

## Bond Refractions, Bond Dispersions and Ring Refractions in Cyclopolymethylenesilanes

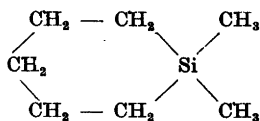
BENGT SMITH

*Institutionen för Organisk Kemi, Chalmers Tekniska Högskola, Göteborg, Sweden*

Bond refractions of the *cyclotrimethylene*, *cyclotetramethylene* and *cyclopentamethylene* groups bonded to silicon have been calculated. Bond dispersions of the last-mentioned group are also given. It is shown that a ring refraction is present in the *cyclotrimethylene*- and *cyclotetramethylenesilane* rings.

Reliable refractometric data for *cyclopolymethylenesilanes* were first given by Bygdén<sup>1</sup> in 1915 for *cyclopentamethylenedichlorosilane* and the corresponding dimethylsilane. Some years ago the present author<sup>2</sup> measured some refractometric constants of *cyclopentamethylenediethoxysilane*. Recently West<sup>3</sup> reported some preparations of *cyclopolymethylenesilanes* with 4, 5 and 6 methylene groups in the heterocyclic ring, together with their refractometric constants. At about the same time Sommer and Baum<sup>4</sup> succeeded in preparing *cyclotrimethylenedimethylsilane*. With the accumulation of these data it seems justified to calculate the bond refractions, bond dispersions and ring refractions of some polymethylene groups bonded to silicon.

The material used in these calculations is listed in Tables 1 and 2. The structural type of the *cyclopolymethylenesilanes* is apparent from the following formula for *cyclopentamethylenedimethylsilane*.



*Bond refractions and bond dispersions.* In the calculation of the bond refractions  $r$  [ $\text{Si}(\text{CH}_2)_n$ ] the principles previously outlined by the author were applied<sup>2</sup>.

Table 1. Molar refractions and molar dispersions of cyclopentamethylenesilanes.

No.	Compound	$MR_C$	$MR_D$	$MR_F$	$MR_g^*$	$MR_{F-C}$	$MR_{g-C}$	Ref.
1	$(CH_2)_5Si(CH_3)_2$	41.80	42.01	42.54	42.95	0.740	1.155	1
2	$(CH_2)_5Si(OC_2H_5)_2$	52.49	52.74	53.32	53.77	0.830	1.282	2

\* Bygdén measured  $MR_G$ . The value of  $MR_g$  was obtained using the "reciprocal plotting method" of Bauer and Fajans<sup>5</sup>.

Table 2. Molar refractions of cyclopolymethylenesilanes.

No.	Compound	$MR_D$	Ref.
3	$(CH_2)_5Si(OCH_3)_2$	43.31	3
4	$(CH_2)_5Si(CH_3)_2$	53.77	3
5	$(CH_2)_5Si(CH_2)_4$	49.27	3
6	$(CH_2)_4Si(CH_3)_4$	44.80	3
7	$(CH_2)_4Si(OCH_3)_2$	38.82	3
8	$(CH_2)_3Si(CH_3)_2$	33.22	4
9	$(CH_2)_3Si(CH_2)_2$	47.45	3

The normal bond refraction\*  $r$  [ $Si(CH_2)_5$ ] is obtained from the molar refraction of compound No. 4, for example, by dividing it by two or from the molar refraction of compound No. 1 by subtraction of  $2r(Si-CH_3)$  \*\*, assuming additivity of the bond refractions of the cyclopentamethylene group and the two methyl groups to be in hand. The fact that the same value of  $r$  [ $Si(CH_2)_5$ ] is obtained in both cases shows this assumption to be correct. The refractometric equivalence of a cyclopentamethylene group with two alkyl groups when bonded to silicon is further demonstrated by the calculation of  $r$  [ $Si(CH_2)_5$ ] from the molar refractions of the two cyclopentamethylenedialkoxysilanes, Nos. 2 and 3. As shown previously<sup>2</sup> the molar refractions of a dialkyldialkoxysilane may be obtained from the normal bond refractions of the alkyl and alkoxy groups bonded to the silicon atom using the formula

$$2r(Si-R) + 2r(Si-OR) - 2K_r^{***} = MR \quad (1)$$

\* The bond refraction of a group X bonded to silicon is written  $r(Si-X)$  and means the sum of the refractions of the group X and the bond Si-X. The normal value of the bond refraction  $r(Si-X)$  is defined as the bond refraction of the group in the compound  $SiX_n$  and is obtained by dividing the molar refraction by n. Usually n equals 4, but in the present case its value is 2. Thus the normal bond refraction of the cyclopentamethylene group bonded to silicon is, by definition, equal to the molar refraction of bis-(cyclopentamethylene)-silane (No. 4) divided by two.

\*\* The bond refractions, bond dispersions and structure corrections used in the derivation of the bond values and ring refractions in this work were, unless otherwise stated, taken from Ref.<sup>2</sup>

\*\*\*  $K_r$  is named "the structure correction for refraction" and is used in silanes which at the same time have alkyl and alkoxy or siloxy groups bonded to the silicon atom (cf. Ref.<sup>2</sup>). The same applies to the structure correction for dispersion  $K_D$ , which is used in the following discussion.

Assuming the same eq. to be valid for a *cyclopentamethylenedialkoxy-silane* we get

$$r [\text{Si} (\text{CH}_2)_5] + 2r (\text{Si}-\text{OR}) - 2K_r = MR \quad (2)$$

When substituting the appropriate values of  $r$  ( $\text{Si}-\text{OR}$ ) and  $K_r$  and of  $MR$  from Table 1,  $r [\text{Si} (\text{CH}_2)_5]$  is obtained. Within the limits of error the same values are arrived at as from the molar refractions of compounds Nos. 1 and 4.

The refraction of the *cyclotetramethylene* group bonded to silicon may be calculated in the same way as described for the *cyclopentamethylene* group using the molar refractions of compounds Nos. 6 and 7. Eq. 2 applies to *cyclotetramethylenedimethoxysilane* (No. 7) as well, if  $r [\text{Si} (\text{CH}_2)_4]$  is substituted for  $r [\text{Si} (\text{CH}_2)_5]$ . From the value of the molar refraction of the spirane, *cyclotetramethylene-cyclopentamethylenesilane* (No. 5), the additivity of the bond refractions of the two *cyclopolymethylene* groups is apparent.

For the calculation of the bond refraction of the *cyclotrimethylene* group bonded to silicon only the molar refraction (D-line) of *cyclotrimethylenedimethylsilane* (No. 8) is available.

The material on *cyclohexamethylenesilanes* includes only the molar refraction (D-line) of *cyclohexamethylenedimethylsilane* (No. 9). As pointed out below there is some doubt as to the accuracy of this value. On that account the calculation of the bond refraction of the *cyclohexamethylene* group is postponed until further experimental results are available.

In the calculation of the bond dispersions of the *cyclopentamethylene* group bonded to silicon,  $d [\text{Si} (\text{CH}_2)_5]^*$ , the same methods were used as for the bond refractions. By subtraction of  $2d(\text{Si}-\text{CH}_3)$  from the molar dispersion of compound No. 1 one value of  $d[\text{Si} (\text{CH}_2)_5]$  is obtained; another results from the molar dispersion of compound No. 2. In this case we get

$$d [\text{Si} (\text{CH}_2)_5] + 2d (\text{Si}-\text{OC}_2\text{H}_5) - 2K_d = MR_{\lambda-\lambda} \quad (3)$$

where  $K_d$  is the structure correction for dispersion. As yet no data exist for calculation of bond dispersions of other *cyclopolymethylene* groups bonded to silicon.

The bond refractions and bond dispersions obtained are collected in Tables 3 and 4.

The difference between the molar refraction (D-line) of a *cyclopentamethylenesilane* and that of the corresponding *cyclotetramethylenesilane* is about 4.50 ml. This value is only about 0.15 ml below the normal refraction of the methylene group the latter being 4.64 ml. (*cf.* Ref.<sup>2</sup>, Table 40). The difference between the molar refraction (D-line) of *cyclohexamethylenedimethylsilane* (No. 9) and that of *cyclopentamethylenedimethylsilane* (No. 1) is 5.45 ml, a value which seems to be abnormally high. As mentioned previously the author has therefore not attempted to calculate the bond refraction of the *cyclohexamethylene* group from the molar refraction of compound No. 9.

\* Previously<sup>2</sup> the bond dispersion of a group X bonded to silicon was written  $\Delta (\text{Si}-\text{X})$ . Here, however, the notation  $d (\text{Si}-\text{X})$  is preferred.

Table 3. Bond refractions.

Bond refraction	c	D	F	g
$r$ [Si(CH <sub>2</sub> ) <sub>5</sub> ]	26.77	26.90	27.22	27.47
$r$ [Si(CH <sub>2</sub> ) <sub>4</sub> ]	—	22.42	—	—
$r$ [Si(CH <sub>2</sub> ) <sub>3</sub> ]	—	18.06	—	—

Table 4. Bond dispersions.

Bond dispersion	F-C	g-C
$d$ [Si(CH <sub>2</sub> ) <sub>5</sub> ]	0.459	0.712

The ring refraction in the cyclotrimethylene-, cyclo-tetramethylene-, and cyclopentamethylenesilanes can be estimated in the following way. A cyclo-trimethylenesilane ring is formed from a methylethylsilane by the breaking of an  $\alpha$  C—H and a  $\beta$  C—H bond and the formation of an  $\alpha$ — $\beta$  C—C bond. In the same way a cyclo-tetramethylenesilane ring is formed from a diethylsilane by the breaking of two  $\beta$  C—H bonds and the formation of a  $\beta$ — $\beta$  C—C bond. A similar procedure applied to an ethyl-*n*-propylsilane furnishes a cyclo-pentamethylenesilane ring. In this case a  $\beta$  C—H and a  $\gamma$  C—H bond are broken and a  $\beta$ — $\gamma$  C—C bond formed. The refractometric modifications involved may be expressed

$$r_D[\text{Si}(\text{CH}_2)_3] = r_D(\text{Si}-\text{CH}_3) + r_D(\text{Si}-\text{C}_2\text{H}_5) - 2r_D(\text{C}-\text{H}) + r_D(\text{C}-\text{C}) + R_1 \quad (4)$$

$$r_D[\text{Si}(\text{CH}_2)_4] = 2r_D(\text{Si}-\text{C}_2\text{H}_5) - 2r_D(\text{C}-\text{H}) + r_D(\text{C}-\text{C}) + R_2 \quad (5)$$

$$r_D[\text{Si}(\text{CH}_2)_5] = r_D(\text{Si}-\text{C}_2\text{H}_5) + r_D(\text{Si}-\text{C}_3\text{H}_7-n) - 2r_D(\text{C}-\text{H}) + r_D(\text{C}-\text{C}) + R_3 \quad (6)$$

where  $R_1$ ,  $R_2$  and  $R_3$  are the ring refractions (D-line). Substitution of the appropriate values in eqs. 4, 5 and 6 gives  $R_1 = 0.51$  ml,  $R_2 = 0.36$  ml and  $R_3 = 0.11$  ml. If the correct values of the C—H and C—C bond refractions were known the exact values of the ring refractions would be obtained. There is reason to assume that the values used in the calculation above for the C—H and C—C bond refractions are somewhat different from the real ones\*. The error in the ring refractions caused from this, however, is not believed to exceed 0.10 ml. Thus it appears that a ring refraction is present in the cyclo-trimethylenesilane and cyclo-tetramethylenesilane rings while the ring refraction in the cyclopentamethylenesilane ring seems to be negligible.

This is in agreement with the result of an inspection of Stuart molecular models of the three rings. While strain-free models may be built of the cyclo-pentamethylenesilane ring this is not the case with the two other rings.

\* The values of Denbigh<sup>6</sup>  $r_D(\text{C}-\text{C}) = 1.25$  and  $r_D(\text{C}-\text{H}) = 1.69$  were used.

It is of interest to note that Eisenlohr <sup>7</sup> in his refractometric investigations of *cyclobutanes*, *cyclopentanes* and *cyclohexanes* found the two latter types to be without ring refraction while the ring refraction of the *cyclobutane* ring was 0.46 ml. In a recent investigation Jeffery and Vogel <sup>8</sup> found the ring refraction of the latter ring to be 0.32 ml, a value which in all probability is more reliable than that of Eisenlohr. The greater strain in the silicon containing rings as compared with the corresponding carbon rings is evident from the calculations above. The considerable strain in the *cyclotrimethylsilylene* ring might explain the unusual reactivity of *cyclotrimethylsilylene* towards concentrated sulfuric acid and 1 N potassium hydroxide, reactions which proceed with ring opening.<sup>4</sup>

*Use of the bond values.* The bond refractions and bond dispersions in Tables 3 and 4 may be used for the calculation of molar refractions and molar dispersions of *cyclopolymethylenedialkylsilanes* and *cyclopolymethylenedialkoxysilanes*. In the former case this is simply made by addition of the bond values of the *cyclopolymethylene* group and those of the alkyl groups. In the latter case eqs. 2 and 3 given in this paper are used. The bond values of the alkyl and alkoxy groups and the  $K_r$ - and  $K_d$ -values are taken from Ref.<sup>2</sup>.

#### REFERENCES

1. Bygdén, A. *Ber.* **48** (1915) 1236; *Diss.* Uppsala 1916.
2. Smith, B. *Diss.* Gothenburg 1951.
3. West, R. *J. Am. Chem. Soc.* **76** (1954) 6012.
4. Sommer, L. H. and Baum, G. A. *J. Am. Chem. Soc.* **76** (1954) 5002.
5. Bauer, N. and Fajans, K. *J. Am. Chem. Soc.* **64** (1942) 3023.
6. Denbigh, K. G. *Trans. Faraday Soc.* **36** (1940) 936.
7. Eisenlohr, F. *Spektrochemie organischer Verbindungen*, Stuttgart 1912, p. 86.
8. Jeffery, G. H. and Vogel, A. J. *J. Chem. Soc.* **1948** 1804.

Received May 21, 1955.