

1. Almenningen, A., Bastiansen, O. and Træt-
teberg, M. *Acta Chem. Scand.* **12** (1958)
1221.
2. Bastiansen, O., Hedberg, L. and Hedberg,
K. *J. Chem. Phys.* **27** (1957) 1311.
3. Haugen, W. and Trætteberg, M. *Acta Chem.*
Scand. **20** (1966) 1726.
4. Almenningen, A., Bastiansen, O. and Fern-
holt, L. *Kgl. Norske Videnskab. Selskabs,*
Skrifter **1958** No. 3.
5. Trætteberg, M. and Bonham, R. A. *J. Chem.*
Phys. **42** (1965) 587.

Received June 30, 1966.

The Molecular Structures of 1,3-Butadiene and 1,3,5-*trans*-Hexatriene

WILLIAM HAUGEN,^{a*} and
MARIT TRÆTTEBERG^b

^a*Kjemisk Institutt C, Universitetet i Oslo,
Blindern, Oslo 3, Norway*

^b*Kjemisk Institutt, Norges Lærerhøgskole,
Trondheim, Norway*

The molecular structures of 1,3-butadiene and 1,3,5-*trans*-hexatriene in the vapour phase have been studied by the sector electron diffraction method, using a modified s^3 sector. The results presented in this work are parts of our endeavour to study the factors determining the lengths of sp^2 - sp^2 carbon-carbon single bonds. The research program also includes molecules like 1,3,5,7-cyclo-octatetraene,¹ 1,3,5-*cis*-hexatriene, 1,3-cyclo-pentadiene and the *cis,cis*-, *cis,trans*- and *trans,trans*-3,4-dimethyl-2,4-hexadienes.

The molecular structure of 1,3-butadiene reported here was determined simultaneously as the molecular structure of 1,3,5,7-cyclo-octatetraene reported elsewhere.¹ The two structures attract interest because of a reported discrepancy between the carbon-carbon single bond lengths^{4,5} which was not in accordance with the current ideas of π -electron delocalization.

* Present address: Harvard University, Cambridge, Mass., U.S.A.

The intensity data were treated according to the usual well-established procedure,² and for both molecules the effective s -region of the resulting molecular intensity functions ($sM(s)$ -functions) extended from $s = 1.25 \text{ \AA}^{-1}$ to about $s = 45 \text{ \AA}^{-1}$. The bonded distances in the molecules were determined by applying auto- and cross-correlation functions³ to the intensity data, while the complete structures in both cases were determined by least-squares refinements of the molecular intensity functions. Tables 1 and 2 give the structural parameters obtained for 1,3-butadiene and 1,3,5-*trans*-hexatriene, respectively.

Table 1. 1,3-Butadiene. Internuclear distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of a least-squares refinement of the molecular intensity data.

Distance	$r_g(1), \text{ \AA}$	$\Delta r_g(1), \text{ \AA}$	$u, \text{ \AA}$	$\Delta u, \text{ \AA}$
C=C	1.343 ₉	0.000 ₅	0.043 ₆	0.000 ₅
C-C	1.467 ₂	0.001 ₃	0.051 ₃	0.001 ₀
C ₁ C ₃	2.469 ₅	0.001 ₃	0.064 ₆	0.001 ₂
C ₁ C ₄	3.698 ₁	0.003 ₄	0.059 ₁	0.002 ₇
C-H	1.094 ₄	0.001 ₃	0.082 ₁	0.001 ₁

$$\angle \text{C}=\text{C}-\text{C}: 122.8^\circ \pm 0.5^\circ$$

$$\angle \text{H}-\text{C}=\text{C}: 119.5^\circ \pm 1.0^\circ$$

Angle of rotation around C-C bond: 0.0°

Table 2. 1,3,5-*trans*-Hexatriene. Internuclear distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of a least-squares refinement of the molecular intensity data.

Distance	$r_g(1), \text{ \AA}$	$\Delta r_g(1), \text{ \AA}$	$u, \text{ \AA}$	$\Delta u, \text{ \AA}$
C=C	1.345 ₂	0.001 ₀	0.043 ₃	0.001 ₄
C-C	1.450 ₄	0.002 ₃	0.052 ₅	0.002 ₅
C ₁ C ₃	2.472 ₀	0.002 ₃	0.058 ₄	0.001 ₇
C ₁ C ₄	3.699 ₂	0.007 ₅	0.067 ₅	0.008 ₈
C ₂ C ₅	3.823 ₆	0.067 ₅	0.067 ₅	0.020 ₀
C ₁ C ₅	4.938 ₇	0.095 ₁	0.095 ₁	0.011 ₉
C ₁ C ₆	6.129 ₄	0.020 ₇	0.084 ₁	0.024 ₈
C-H	1.102 ₇	0.003 ₃	0.080 ₇	0.002 ₆

$$\angle \text{C}=\text{C}-\text{C}: 124.3^\circ \pm 1.5^\circ$$

$$\angle \text{H}-\text{C}=\text{C}: 117.8^\circ \pm 1.5^\circ$$

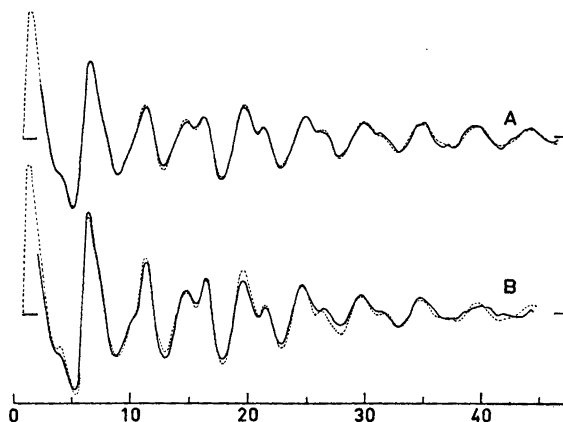


Fig. 1. Experimental (—) and theoretical (---) molecular intensity functions for 1,3-butadiene (A) and 1,3,5-*trans*-hexatriene (B).

The experimental $sM(s)$ -functions for both molecules are shown in Fig. 1, which also indicate the two theoretical $sM(s)$ -functions calculated on the basis of the structural parameters listed in Tables 1 and 2. The Fourier transforms of the modified molecular functions (modification function: $\exp(-0.0009s^2)$) are presented in Fig. 2 along with their theoretical counterparts.

The correspondence between the various experimental and theoretical functions for 1,3-butadiene is exceptionally good, a fact which is reflected in the small standard

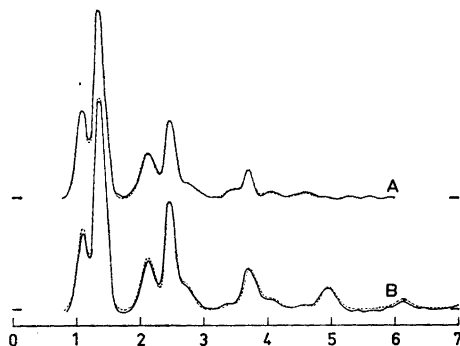


Fig. 2. Experimental (—) and theoretical (---) radial distribution functions for 1,3-butadiene (A) and 1,3,5-*trans*-hexatriene (B). Damping constant $k = 0.0009$.

deviations resulting from the least-squares refinement. The two vinyl groups were allowed to rotate around the C—C single bond during the least-squares refinement. The best fit between the experimental and theoretical $sM(s)$ -functions was however obtained for a planar *trans* model with no rotation around the central carbon-carbon bond. The longer distances in the molecule are, however, only slightly influenced by a moderate oscillation of the vinyl groups around the *trans*-position and an oscillation around the *trans*-conformation with a root-mean-square amplitude of about 10° can not be excluded on the basis of the present electron diffraction investigation. The structural parameters of 1,3-butadiene and 1,3,5,7-cyclo-octatetraene are briefly compared elsewhere.¹

For 1,3,5-*trans*-hexatriene the correspondence between the experimental and theoretical $sM(s)$ -functions and between the radial distribution functions is satisfactory, but not as good as in the 1,3-butadiene case. The longer distances in the molecule correspond to an out-of-plane motion that can formally be described as rotations of the vinyl groups of about 11.9° around the carbon-carbon single bonds, so that the molecule assumes a "boat" conformation.

A full account of the work will be published later together with a thorough discussion of the sp^2 - sp^2 carbon-carbon single bond length.

The authors wish to thank professor Otto Bastiansen for his inspiring interest in the project and for valuable discussions. Thanks are also due to cand. real. Arne Almenningen for making all the electron diffraction diagrams, to Miss Anne Reitan for skillful technical assistance, and to *Norges Almenvitenskapelige Forskningsråd* for financial support.

1. Trøttestad, M. *Acta Chem. Scand.* **20** (1966) 1724.
2. Almenningen, A., Bastiansen, O. and Fernholt, L. *Kgl. Norske Videnskab. Selskabs, Skrifter* **1958** No. 3.
3. Trøttestad, M. and Bonham, R. A. *J. Chem. Phys.* **42** (1965) 587.
4. Almenningen, A., Bastiansen, O. and Trøttestad, M. *Acta Chem. Scand.* **12** (1958) 1221.
5. Bastiansen, O., Hedberg, L. and Hedberg, K. *J. Chem. Phys.* **27** (1957) 1311.

Received June 30, 1966.

Algal Carotenoids

V. Iso-fucoxanthin — a Rearrangement Product of Fucoxanthin

ARNE JENSEN

Norwegian Institute of Seaweed Research, N.T.H., Trondheim, Norway

The use of seaweed meal as a feed ingredient in rations to poultry prompted us to investigate the fate of fucoxanthin, the characteristic carotenoid of brown seaweeds, when fed to the laying hen. Seaweed meal feeding was found to increase the yellow colour of the egg yolk.¹ Most of the colour was caused by a transformation product of fucoxanthin and no unchanged fucoxanthin could be detected in the egg yolk.

During studies on the structure of fucoxanthin we observed the formation of a similar, probably identical pigment, upon chromatographic purification of fucoxanthin on alkaline adsorbents. Since studies of the latter rearrangement product might

shed some light on the nature of the egg yolk pigment, work on the artefact formed on alkaline adsorbents was undertaken.

Fucoxanthin was adsorbed to a column of magnesium oxide from a petroleum ether:acetone (10:1) solution and left on the column overnight at room temperature. Extensive conversion to more polar pigments took place, and no unchanged fucoxanthin could be eluted from the column. The main product, for which we suggest the name iso-fucoxanthin, was rechromatographed on calcium carbonate and gave, after two crystallisations from diethyl ether-petroleum ether dark red-violet needles which melted at 140°C (uncorr.), λ_{\max} (430), 453 ($E_{1\text{ cm}}^{1\%} = 1600$), 482 m μ (petroleum ether); λ_{\max} 3450, 2940, 1930, 1730, 1606, 1530, 1450, 1355, 1240, 1150, 1030, 960 cm^{-1} (KBr-disc); τ -values: 8.92, 8.75, 8.64, 8.62, 8.46, 8.18, 8.02, and 7.97. The compound was spectroscopically and chromatographically inseparable from one of the main egg yolk pigments obtained from hens on seaweed meal rations.

By following the acetylation of iso-fucoxanthin on paper chromatograms it was established that the compound formed a monoacetate under standard conditions (acetic anhydride-pyridine at room temperature overnight). The R_F -values of the original pigment (0.24, on Schleicher & Schüll, No. 287 paper using petroleum ether containing 10% of acetone as solvent) and of the acetate (0.46) indicated the presence of (one) more hydroxy group in these compounds over the corresponding members of the fucoxanthin series ($R_F = 0.49$ for fucoxanthin and $R_F = 0.72$ for fucoxanthin acetate). In an attempt to establish the character of the additional hydroxy functions the two acetates were treated with hexamethyldisilazane and trimethylchlorosilane and the course of the ether formation was followed by paper chromatography. Samples were taken from the reaction mixtures at intervals and subjected directly to paper chromatography. The triacetate of fucoxanthol *b*⁶ was also included in the experiment. The results are shown in Table 1 and indicate that fucoxanthin acetate and fucoxanthol *b* acetate had only one accessible hydroxy group each, while a diether was formed from iso-fucoxanthin acetate.

The mass spectrum of iso-fucoxanthin showed parent ion peak at mass number 658; further peaks at mass numbers 640 (P-18, water); 622 (P-(2 × 18)); 580