

NMR Studies of Conjugated Linear Trienes

II.* Hexatriene and 1,6-Dimethylhexatriene

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The 100 MHz NMR spectra of *cis*-1,3,5-hexatriene, *trans*-1,3,5-hexatriene, and 1,6-dimethyl-1,3,5-hexatriene have been analysed. The assignment of configuration and conformation of the *cis*-triene is discussed in relation to buta- and pentadiene NMR parameters and to published electron diffraction data on dienes and trienes. The NMR data for *cis*-1,3,5-hexatriene is not inconsistent with slight non-planarity. The existence of long range coupling constants, ${}^6J \sim -0.14$ Hz and ${}^7J \sim +0.1$ Hz, are shown.

An investigation of 1,3,5-hexatrienes by NMR is of interest both from the theoretical aspect of comparing the coupling constants with those obtained for penta- and buta-dienes¹ and from the stereochemical point of view. Apart from some cases of heavily substituted hexatrienes^{2,3} no detailed NMR analyses of conjugated trienes have been reported. The simplest conjugated triene, 1,3,5-hexatriene, has been studied by electron diffraction^{4,5} and by infrared and Raman spectroscopy.^{6,7} The infrared spectra of *cis*- and *trans*-1,3,5-hexatriene^{6,7} have been analysed under the assumption that the isomers have C_{2v} and C_{2h} symmetry, respectively. Contributions from non-planar or *s-cis* structures could not be entirely ruled out by infrared and Raman spectroscopic evidence. Trættestad *et al.*^{4,5} suggested from electron diffraction studies that *trans*-1,3,5-hexatriene has an all-*s-trans* conformation, whereas the *cis*-isomer is non-planar. The present NMR investigation was undertaken to obtain more information on the structure of hexatrienes, and on long-range (H,H) coupling in conjugated systems. The spectra of three compounds have been analysed: *cis*-1,3,5-hexatriene (I), *trans*-1,3,5-hexatriene (II), and 1,6-dimethyl-1,3,5-hexatriene (III).

* Part I: Ref. 2.

EXPERIMENTAL

The *cis*- and *trans*-1,3,5-hexatrienes were obtained from a commercially available isomer mixture by the method of Hwa *et al.*⁸ The *cis* isomer was obtained pure, but the *trans* isomer contained about 5 % of the *cis*-triene. The NMR spectra were used as evidence of purity.

The all-*trans* 1,6-dimethyl-hexatriene was prepared by dehydration of 2,4-octadien-6-ol with *p*-toluene sulphonic acid: b.p. 44–45°/12 mmHg. The triene was recrystallized from methanol at –30°C. 2,4-Octadien-6-ol was obtained from sorbaldehyde and ethylbromide by a Grignard reaction: b.p. 85–86°/13 mmHg.

The materials were introduced into 5 mm o.d. sample tubes; a small quantity of TMS was added to serve as NMR reference and locking substance. For double resonance experiments benzene was also added to serve as locking substance in preference to TMS. The samples were degassed by freezing and thawing under vacuum and the tubes were sealed in the evacuated condition. The spectra of *trans*-hexatriene were recorded for the neat liquid whereas the spectra of *cis*-hexatriene and 1,6-dimethylhexatriene were obtained for samples dissolved in CCl₄ (about 50 % v/v).

The spectra were recorded using a Varian Associates HA 100 spectrometer operating at 100 MHz in the field/frequency lock mode, at ambient temperature (*ca.* 35°C) with frequency sweep. Spectra of the two 1,3,5-hexatriene isomers for detailed measurement were recorded at 50 Hz sweep width at scan rate 0.02 Hz s⁻¹, calibrated every 5 Hz using a Hewlett-Packard 5212A frequency counter. The methyl decoupled spectra of *trans*-1,6-dimethyl-hexatriene were recorded at 100 Hz sweep width.

The computations were carried out using the IBM 360/50 computer at the University of Bergen and the Atlas computer at the Science Research Council Atlas Laboratory, Chilton, Didcot, England. The results were plotted with a Calcomp Plotter.

SPECTRAL ANALYSIS

The spectrum of *cis*-1,3,5-hexatriene (Fig. 1) consists of three bands at $\delta \sim 5.1$, ~ 5.9 and ~ 6.7 . The separations between the bands are considerably greater than any coupling constants. This enables initial assignments and estimates of some NMR parameters to be made on a quasi first-order basis, but second-order effects are observable (in addition to those caused by symmetry). The spectrum was therefore analysed on the basis of an [ABCD]₂ spin system. The total spectrum is complex, but the low frequency band ($\delta \sim 5.1$) is clearly assignable to the geminal protons with major structure due to splittings by 3J_c and 3J_t . The main pattern within the band at $\delta \sim 5.9$ can be explained as the D part of an [ABCD]₂ spin system with $J_{AD} \simeq J_{A'D}$ and $J_{BD} \simeq J_{B'D}$ small, but J_{CD} large. The total spectrum was analysed using the iterative computer program LACX.⁹ This procedure gave reasonably accurate values for the triene coupling constants and chemical shifts. The final RMS error of fitting observed to calculated transitions was 0.14 when all 20 parameters were allowed to vary. The computed probable errors on the coupling constants are 0.01 to 0.02 Hz when 800 computed transitions were fitted to 135 observed lines. The errors in the parameters are probably greater than those computed and it might also be possible to iterate onto another solution. However, we believe that our solution is correct, taking into account the number of transitions fitted and the analogous values of NMR parameters obtained for buta-, penta-, and hexa-dienes,^{1,10,11} and trienes.²

The spectrum of *trans*-1,3,5-hexatriene (Fig. 2) consists of two bands at $\delta \sim 5.1$ and ~ 6.2 , respectively. The band at $\delta \sim 5.1$ was assignable to the geminal protons split by 3J_c and 3J_t . The band at $\delta \sim 6.2$ was very complex

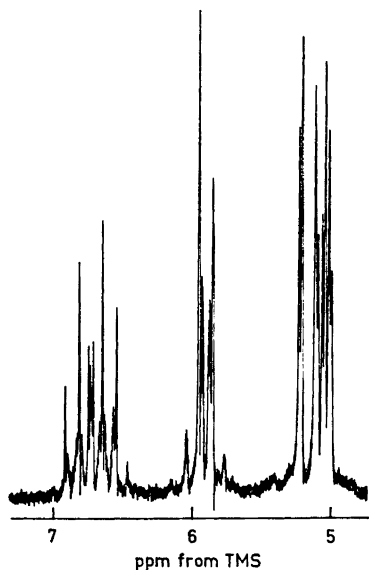


Fig. 1. 100 MHz spectrum of *cis*-1,3,5-hexatriene.

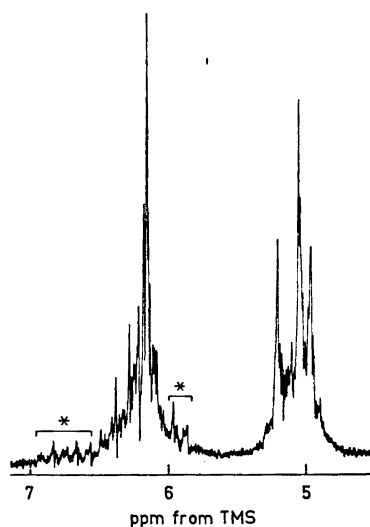


Fig. 2. 100 MHz spectrum of *trans*-1,3,5-hexatriene. Signals due to the *cis*-isomer (see text) are marked by asterisks.

due to the small chemical shift difference between the two pairs of inner protons compared to the coupling constants involved. The spectrum was simulated by computer and the parameters involved were adjusted to give a reasonable fit without any iterative procedure.

The spectrum of all-*trans*-1,6-dimethyl-1,3,5-hexatriene was very complex. Even the methyl decoupled spectrum gave too little resolved fine structure to make an iterative calculation feasible. The spectrum calculated with the parameters in Table 1 gave a reasonable correlation with the observed spectra. The parameters in Table 1 were taken from values obtained for butadienes¹ and trienes^{2,3} as model compounds, and the coupling constants are assumed to be correct to *ca.* 0.3 Hz.

RESULTS AND DISCUSSION

The data for the coupling constants in the trienes are in the range of analogous values for penta- and hexa-dienes,¹ and it may be assumed that the trienes have the configurations shown in Fig. 3, and are in planar or nearly planar conformations. The NMR parameters for 1,6-dimethyl-1,3,5-hexatriene suggest an all-*trans* planar or nearly planar structure. Lippincott *et al.*^{6,7} studied *cis*- and *trans*-1,3,5-hexatriene by IR and Raman spectroscopy, and they assumed the structures I and II.

Table 1. Coupling constants (in Hz) for trienes and related compounds.^a

Compound	² J	³ J _s	³ J _c	³ J _t	⁴ J _c	⁴ J _t	⁵ J _{cc}	⁵ J _{ct}	⁵ J _{tt}
<i>cis</i> -Hexatriene (I)	1.91	11.14	10.77(3,4) 10.15(1',2)	16.77	-0.71	-0.77(1',3) -1.04(2,4)	-	0.56	1.36
<i>trans</i> -Hexatriene (II) ^b	1.9	10.5	9.5 ^c	16.2(3,4) 15.2(1,2) ^c	-0.8(1.3) -0.8(2,4)	-0.8	0.7	0.7	-
all- <i>trans</i> -1,6-Dimethylhexatriene (III) ^b	-	10.8	-	16.2(3,4) 15.6(1,2)	-0.6(1,3) -0.9(2,4)	-	0.8	-	-
<i>cis</i> -Allo-ocimene ^d	-	11.16	-	15.20	-1.04(2,4) -0.94(4,6)	-	-	0.79	-
<i>trans</i> -Allo-ocimene ^d	-	11.01	-	15.28	-0.91	-0.82	0.55	-	-
Methyl 2,7-dimethyloctatrienoate- <i>trans</i> -2, <i>cis</i> -4, <i>trans</i> -6 ^e	-	12.5	10.7	-	-	-1.0	-	-	-
all- <i>trans</i> -Octatrienoate ^e	-	11.5	-	14.6	-0.6	-	-	-	-
Butadiene ^f	1.74	10.41	10.17	17.05	-0.83	-0.86	0.69	0.60	1.30
<i>trans</i> -Pentadiene ^g	1.89	10.30	10.22	16.93(1,2) 15.06(2,4)	-0.79 -0.78	-0.81	0.74	0.61	-
all- <i>trans</i> -Hexadiene ^g	-	10.30	-	15.01	-	-0.84	0.68	-	-
<i>cis</i> -Pentadiene ^g	2.12	10.95	10.24(1',2) 10.86(3,4')	16.89	-0.85	-0.81(1',3) -1.14(2,4')	-	0.81	1.53
<i>cis</i> -2-Butene ^h	-	-	10.88	-	-	-	-	-	-
Ethylene ⁱ	2.08	-	10.02	16.81	-	-	-	-	-

Compound	⁵ J _{s_{cs}}	⁵ J _{s_{ts}}	⁶ J _{cc}	⁶ J _{ct}	⁶ J _{tt}	⁷ J _{ccc}	⁷ J _{cct}	⁷ J _{tct}	⁷ J _{ctc}	⁷ J _{t_{tt}}
I	0.21	-	-0.14	-0.14	-	0.09	0.10	0.09	-	-
II ^b	-	0.25	-	-0.2	-0.2	-	-	-	0.15	0.15
III ^b	-	0.25	-	-0.2	-	-	-	-	0.15	-
<i>cis</i> -Allo-ocimene ^d	-	-	-	-	-0.13	-	-	-	-	-
<i>trans</i> -Allo-ocimene ^d	-	-	-0.09	-	-	-	-	-	-	-
Methyl 2,7-dimethyloctatrienoate- <i>trans</i> -2, <i>cis</i> -4, <i>trans</i> -6 ^e	±0.2	-	-	-	-	-	-	-	-	-
all- <i>trans</i> -Octatrienoate ^e	-	±0.3	-	-	-	-	-	-	-	-

^a The signs are chosen to be consistent with published values on dienes.¹ ^b The errors in the parameters for compounds II and III are *ca.* 0.3 Hz. These results were not derived from iterative spectral analysis (see text). These values appear to be unreasonably low, but computations using higher values gave poorer agreement with the experimental spectrum. We suspect the errors in these parameters are, however, substantial. One of the difficulties in obtaining more accurate parameters for II is the small amount of *cis*-isomer also present in the sample. ^d Ref. 2. The *cis* and *trans* isomers are those assumed by Cunliffe *et al.*² ^e Ref. 3. ^f Ref. 10. ^g Position notation according to Ref. 1. ^h Ref. 14. ⁱ Ref. 19.

Since planarity is required for resonance it is expected that these structures should be the most stable as compared to other possible isomers. It is, however, not possible to rule out any *s-cis* structures from IR and Raman evidence

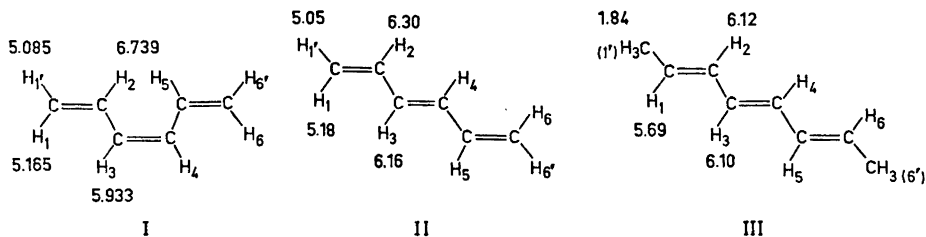


Fig. 3. Notation and chemical shifts (ppm from TMS) for the hexatrienes studied.

alone.^{6,7} The *cis*-1,3,5-hexatriene is strained because of steric interaction between the central C–H groups in a similar manner to that discussed for *cis*-pentadiene.^{1,12} For a planar conformation, with normal valence angles, the distance between H₂ and H₅ will be close to the sum of the van der Waals radii. Similar strain is not expected for the all-*trans*-1,3,5-hexatrienes.

Some of the coupling constants obtained for the *cis*-hexatriene (I) show significant deviations from the butadiene¹⁰ and propene¹³ values. They are, however, close to the values reported for *cis*-pentadiene.^{1,11} The value of 3J_c for the vinyl groups in the *cis*-triene, 10.15 Hz, is similar to the values obtained for butadiene,¹⁰ 10.17 Hz, *cis*-pentadiene,¹ 10.24 Hz, and *trans*-pentadiene,¹ 10.22 Hz. It seems clear that the vinyl group angles in the triene are close to those of the dienes. This assumption is also supported by electron diffraction measurements^{4,5} which show that the C₁C₂C₃ angle in the *cis*-triene (122.1°) is close to the butadiene value (122.8°). Moreover, 3J_c for the protons at the disubstituted double bond, 10.77 Hz, parallels the values obtained for *cis*-pentadiene,¹ 10.86 Hz, *cis*-2-butene,¹⁴ 10.88 Hz, and methyl 2,7-dimethylocta-2,4,6-trienoate,³ 10.7 Hz. The C₂C₃C₄ angle in the *cis*-triene, 125.9°, is, however, significantly different from the butadiene value.^{4,5} This angle distortion, *ca.* 4°, is comparable to the distortion of *ca.* 5° suggested for the *cis*-butene due to steric interaction between the methyl groups.¹⁵ An “in-plane-deformation” of *cis*-1,3,5-hexatriene is also supported by observations on *cis*-pentadiene.¹ The values of 3J_c show no significant variation due to the differences between methyl or vinyl groups substituted *cis* into ethylene, but any substituent effects might be obscured by effects arising from distortion. The proposed in-plane-distortion in *cis*-pentadiene has been treated theoretically by Bacon and Maciel.¹² They showed that all of the pertinent couplings are increased in magnitude by this deformation. Such a deformation may therefore have a significant effect on the observed coupling constants for *cis*-1,3,5-hexatriene. The value of 3J_t for the *cis*-triene, 16.77 Hz, is slightly smaller than that for butadiene (17.05 Hz) but it is nearer to the values observed for the vinyl groups of *cis*- and *trans*-pentadiene,¹ 16.89 Hz and 16.93 Hz, respectively.

The value of 3J_s for *trans*-1,6-dimethyl-1,3,5-hexatriene is increased by *ca.* 0.5 Hz compared to *trans*-penta- and hexa-diene.¹ This could be an effect due to extended conjugation rather than any difference in population of rotamers. Dodziuk¹⁶ has pointed out from theoretical calculations that the torsional barrier height for the methyl group of *cis*-pentadiene is substantially higher than that for *trans*-pentadiene, a fact which is consistent with the steric in-

teractions deduced from NMR experiments on penta- and hexa-dienes.¹ Segre *et al.*¹¹ found a variation in 3J_s *ca.* 0.2 Hz for *trans*-pentadiene and *ca.* 0.05 Hz for *cis*-pentadiene over a temperature range of *ca.* 75°C. The increase in 3J_s for *cis*-1,3,5-hexatriene relative to butadiene^{10,11} could be due to deformations of the triene. Barber *et al.*³ report a value of 12.5 Hz for 3J_s in methyl 2,7-dimethylocta-*trans*-2,*cis*-4,*trans*-6-trienoate. The increase in 3J_s relative to *cis*-1,3,5-hexatriene could be explained by a substituent effect similar to that proposed for butadiene,¹ where 3J_s increases by *ca.* 0.55 Hz for each *cis* methyl group present. The value of 3J_s in butadiene is also increased by the presence of ester groups. The effect of two *trans* ester groups¹⁷ is an increase of 1.0 Hz. Calculations¹² of 3J_s in butadiene show that this coupling is increased substantially by out-of-plane deformations about the double bond.* Substitution of *trans* terminal methyl groups into butadiene has only a minor effect on 3J_s whereas *cis* substitution increases this coupling significantly (in-plane deformation does not affect 3J_s significantly¹²). This suggests that the observed *cis*-methyl effect is due to an out-of-plane distortion.

The values of 4J are essentially the same as observed for *cis*-pentadiene.¹ The variations of 4J in a *cis*-triene caused by in-plane-deformation and out-of-plane twist are expected to be of the same magnitude and sign, for similar degree of distortion, as suggested for *cis*-pentadiene.¹² Out-of-plane distortion about the central C=C double bond in *cis*-1,3,5-hexatriene, however, affects conjugation to a different extent from that of the analogous distortion for *cis*-pentadiene. It is difficult to distinguish between the in-plane and out-of-plane distortions for hexatriene by measurements of 4J . Electron diffraction measurements⁵ suggest that the angle of distortion for *cis*-hexatriene about the central double bond (out-of-plane twist) is *ca.* 10°. A similar suggestion is made by Hecht and Victor¹⁵ for *cis*-2-butene, where the assumed angle is *ca.* 14°.

The value of ${}^5J_{tt}$ (1.36 Hz) lies between those for butadiene (1.30 Hz) and *cis*-pentadiene (1.53 Hz). The high value for *cis*-pentadiene may be connected with a proposed in-plane distortion.^{1,12} Theoretical work¹² shows that ${}^5J_{tt}$ should drop if an out-of-plane twist occurs, and the value for *cis*-hexatriene (compared to that for *cis*-pentadiene) might indicate the presence of such a twist. The values of ${}^5J_{ct}$ show similar effects (0.56 Hz for *cis*-hexatriene, 0.60 Hz for butadiene, and 0.81 Hz for *cis*-pentadiene).

Table 2. Calculated and observed coupling constants (in Hz) for *cis*-hexatriene.

	${}^5J_{ct}$	${}^5J_{scs}$	6J	7J
Calculated FP ^a	0.92	0.17	-0.29	0.50
Calculated MK/CI ^a	0.81	0.09	-0.23	0.62
Observed	0.56	0.21	-0.14	0.10

^a π contributions (see Ref. 18).

* Haugen and Trættestad⁴ do not discuss out-of-plane distortions arising from internal rotation about formal single bonds of the polyenes.

It is anticipated that the values of 5J (except ${}^5J_{tt}$), 6J , and 7J will be π -dominated,^{1,12} since σ -contributions to J attenuate rapidly with the number of bonds separating the nuclei. In Table 2 the observed values are compared to those calculated by Cunliffe *et al.*¹⁸ The five-bond coupling constant through two formal single bonds, designated ${}^5J_{scs}$, is slightly greater than predicted. The only previous report of such a coupling is by Barber *et al.*³, who list ± 0.2 Hz for ${}^5J_{scs}$ and ± 0.3 Hz for ${}^5J_{sts}$ in heavily substituted trienes. Our results for 6J , on the other hand, are smaller by a factor of two than that calculated, though the deviation is not greatly outside experimental error. However, similar values have been reported² for allo-ocimene. The experimental values for 7J in *cis*-hexatriene are a factor of five smaller than the predicted magnitude, the difference being well outside experimental uncertainty. No measurements of 7J in a triene system have been reported previously. The assumed domination of 6J and 7J by the π -contribution leads to the conclusion that any out-of-plane distortion will reduce their magnitude. Our observations are therefore consistent with some out-of-plane twisting. It should be noted that the signs of the experimental six- and seven-bond coupling constants agree with those calculated.¹⁸ Also as predicted, the values of 6J and 7J do not depend on configuration.

The uncertainty in the coupling constants reported here for compounds II and III argues against any detailed discussion beyond the comment that the results support the configurations illustrated.

The chemical shifts in dienes¹ are affected by the substituents. For the trienes, however, quantitative conclusions cannot be made from the available data, but certain trends are apparent. However, it should be noted that the shifts we report are for varying solvent conditions, and none of the values are extrapolated to infinite dilution. The shifts of the terminal vinyl protons in 1,3,5-hexatriene are hardly affected by the relative position of the two vinyl groups, *i.e.* the chemical shifts are nearly the same in the *cis* and *trans*-isomers. A terminal methyl group in the triene causes a high frequency shift of H_1 , $+0.54$ ppm, compared to the unsubstituted compound. This shift is similar to those between butadiene¹⁰ and *cis*- and *trans*-pentadiene,¹ and to the shift between ethylene¹⁹ and propene.¹³ Protons attached to carbon atoms at a distant C=C double bond are apparently very little affected (by <0.1 ppm).

The shift of H_2 in *cis*-hexatriene is $+0.44$ ppm to high frequency compared to that for the *trans* isomer. This observation parallels that made for *cis*-pentadiene¹ compared to butadiene. A *cis* substituent at C_4 , whether it is a methyl group or a vinyl group, causes a high frequency shift of H_2 by *ca.* 0.4 ppm. This effect is probably caused by steric influences^{20,21} and this provides further evidence for a deformation due to the interaction between *cis* C—C bonds. The methyl group in *cis*-pentadiene does not show any steric shift,¹ probably due to the effect of internal rotation. The very small increase, *ca.* 0.1 ppm, of the shift for H_2 in *cis*-hexatriene compared to *cis*-penta-diene might be attributed to the different shielding effect caused by a vinyl group compared to a methyl group.

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