Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURE OF TRIMETHYLCYCLOPENTADIENYLSILANE

N. N. VENIAMINOV, YU. A. USTYNYUK, N. V. ALEKSEEV, I. A. RONOVA AND YU. T. STRUCHKOV

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

(Received December 16th, 1969)

SUMMARY

The molecular structure of trimethylcyclopentadienylsilane, $C_5H_5Si(CH_3)_3$, has been studied by electron diffraction in the vapour phase. The Si atom is found to be bonded by the localized σ-bond with one of the cyclopentadienyl carbon atoms. The Si–C bond distances are 1.90 ± 0.01 Å. The cyclopentadienyl ring has an "envelope" conformation, the dihedral angle between planar four- and three-membered fragments of the ring being $22 \pm 4°$. The Si–C bond makes an angle of $56 \pm 4°$ with the plane of the bent-out "envelope flap". Assuming the equality of all C–H bond lengths and also of three C–C bond lengths within the planar four-membered fragment of the cyclopentadienyl ring, the following values are obtained: $r(\text{C–H}) = 1.11 \pm 0.02$, $r(\text{C–C}) = 1.53 \pm 0.03$, $r(\text{C=C}) = 1.40 \pm 0.02$ Å.

INTRODUCTION

In continuation of the molecular structure investigation[1] of cyclopentadienyl derivatives having the general formula $C_5H_5AX_3$ (where A = Sn, Ge, or Si) we have now undertaken the electron diffraction study of trimethylcyclopentadienylsilane in the vapour phase.

EXPERIMENTAL

The electron diffraction patterns were recorded with the EG-100A electronograph having the r^3-sector. The nozzle-to-plate distance was ca. 400 mm. A densitometric processing was carried out according to the previously described procedure[2]. Four and eight series of plates taken at accelerating potentials of 40 and 100 kV respectively were selected for processing.

STRUCTURE ANALYSIS

To separate out the molecular part of the scattering intensity the algorithm proposed earlier was used[3]. The resulting molecular intensity curve $sM(s)$ covers the interval from 4.8 to 24 Å^{-1} (Fig. 1).

In the region of small scattering angles this curve was extrapolated by the theoretical function calculated for the model the type of which (a molecule with the localized cyclopentadienyl carbon–silicon bond) was unambiguoŭsly determined in the first stages of the investigation. Later, with the continuous refinement of the geometrical parameters, this procedure was repeated, the correction of the $sM(s)$ curve in the region of small s-values being accompanied by any appreciable alteration of the resulting radial distribution (RD) curve. The experimental RD curve is shown in Fig. 2.

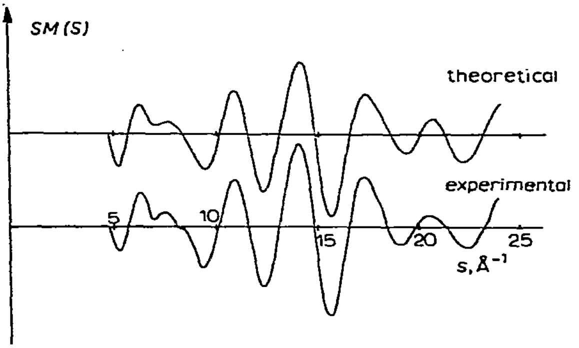


Fig. 1. Theoretical and experimental molecular intensity curves.

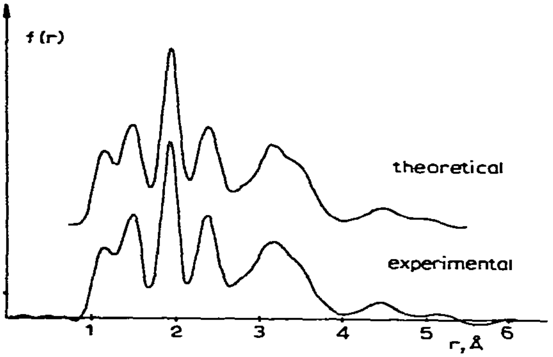


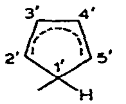
Fig. 2. Theoretical and experimental RD curves.

Its first peak corresponds to the C–C and C–H bond distances. Generally speaking, one may propose three types of bond distribution in the cyclopentadienyl ligand:

(*a*). One corresponding to the cyclopentadiene itself, (I).
(*b*). The other one with "antibutadiene" four-membered fragment, (II).
(*c*). The third one with equalized C(2')–C(3'), C(3')–C(4') and C(4')–C(5') bonds.

(I)

(II)



(III)

According to previous structural data[4–6] the system (I) tends to retain a planar configuration. Meanwhile, according to the present study (see below) the distances from the Si atom to the C(3′) and C(4′) carbon atoms of the ring have such values that the model with the planar cyclopentadienyl fragment turns out to be unacceptable. Therefore, the bond distribution as represented in the system (I) seems to be hardly probable.

The results[7] of the X-ray study of $[(\pi\text{-}C_5H_5)Fe(CO)_2]\cdot Sn(\sigma\text{-}C_5H_5)_2$ (IV) indicate a rather complicated bond distribution in the non-planar cyclopentadienyl ring approaching the type (II) system [1.53, 1.44 and 1.37 Å for the C(1′)–C(2′), C(2′)–C(3′) and C(3′)–C(4′) bonds, respectively]. However, taking into account the accuracy of this determination (±0.03 Å) one cannot exclude the possibility that the C(2′)–C(3′) and C(3′)–C(4′) internuclear distances are in effect very close to each other.

Considering this point and also limited possibilities of the electron diffraction to resolve composite peaks we accepted as an initial approximation the model (III) with the equal C(2′)–C(3′) and C(3′)–C(4′) bond distances. Also, the equality of all C–H bond distances was assumed. In this approximation the following values were found:

$r(\text{C–H}) = 1.11 \pm 0.02$ Å

$r(\text{C–C}) = 1.53 \pm 0.03$ Å

$r(\text{C=C}) = 1.40 \pm 0.02$ Å

The second and highest peak of the RD curve corresponds to the Si–C bond distances. This peak being quite symmetrical, one naturally may assume that all Si–C bond distances are equal. However, if we suppose that the Si–C(1) and Si–C(1′) distances are different, then the least-square procedure leads to two equally probable sets of parameters:

(1) $r[\text{Si–C(1)}] = 1.89 \pm 0.01$ Å and $r[\text{Si–C(1′)}] = 1.93 \pm 0.03$ Å

(2) $r[\text{Si–C(1)}] = 1.91 \pm 0.01$ Å and $r[\text{Si–C(1′)}] = 1.87 \pm 0.03$ Å

Thus, within the accuracy of investigation all Si–C bond distances are very close to each other. Finally, if the C–H, C–C and Si–C structural peaks are considered jointly the best agreement between theoretical and experimental RD curves is achieved in the case where all Si–C bond distances are equal to 1.90±0.01 Å.

The value is in a good agreement with results of the earlier electron diffraction investigations of molecules having the Si–C σ-bond: thus, the Si–C bond length was found to be equal to 1.93±0.03 Å[8] or 1.888±0.02 Å[9] in $(CH_3)_4Si$ and 1.90±0.02 Å[10] in $[(CH_3)_3Si]_2$.

The following assumptions were made in the course of the determination of the molecular geometry as a whole:

(1). The silicon atom has a non-distorted tetrahedral valence configuration.

(2). The $(CH_3)_3Si$ group orientation around the Si–C(1′) bond is such that the Si–C(1) bond is directed towards the ring and lies in the molecule symmetry plane passing through the Si and C(1′) atoms and the middle point of the C(3′)–C(4′) bond.

(3). The C(2′)–C(1′)–C(5′) angle (γ) is equal to 109° (see Fig. 3).

The simple geometrical analysis shows that variation of this parameter within reasonable limits has only a little effect on the angles α and β (see below), while a direct determination of γ is practically impossible due to small contributions of the corresponding distances into the experimental RD curve. The value $\gamma = 109°$ was taken as an average between 103° in the molecule of cyclopentadiene[5] and 115° in the molecule (IV)[7].

Thus, the following two parameters are to be determined (Fig. 3): the dihedral angle α between the C(2′)C(1′)C(5′) and C(2′)C(3′)C(4′)C(5′) planes and the angle β between the Si–C(1′) bond and the C(2′)C(1′)C(5′) plane. The angle β can be readily estimated from the distances r[Si–C(2′)] and r[Si–C(5′)] (equal to 2.80±0.03 Å) which were obtained by the analysis of the RD curve part from 2.5 to 3 Å. Thus, β is found to be equal to 55.7±4°. Then, the variation of α showed that the model with $\alpha = 22 \pm 4°$ meets the experimental RD curve in the best way, the distance r[Si–C(3′)] = r[Si–C(4′)] being equal to 3.41±0.05 Å in this case.

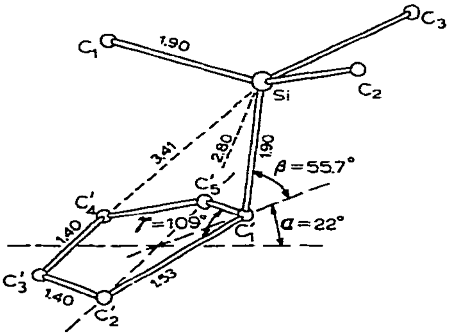


Fig. 3. The molecular model of $C_5H_5Si(CH_3)_3$.

It is interesting to note that for the best agreement between theoretical and experimental data the great root-mean-square vibration amplitudes should be attributed to the long distances from the atoms of the $Si(CH_3)_3$ fragment to the atoms C(2′), C(5′) and also C(3′), C(4′) (about 0.15 Å for the first group of distances and about 0.20 Å for the second). Such a situation was already observed earlier in the electron diffraction study of trimethylcyclopentadienylgermane[1]. Generally speaking, this feature may be interpreted in two ways. On one hand, it may be caused by certain asymmetry of the molecule, although there are no evident reasons for the symmetry distortion [*e.g.*, as steric hindrance in the structure of (IV)[7]]. On the other hand, the assumption of vibrations of a deformational type with the amplitudes mentioned is fully justified. It should be noted also that the compound studied undergoes an intramolecular metallotropic rearrangement in liquid phase at sufficiently high temperature[11,12]. Since the occurrence of such a process in vapour phase is also quite probable one should keep in mind a possibility of the corresponding distortion in the distribution of internuclear distances.

To estimate the degree of a possible molecular symmetry distortion we tested a model in which the Si atom is not situated in the symmetry plane of the ring but is slightly displaced aside so that the distances Si–C(2′) and Si–C(5′) and also Si–C(3′) and Si–C(4′) are no longer equal. For this purpose at first the position of the Si atom relative to the group of C(2′), C(2′), and C(5′) atoms was located by analysis of the

RD curve in the region from 2.5 to 3 Å on the assumption of inequality of the Si–C(2′) and Si–C(5′) distances. Root-mean-square vibration amplitudes for these distances were adopted equal to 0.09 Å. The resulting distances 2.72 Å for Si–C(2′) and 2.89 Å for Si–C(5′) correspond to the angles of 105° and 114.5° for Si–C(1′)–C(2′) and Si–C(1′)–C(5′), respectively (instead of 109.1° for both in the case of the symmetrical model), β is equal to 54.9° (instead of 55.7°). The subsequent variation of α indicated that in this case it also should be equal to 22±4° [as before, the C(1) atom was assumed to lie in the symmetry plane of the cyclopentadienyl ring].

The difference between the theoretical RD and $sM(s)$ curves for symmetrical and distorted models is so small that it seems unnecessary to present plots for each model separately.

ACKNOWLEDGEMENT

We are greatly indebted to Dr. A. V. Kisin for providing a sample of trimethylcyclopentadienylsilane.

REFERENCES

1 N. N. Veniaminov, Yu. A. Ustynyuk, Yu. T. Struchkov, N. V. Alekseev and I. A. Ronova, *Zh. Strukt. Khim.*, 11 (1970) in press.
2 N. V. Alekseev, P. P. Barzdain and I. A. Ronova, *Prib. Tekh. Eksp.*, 1 (1969) 150.
3 N. G. Rambidi, E. Z. Zasorin and B. M. Shchedrin, *Zh. Strukt. Khim.*, 5 (1964) 503; N. G. Rambidi and B. M. Shchedrin, *Zh. Strukt. Khim.*, 5 (1964) 663; B. M. Shchedrin and N. G. Rambidi, *Zh. Strukt. Khim.*, 6 (1965) 3.
4 G. Liebling and R. E. Marsh, *Acta Crystallogr.*, 19 (1965) 202.
5 L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 43 (1965) 2765.
6 J. L. Calderon, F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, 91 (1969) 2528.
7 B. P. Bir'yukov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 10 (1969) 95.
8 L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 58 (1936) 2036.
9 W. F. Sheehan and V. Schomaker, *J. Amer. Chem. Soc.*, 74 (1952) 3956.
10 L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 63 (1941) 3287.
11 H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, 1 (1964) 323.
12 Yu. A. Ustynyuk, A. V. Kisin and O. E. Oksinoid, *Zh. Obshch. Khim.*, 38 (1968) 391.