

Short Communications

Some Electron Diffraction Studies
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Heat capacity measurements^{1,2} of $\text{HCH}_3\text{-C}\equiv\text{C-CH}_3$ have indicated an almost free rotation between the methyl groups. In the case of $\text{CH}_3\text{-C}\equiv\text{C-CF}_3$ there have been contraversial views³⁻⁵ over the possibility of internal free rotation. It seemed of interest to study the internal rotation in a similar molecule by electron diffraction. The diffraction power of bromine made $\text{CBrH}_2\text{-C}\equiv\text{C-CBrH}_2$ suitable for our studies.

The diagrams were taken by the Oslo electron diffraction apparatus⁶ using distances between the diffraction point and photographic plate of 48 cm and 19 cm. The intensity data went out to $s = 27$. The data were treated in our usual manner⁷, but with a very strong damping factor of 0.006, as we were primarily interested in the longer distances. The information about these distances is found in the inner part of the intensity curve.

The radial distribution curve is presented in Fig. 1 and is compared with the

theoretically determined distances. The positions of the distances are indicated by perpendicular lines. These values were calculated using the following parameters: $\text{C}_1\text{-H}_1 = 1.09 \text{ \AA}$, $\text{C}_2\text{-C}_3 = 1.21 \text{ \AA}$, $\text{C}_1\text{-C}_2 = 1.45 \text{ \AA}$ and $\text{Br}_1\text{C}_1\text{C}_2 = 111.5^\circ$. The height of each line is proportional to $n Z_1 Z_2 / r$, where Z_1 is the atomic number of one atom, Z_2 is the atomic number of the second atom, n is the number of times the distance occurs in the molecule, and r is the distance.

If we subtract from the radial distribution curve the contribution of distances which would be invariable under rotation, we obtain the contribution of the distances which are dependent upon the rotation. This curve is presented in Fig. 2 as the solid line and should give information about the $\text{Br}_1\text{-Br}_4$ and the $\text{Br}_1\text{-H}_4$ distances.

If the molecule were rigid, there would be only one Br-Br peak. For a *cis* molecule the peak would occur at 5.55 \AA and for a *trans* molecule at 6.63 \AA . The difference curve shows no single simple peak. On the contrary, the double peak in Fig. 2 suggests free rotation.

The theoretical radial distribution curves for the $\text{Br}_1\text{-Br}_4$ distance were calculated assuming free rotation. These curves were made by assuming normal curves whose areas were proportional to the probability of the corresponding r -value. Gaussian normal curves were used. The three different theoretical curves (Fig. 2)

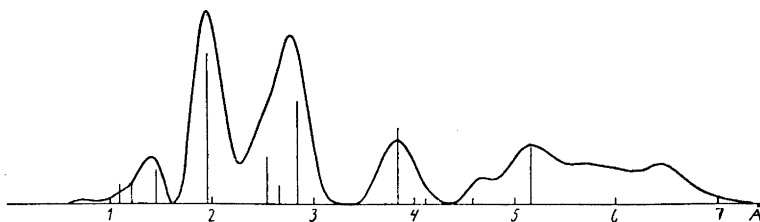


Fig. 1. Radial distribution curve for $\text{BrH}_2\text{C-C}\equiv\text{C-CH}_2\text{Br}$ ($k = 0.006$).

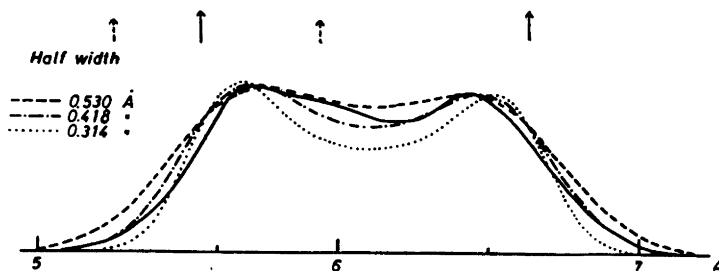


Fig. 2. Experimental difference curve and theoretical curves calculated on the assumption of free rotation.

represent three different choices for the half-width, *i. e.*, 0.314 Å, 0.418 Å, and 0.530 Å. The theoretical curves were normalized to the experimental curve.

The agreement between the theoretical and experimental curves is good. The discrepancies are easily understood: 1) The choice of the subtracted envelope⁷ is somewhat arbitrary, 2) the subtraction of the invariable distances leaves some uncertainty, and 3) the Br_1-H_4 distances are expected to give rise to a detectable effect. The Br_1-H_4 distances should have a probability curve similar to that for Br_1-Br_4 , but with peaks at about 5.37 Å and 5.87 Å and a total area about 15 % of the Br_1-Br_4 area. The maximum and minimum Br_1-H_4 distances are marked by dashed arrows in Fig. 2. The maximum and minimum Br_1-Br_4 distances are marked by solid arrows.

There remains one unexplained point in the radial distribution curve, namely the comparatively large area located at 4.67 Å. The C_1-H_4 distance at 4.58 Å should not give rise to such a large area. Even though we are not able to interpret this point, we feel it has no essential effect on our conclusion that there is internal rotation in the gaseous $\text{CBrH}_2-\text{C}\equiv\text{C}-\text{CBrH}_2$ molecule.

One of the authors (F. H.) wishes to express his gratitude to the *United States Educational Foundation in Norway* for a stipend during the 1956—57 academic year.

We also wish to thank *siv.ing. Marit Trætterberg* for the preparative work.

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Received June 20, 1957.

Phenol Dehydrogenations

VII. *. Dehydrogenation of Chavicol to Magnolol

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The biosynthetic importance of dehydrogenative coupling of phenols with the formation of diphenyl or diphenyl-oxide derivatives has been discussed by Erdtman and Wachtmeister¹. Magnolol (II) is a particularly simple example with a structure indicating that it has been formed by the coupling of two molecules of chavicol (I) or an aromatic precursor.

* Part VI: *Svensk Kem. Tidskr.* **47** (1935) 223.