Short Communications

The Structure of Divinyl Ether

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The study of the diethyl and divinyl ether by Fischer and Ehrenberg has given rise to a discussion of the structure of the gaseous divinyl ether. Usually the structure of this compound is explained by assuming a resonance which gives a certain degree of double bond character to the C—O-bonds. The molecule should accordingly be expected to be planar. On the other hand the short $H_2—H_3$-distance in the planar model is unfavourable and will counteract the tendency to coplanarity. The van der Waals distance between two hydrogen atoms is 2.4—2.5 Å, while the $H_2—H_3$-distance for an undistorted model would be about 2.0 Å.

In order to decide whether one of the two effects predominates or an intermediate equilibrium position might exist, we have carried through an electron diffraction investigation by the aid of the sector method.

In Fig. 1 the $\sigma(r)$-curve of divinyl ether is given. The peaks with Roman numerals are due to the C—C- and C—O-distances. The other maxima are mainly caused by the C—H- and O—H-distances which give a relatively important contribution in this case. These maxima are, however, also somewhat influenced by the diffraction effect.

We are not able to determine separately the C—C- and C—O-bond distances from the $\sigma(r)$-curve. The same difficulty also occurs for the distances $C_1—O$ and $C_2—C_3$. An accurate determination of the parameters in the molecule can therefore not be expected. The following bond distances are

Fig. 1. $\sigma(r)$-curve for divinyl ether.
and valency angles seem, however, to give best agreement with the $\sigma(r)$-curve:

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\begin{align*}
C_1C_2 & : 1.35 \text{ Å} \\
C_2O & : 1.42 \text{ Å} \\
\angle C_2OC_3 & : 107^\circ \\
\angle C_1C_2O & : 123^\circ
\end{align*}
\]

The $C-C$ and $C-O$-distances occurring in a planar molecule with these parameters are indicated below the $\sigma(r)$-curve by a line diagram. (Full-drawn lines). The maximum IV does not fit with the $C_1-C_4$-distance. If we give up the claim of coplanarity, however, and for instance rotate the vinyl groups about the $C-O$-bonds an angle of $20^\circ$ in such a way that the $C_1$- and $C_4$-atoms move in the same direction, a relatively good agreement may be obtained. (Dotted lines in the line diagram.) Because of the uncertainty in the determination of the bond distances and valency angles an accurate determination of the magnitude and form of the deviation from coplanarity is impossible. By varying the distances and angles within reasonable limits we have, however, not been able to find a planar model which can be brought in accordance with the $\sigma(r)$-curve. We feel therefore justified in concluding that the deviation from coplanarity is real and that this deviation must be ascribed to the short $H_2-H_3$-distance in the undistorted planar model.

In this connection another question related to our problem may be mentioned. Wheland $^3$ has drawn attention to the surprising fact that the resonance energy of ethyl vinyl ether seems to be slightly greater than that of divinyl ether; it would have been expected to be somewhat smaller since only a single unstable structure takes part in the resonance in the ethyl vinyl ether molecule, while two such structures take part in the resonance of the divinyl ether molecule. This fact might be brought in relation to the unfavourable $H_2-H_3$-distance in the planar divinyl ether molecule model. If our assumption of a deviation from coplanarity is correct, the $\pi$-orbitals will overlap less completely causing a reduction of the resonance energy. But even if the molecule was assumed to be strictly planar the unfavourable $H_2-H_3$-distance would have decreased the stability of the divinyl ether molecule. In the case of the ethyl vinyl ether, on the other hand, the planar configuration is stabilized by the favourable $H_2-H_3$-distances. In an ethyl vinyl ether molecule with a planar carbon-oxygen skeleton the $H_2-H_3$-distances are approximately 2.3 Å. If any of the carbon atoms are brought out of the plane, one of the $H_2-H_3$-distances will decrease and might therefore oppose the deviation from coplanarity.

We wish to express our gratitude to fil.mæg. Inga Fischer, University of Stockholm, who has suggested this investigation and placed a sample of divinyl ether at our disposal. We also wish to thank Prof. O. Hassel for having read the manuscript.


Received March 7, 1949.