\nu_1 - \nu_3 = 74.39 \pm 0.18$ Hz	
	<i>x</i>	<i>y</i>	<i>z</i>
$S_{xx} = -0.07405 \pm 0.00058$	H ₁ : 0.6086	3.5693	0.9519
$S_{zz} = -0.11616 \pm 0.00001$	H ₃ : 1.6777	-0.0921	0
$S_{xy} = 0.06607 \pm 0.00136$			

^a Ref. 11.

iteration converged to a final r.m.s. error of 1.2 Hz. In Table 1 the final direct coupling constants and chemical shift are given together with the indirect spin-spin coupling constants used.

From the data in Table 1 it is clear that the separation of D_{13} and $D_{13'}$ is still uncertain and the values of the two are correlated. The estimated error in the sum is only 1/10 of the error in the individual values. Otherwise the final values are satisfactory and the agreement between the observed and the calculated spectrum is very good.

The chemical shift difference, 74.4 ± 0.2 Hz, between the terminal and the inner protons is 3.0 Hz larger than observed in the isotropic spectrum.¹¹ This can be due to the difference between the solvents or might indicate anisotropy of the chemical shift.⁶

Seven of the lines in the observed spectrum could not be matched by a line in the calculated spectrum. These lines are marked in Fig. 1. The lines are probably from an impurity. The interpretation of the spectrum is straightforward. It is the spectrum of an A_2X system where the two outermost doublets are from the A_2 protons and the central triplet is from the X -proton. The obtained chemical shifts are $\nu_A = 74$ Hz, $\nu_X = 49$ Hz (to low field relative to ν_3), $D_{AA} = 1030$ Hz and $D_{AX} = 109$ Hz.

The impurity is most likely $CH_2=C=CHX$ oriented in the nematic solvent similarly to biallenyl. X is probably Br and the same impurity was also detected in the isotropic spectrum.¹¹ However, in the isotropic spectrum only the low field triplet from $=CHBr$ could be seen, but here all lines are separated. Furthermore, as biallenyl contributes to many more lines the relative intensities of the impurity lines are comparable to the intensities of the lines from biallenyl. The only symmetry for bromoallene is a mirror plane. It is therefore necessary with three elements in the S -matrix to specify the orientation of the molecule, and with only two direct coupling constants no structural information can be obtained.

STRUCTURAL INFORMATION

The good agreement between the calculated and observed spectrum is a further support for the structure (I). However, the direct coupling constants also carry quantitative information on the molecular structure of biallenyl. The direct coupling constant between proton i and j is given as⁶

$$D_{ij} = -\frac{\hbar\gamma^2}{4\pi^2r_{ij}^3} S_{ij}$$

γ is the gyromagnetic ratio of the proton, r_{ij} the distance between proton i and j and S_{ij} is the degree of orientation of the axis passing through i and j . For a molecule of symmetry C_{2h} , S_{ij} can be calculated from an **S**-matrix containing three independent elements: S_{xx} , S_{zz} and S_{xy} . (The coordinate system used has its origin at the centre of symmetry with the z -axis normal to the molecular plane and the y -axis parallel to the double bonds.)

The positions of the protons are determined completely by five coordinates: xyz for H_1 and xy for H_3 . The positions of the other protons then follow from the symmetry. The direct coupling constants therefore depend on eight unknowns: five position coordinates and three **S**-matrix elements. We have only six different direct coupling constants, and two of these might be coupled, hence, we can only determine three, or two, proton coordinates. It is therefore necessary to find two or three reasonable constraints. After trying several alternatives we have settled on the following: we have varied x and y for H_3 and used the coordinates calculated from the electron diffraction study for H_1 .

The calculations were done using the least squares program SHAPE.¹² The observed direct coupling constants were given weights inversely proportional to the estimated standard deviations. The final calculated direct coupling constants are given in Table 1 together with the obtained coordinates for H_3 and the assumed coordinates for H_1 . The largest differences between calculated and observed coupling constants are for the coupling between the terminal protons across the molecule, D_{12} , and $D_{11'}$, where the difference is about eight standard deviations.

In the refinement the H_3 -C distance is stretched from 1.10 Å to 1.18 Å and the H_3 -C=C angle is reduced from 118° to 115.2°. These changes are not physically reasonable. Extrapolating from related structures^{4,5} it is expected that the C-H distance should be about 1.1 Å and the H-C=C angle somewhat larger than 120°. This displacement of H_3 relative to the carbon skeleton probably follows from keeping the position of the terminal atoms fixed.* As the direct coupling constants depend only on the inter-proton distances it is more appropriate to look directly at the proton-proton distances calculated from the final coordinates. These distances are given in Table 2 together with corresponding distances in the related molecules allene and 1,3-butadiene.

The best comparison between allene and biallenyl is probably made by comparing the ratio R_{13}/R_{12} . This ratio is 2.065 for biallenyl and 1.961 for allene⁹ (both values from NMR data) indicating that R_{13} is larger in biallenyl. A similar but much larger effect is found comparing 1,3-butadiene¹³ and ethene¹⁴ where the ratio R_{trans}/R_{gem} is 1.677 and 1.320, respectively.

The distance between the inner protons, $R_{33'}$, is found to be 0.2 Å larger here than in the electron diffraction study.² This difference might not be significant, but, at least, it is a support for the assumed structure as any contribution from another conformer would lead to a reduction in this distance.

* However, this unreasonable distortion of the geometry indicates that the conclusions we can draw are at most semiquantitative.

Table 2. Comparison of corresponding distances (Å) in biallenyl, allene, and 1,3-butadiene obtained by electron diffraction and NMR.

Distance	Biallenyl NMR	ED ^a	Allene NMR ^b	ED ^c	1,3-Butadiene NMR ^d	ED ^e
R_{13}	3.931	3.918	3.7782	3.7250		
$R_{13'}$	4.269	4.206				
$R_{33'}$	3.360	3.167			3.188	3.095
R_{12}	(1.9038)	1.9038	1.9269	1.8582	1.806	1.853

^a Ref. 2. ^b Ref. 9. ^c Ref. 3. ^d Ref. 5.

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