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## Atoomafstanden in $\alpha,\omega$ -Diphenyl-polyenen

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## SUMMARY

The careful X-ray examination of naphthalene by Robertson et al. allowed a detailed comparison of calculated bond lengths with experimental ones. The underlying idea of the present investigation was to give a similar comparison for a polyene compound consisting of a chain of alternating single and double bonds. Molecular orbital calculations by Coulson predicted a considerable decrease of the lengths of the single bonds and some increase of the lengths of the double bonds, especially in the centre of the chains. Unsubstituted polyenes are unstable and hence less suitable for an X-ray examination. The  $\alpha, \omega$ -diphenyl-compounds, however, are crystalline and stable at room-temperature. The  $\alpha, \omega$ -diphenyl-polyenes were therefore chosen for the present investigation.

The results of molecular orbital calculations on the series of  $\alpha, \omega$ -diphenyl-polyenes,  $\text{Ph}-(\text{CH}=\text{CH})_n\text{Ph}$  with  $n = 0 - 5$  are given in chapter 3. In addition to the atomic distances the energies of the molecular orbitals were calculated. Semi-empirical values for the exchange integral  $\beta$  were deduced from a comparison of calculated with observed resonance energies and electronic transition energies. The molecular orbital calculations on biphenyl, stilbene and diphenyl-butadiene were extended to a second order approximation, in which the variation of  $\beta$  with distance was introduced. The effect of this variation on the calculated bond distances was small.

Some crystallographic properties of the members of the series with  $n = 2 - 5$  are described in chapter 5. Each of these compounds can crystallize in an orthorhombic and in a monoclinic modification. The orthorhombic modification is the most stable one at and above room-temperature. These orthorhombic modifications constitute a homologous series as do the monoclinic modifications of the terms  $n = 3, 4$  and  $5$ . The orientations of the molecules in the orthorhombic and in the monoclinic crystals appear from the structure analyses of 1,10-diphenyl-1,3,5,7,9-decapentaene (chapter 6). These orientations were found by trial and error, making use of the change of the lattice constants observed in this series of compounds and of the optical properties. The

co-ordinates of the carbon atoms were refined by Fourier projections. The available crystals were rather thin, however, and consequently the number of observed reflections was small. The experimental bond lengths were subject to a standard deviation of approximately 0,03 Å. Therefore a detailed comparison of observed with calculated bond lengths is not possible.

Thicker, well-developed orthorhombic crystals of 1,8-diphenyl-1,3,5,7-octatetraene were available. These crystals were used for an X-ray structure determination described in chapter 7. In order to increase the number of observable reflections the crystals were cooled down to -100°C by means of a stream of evaporated liquid air. All  $h k l$  reflections observed within the region of copper radiation were used for the structure determination.

The molecules possess a centre of symmetry. Starting from a series of approximate co-ordinates, found by two-dimensional methods, the signs of the observed  $h k l$  structure factors were calculated and used in a three-dimensional Fourier synthesis of the electron density distribution throughout the unit cell. The carbon atoms of the polyene chain are located in a plane, as are the atoms of a phenyl group. These two planes make an angle of 5,4° with each other. The hydrogen atoms are clearly visible in the electron density sections according to these planes.

A final refinement of the co-ordinates of the carbon atoms was obtained by computing two differential syntheses; in one of them the observed and in the other one the calculated structure factors were used. The standard deviation of the experimental bond lengths amounted to 0,004 Å.

There is not a close agreement between calculated and observed bond lengths in diphenyl-octatetraene. The lengths of the C-C single bonds of the polyene chain are significantly smaller than the length of a true single bond, but the differences are not as large as predicted theoretically. The calculated increase of the lengths of the double bonds in the chain with respect to a true double bond appears hardly or not at all. The C-C bonds of the polyene chain contain angles of approximately 124°, but two of these angles are increased to 127°, probably due to a mutual repulsion of hydrogen atoms.