PPP (Fig. 2). The temperature optimum was also unaltered in the presence of PPP (Fig.2).

Fig. 1 shows that the lipase activity of duodenal contents was found to be incompletely inhibited by relatively high concentrations of PPP. The inhibitory effect with a concentration of 100 μg PPP/ml substrate solution was 25 % while it was 50 % with 500 μg PPP/ml.

A maximal inhibition of the trypsin activity of duodenal contents of about 10 % was found even with high concentrations of PPP.

Discussion. The results of the present study indicate that PPP is a potent inhibitor of pancreatic phospholipase A in intestinal contents. This inhibitions seems to be independent of the bile salt concentrations, the calcium concentration, the pH, and the temperature of the incubation medium. Also duodenal pancreatic lipase was inhibited to a certain extent, whereas only slight inhibition, if any, of trypsin was found. PPP has been shown to exert a beneficial effect upon the protein losses *via* the colonic mucosa in patients with ulcerative colitis.[2] A subdivided dose of 2 g PPP/day was given. Under such circumstances a total inhibition of the intestinal phospholipase A_2 activity and, in addition, an moderate inhibition of the lipase activity should be expected. This latter possibility might explain that in cases with non-tropical sprue a beneficial effect on the protein leakage but no effect on the feacal fat excretion was obtained after peroral PPP administration.[2]

The membrane tightening effect of PPP has been ascribed its capability of inhibiting hyaluronidase.[1] Considering the fact that lecithin is a main component of cell membranes and that it is split by phospholipase A the beneficial effect of PPP in cases of ulcerative colitis may also be ascribed an inhibition of this latter enzyme by PPP.

1. Fredholm, B. AB Leo, Helsingborg, Sweden. *Personal communication.*
2. Krook, H. *Personal communication.*
3. Ihse, I. and Arnesjö ,B. *Acta Chem. Scand.* **27** (1973). *In press.*
4. Erlansson, C. and Borgström, B. *Scand. J. Gastroenterol.* **5** (1970) 293.
5. Hummel, B. C. W. *Can. J. Biochem. Physiol.* **37** (1959) 1393.
6. Norman, A. *Arkiv Kemi* **32** (1955) 331.
7. Hofman, A. F. Thesis, Lund 1964, p. 32.
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An Electron-Diffraction Investigation of the Molecular Structure of 1,2,4,5-Hexatetraene (Biallenyl) in the Vapour Phase

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The molecular structure of 1,2,4,5-hexatetraene (in the following called biallenyl) has been studied by the gas electron diffraction method. The compound used in the present study was synthesized from 3-bromo-1-propyne and magnesium metal with tetrahydrofuran as solvent.[1]
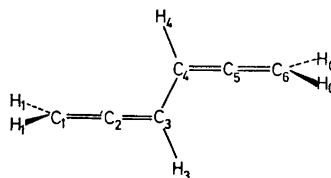

Fig. 1. Biallenyl. Molecular model which shows the numbering of the atoms.

A complete spectroscopic study of the compound was recently carried out by Powell *et al.*,[2] based on a sample originating from the same source. They concluded from examination of the infrared and Raman spectra that the molecule has a center of symmetry corresponding to C_{2h} symmetry in which the hydrogen atoms of the CH_2 groups are twisted out of the molecular plane by 90°.

The electron-diffraction intensity data were obtained with the Oslo diffraction camera.[3] Diffraction photographs were taken at two camera lengths (approximately 48 cm and 20 cm) at room temperature. For each camera length four plates were selected for the structure analyses. The data were treated in the usual way [4] and yielded an experimental molecular intensity ($sM(s)$) function in the region from $s = 1.25$ $Å^{-1}$ to about 44 $Å^{-1}$.

Preliminary values for the bond distances and bond angles were obtained from the experimental radial distribution curve (Fig. 3). The peak at about 1.3 Å corresponds to the carbon carbon bond distances, while the shoulder at the short distance side of this peak contains contributions from the carbon-hydrogen bonds. Non-bonded $C\cdots H$ distances over one bond angle are found at 2.1 Å, while the composite peak at about 2.5 Å contains contributions from the C_1C_3 and C_2C_4 distances. The other nonbonded carbon carbon distances are found at 3.6 Å (C_1C_4 and C_2C_5), 4.9 Å (C_1C_5) and 6.1 Å (C_1C_6).

The molecular structure was determined by a least squares analysis of the diffraction data. During this procedure the r_a, r_g, and r_α structures were studied independently. This implies that for example in an r_a structure study the dependent distances and derivatives were calculated from r_a-parameters. As the $C_1=C_2$ and $C_2=C_3$ distances were assumed to be equal during the refinements, the r_a values for these bonds will be different in an r_α refinement and so on.

The following approximate relationships exist between the different r values:

$$r_a \approx r_e + \langle \Delta z \rangle + K - u^2/r_e \approx r_\alpha + K - u^2/r_e$$
$$\simeq r_g - u^2/r_e$$

where $\Delta z(=r-r_e)$ is directed along the internuclear distance.[9] r_α gives the distance between average positions of two atoms. An r_α structure is therefore geometrical consistent. r_g represents an average internuclear distance. r_g and r_a structures are not geometrical consistent and shrinkage effects might be observed.

In order to determine an r_α structure it is necessary to know the perpendicular amplitude correction coefficients (K values) and the mean amplitudes of vibrations (u values). The u values for the most dominant internuclear distances are usually obtained quite accurately from electron diffraction data. It is, however, ordinarily not possible to determine all vibrational amplitudes by this method. Both u and K values may be calculated from spectroscopic data. In the present case these quantities have been calculated by Gwinn's method[5] which is based on an expansion of interatomic distances in terms of cartesian displacement coordinates. The computer program has been adjusted for use in an electron diffraction analysis by Stölevik et al.[6] The assumed force field was taken from data published by Allinger et al.[7] The results of the calculations are

Table 1. Biallenyl. Observed and calculated mean amplitudes of vibrations (u_{ij}) and calculated perpendicular amplitude correction coefficients (K_{ij}) for distances between carbon atoms. The numbers in parentheses are standard deviation values as obtained in the least squares analyses. All values are given in Å.

Distance	u_{ij}obs.	u_{ij}calc.	K_{ij}calc.
$C_1=C_2$	0.0423(6)	0.0404	0.01113
$C_2=C_3$		0.0403	0.00807
C_3-C_4	0.0595(30)	0.0494	0.00253
C_1-H_1	0.0841(26)	0.0790	0.01382
C_3-H_3		0.0790	0.01210
C_2C_7	0.0784(36)	0.0929	0.00344
C_1C_3	0.0573(26)	0.0487	0.00678
C_1C_4	0.0976(66)	0.0961	0.00439
C_2C_5		0.0911	0.00257
C_1C_5	0.1019(91)	0.0910	0.00199
C_1C_6	0.1065(240)	0.0902	0.00039

presented in Table 1, which also lists the experimentally determined mean vibrational amplitudes (u_{ij}obs.).

The correspondence between observed and calculated mean vibrational amplitudes is reasonably good. The observed u values for bond distances are often found to be higher than those calculated by

Table 2. Structural parameters for biallenyl. The results in columns 2−4 represent values obtained from least squares intensity refinements based on an r_α-structure, while column 5 shows results based on an r_a-structure. The values in brackets are standard deviation values obtained when the geometrical and vibrational parameters were varied simultaneously.

	r_a, Å	r_g, Å	r_α, Å	r_a, Å
$C_1=C_2$	1.3144	1.3158	1.3046(5)	1.3123(5)
$C_2=C_3$	1.3113	1.3127	1.3046(5)	1.3123(5)
$C-C$	1.4682	1.4706	1.4681(35)	1.4656(40)
$C-H$	1.1058	1.1122	1.0992(32)	1.1043(36)
$\angle C=C-C$			124.0° (0.31°)	123.5° (0.35°)
$\angle C=C=C$			(180°)	(180°)
$\angle C_2=C_1-H_1$			(120°)	(120°)
$\angle C_2=C_3-H_3$			(118°)	(118°)

Gwinn's method, while the opposite is more often true for the non-bonded distances. The same trend is observed for the bond distance amplitudes of biallenyl, while the differences between observed and calculated u values for non-bonded distances are scattered in both directions.

Table 2 shows results based on refinements on r_α and r_a structures, respectively. The experimental data are consistent with a molecular structure with C_{2h} symmetry, a planar carbon skeleton with CH_2 groups that lie in planes at right angles to this plane. The carbon skeleton is well determined, but it was not possible to determine the $C=C-H$ bond angles accurately. The length of the carbon-carbon double bond is found to be the same as in allene (r_a: 1.312 Å).[9]

The experimental and theoretical molecular intensity curves are shown in Fig. 2, while Fig. 3 shows the corresponding
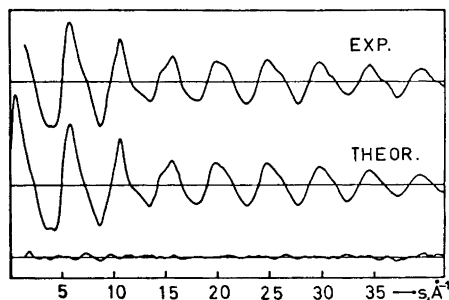

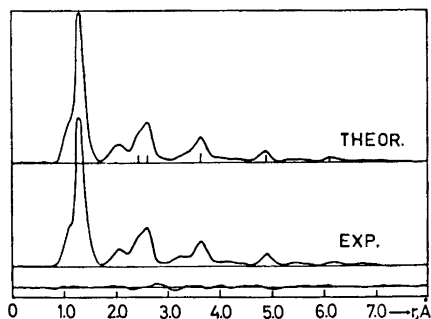*Fig. 2.* Biallenyl. Experimental and theoretical molecular intensity functions and the differences between the two.

Fig. 3. Biallenyl. Experimental and theoretical radial distribution functions. Artificial damping constant $k = 0.0015$ Å².

radial-distribution (RD) curves. It is seen that the deviation between the experimental and theoretical RD functions is quite large in some regions. This fairly large deviation is, however, mostly outside the regions where the CC distances contribute and are probably connected with the difficulties in obtaining reliable CCH bond angles.

Several factors may contribute to explain the fact that shrinkage effects within the allenyl groups could not be clearly demonstrated in the present case. The important C_1C_3 distance is not very different from another carbon carbon distance (C_2C_4), and the accuracy with which each of them is determined is therefore reduced. Further the assumed force field that was applied in calculating the perpendicular amplitude correction coefficients might not be accurate enough to give K values of the required precision. Finally experimental errors in the scattering data should be mentioned.

The investigation will be continued by carrying out a more elaborate calculation of K and u values from spectroscopic data for application in further refinements of the electron-diffraction data.

1. Hopf, H. *Angew. Chem.* 17 (1970) 703.
2. Powell, D. L., Klœboe, P., Christensen, D. H. and Hopf, H. *Spectrochim. Acta* A 29 (1973) 7.
3. Almenningen, A., Bastiansen, O., Haaland, A. and Seip, H. M. *Angew. Chem.* 77 (1965) 877.
4. Andersen, B., Seip, H. M., Strand, T. G. and Stölevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
5. Gwinn, W. D. *J. Chem. Phys.* 55 (1971) 477.
6. Stölevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Letters* 15 (1972) 263.
7. Allinger, N. L. and Sprague, J. T. *J. Am. Chem. Soc.* 94 (1972) 5734.
8. Almenningen, A., Bastiansen, O. and Trætteberg, M. *Acta Chem. Scand.* 13 (1959) 1699.
9. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo and Elsevier, Amsterdam 1968.