

Fig. 1. Bond lengths (Å) and bond angles (°) in the hexasulphide ion.

procedure. A least squares refinement of the structure, based on the structure factor data published by Abrahams and Grison,¹ has been carried out on the IBM 1620 II computer using Mair's³ program.

Atomic coordinates and temperature parameters from the least squares refinement are listed in Tables 1 and 2, and corresponding bond lengths and bond angles in the hexasulphide ion are given in Fig. 1. The standard deviation in bond lengths is 0.03 Å and in angles 1.3°. The dihedral angles are found to be: $S_1S_2S_3/S_2S_3S_4 = 74.6^\circ$, $S_2S_3S_4/S_3S_4S_5 = 83.1^\circ$ and $S_3S_4S_5/S_4S_5S_6 = 60.9^\circ$.

Our value for the length of the S_2-S_3 bond is 0.06 Å smaller than the value reported by Abrahams and Grison. The S_4-S_5 bond is also by the present refinement found to be the longest in the sulphur chain. This may be explained by taking into account the dependence of sulphur-sulphur bond length on dihedral angle; the dihedral angle associated with S_4-S_5 is as low as 60.9° .

On the basis of the dihedral angles and the bond-length/dihedral-angle relationship,² the values predicted for the lengths of the three central bonds in the hexasulphide ion are: $S_2-S_3 = 2.04$ Å, $S_3-S_4 = 2.03$ Å, and $S_4-S_5 = 2.07$ Å. These agree within the error with the bond lengths in Fig. 1.

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On the Molecular Structure of Di-cyclopentadienylberyllium (C_5H_5)₂Be

II. Least Squares Refinement

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The molecular structure of gaseous dicyclopentadienylberyllium as determined by Almenningen, Bastiansen and Haaland¹ by means of electron diffraction is shown in Fig. 1. The molecule consists of two regular C_5H_5 rings that lie parallel and staggered with a vertical ring-to-ring distance of $h = 3.37 \pm 0.03$ Å. The beryllium atom was found to occupy a position on the fivefold symmetry axis $h_1 = 1.485 \pm 0.005$ Å from one ring and $h_2 = 1.980 \pm 0.010$ Å from the other. The molecular symmetry is thus C_{5v} .

Since Almenningen *et al.*¹ found it necessary to invoke shrinkage effects of the order of 0.1 Å in order to obtain satisfactory agreement with the experimental data, and since the molecular structure is highly unusual, we have considered it worth while to repeat the structure determination using the experimental material of Almenningen *et al.*¹ and the more advanced calculation methods that now are available.

The complex atomic scattering factors $f(s) = |f(s)|\exp(i\eta(s))$ of H, Be, and C were computed under the partial wave approximation with a program written by Peacher.² The experimental intensities recorded by Almenningen *et al.*¹ had been

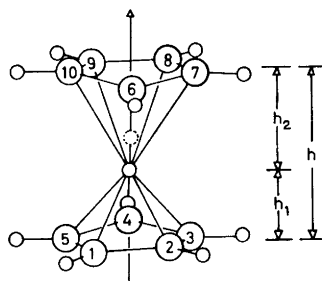


Fig. 1. The molecular structure of (C_5H_5)₂Be with the two positions of the beryllium atom drawn in.

corrected for nonlinearity of plate response, plate flatness and the screening effect of the rotating sector. The corrected intensities were multiplied with

$$s^6/|f_C(s)|^2$$

and empirical backgrounds were subtracted. After the molecular intensities from different plates had been scaled and connected, the experimental material consisted of modified molecular intensity points extending from $s=4.25 \text{ \AA}^{-1}$ to 44.00 \AA^{-1} , the interval between the points being 0.25 \AA^{-1} .

Theoretical intensities were calculated from

$$I^{CC}(s) = \text{const} \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)|^2} \frac{\sin(\eta_i(s) - \eta_j(s))}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2 s^2) \quad (1)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. The molecular structure was refined by least-squares calculations on the intensity data with a program written by H.M. Seip.

Refinement of a model in which the two C_5H_5 rings are staggered converged to give the parameters listed in Table I. The

Table I. Bond distances and vibrational amplitudes of $(C_5H_5)_2Be$. The standard deviations include the uncertainty in the electron wavelength. The distances are given as $r_g(1)$.⁵

	R (Å)	u (Å)
Be—Cl	1.907 (0.005)	0.098 (0.004)
Be—C6	2.256 (0.007)	0.115 (0.007)
Cl—C2	1.425 (0.002)	0.052 (0.001)
Cl—H1	1.103 (0.003)	0.073 (0.003)
Be...H1	2.743 (0.004)	0.15 ^a
Be...H6	2.997 (0.005)	0.15 ^a
Cl...C3	2.305 (0.002)	0.051 (0.001)
Cl...C6	3.457 (0.009)	0.181 (0.008)
Cl...C7	3.903 (0.008)	0.292 (0.025)
Cl...C8	4.155 (0.008)	0.222 (0.023)
Cl...H2	2.257 (0.003)	0.308 (0.046)
Cl...H3	3.371 (0.003)	0.094 (0.006)
Cl...H6	3.698 (0.007)	0.25 ^a
Cl...H7	4.466 (0.007)	0.30 ^a
Cl...H8	4.811 (0.009)	0.25 ^a
h_1	1.472 (0.006)	
h_2	1.903 (0.008)	
h	3.375 (0.010)	

^a assumed

standard deviations include the uncertainty in the electron wavelength. The weighted square-error sum for this model is 3.32. Refinement on a model in which the ligand rings are eclipsed gave a minimum weighted square-error sum of 3.47. Hence it would appear that the eclipsed model may be rejected at the 0.05 significance level.³ We should, however, like to strike a note of caution at this point; it has not been demonstrated that electron-diffraction data satisfy the statistical model on which Hamilton's discussion is based.

An experimental radial distribution curve⁴ and a theoretical curve calculated from the parameters listed in Table I is shown in Fig. 2. The agreement between the two curves is very good. Hence the need for introduction of large shrinkage effects does not arise.

The unexpectedly large value obtained for $u(Cl \cdots H2)$ deserves comment. This parameter is strongly correlated with the bond distance and vibrational amplitude of Be—C6. If the probability distribution curve⁵ of this distance is asymmetric, the use of eqn. (1) could easily introduce a large systematic error in $u(Cl \cdots H2)$. With this exception all the parameters in Table I fall in the range expected after the investigations of $(C_5H_5)_2Pb$,⁶ $(C_5H_5)_2Sn$,⁶ and $(C_5H_5)_2Mn$.⁷

The two Be—C vibrational amplitudes, 0.098(0.004) Å and 0.115(0.007) Å, are similar to the metal-carbon vibrational amplitudes of $(C_5H_5)_2Pb$,⁶ $(C_5H_5)_2Sn$, and $(C_5H_5)_2Mn$.⁷ In these compounds $u(M—C) = 0.142(0.013)$ Å, 0.156(0.027) Å, and 0.135

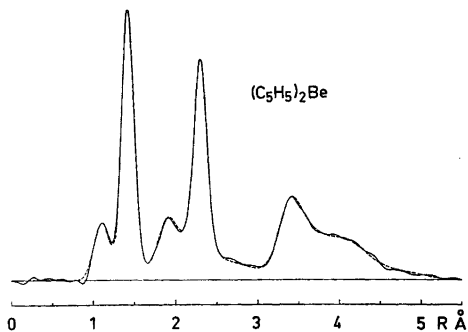


Fig. 2. Radial distribution curves of $(C_5H_5)_2Be$. Full line; experimental; stippled line: theoretical curve calculated from the parameter values in Table I. The artificial damping constant $k=0.0015 \text{ \AA}^2$.

(0.005) Å, respectively. These four dicyclopentadienyl compounds are also similar in their chemical reactivity; in contrast to, e.g., ferrocene and ruthenocene they react with air or moisture. The difference in the stability of the two classes of compounds is reflected in the vibrational amplitudes of the M—C distances; in the unstable compounds they are twice as large as in the stable ones;⁸ $u(\text{Fe—C})=0.062(0.001)$ Å and $u(\text{Ru—C})=0.060(0.001)$ Å.

It has been pointed out⁷ that the M—C bond distances in $(\text{C}_5\text{H}_5)_2\text{Sn}$, $(\text{C}_5\text{H}_5)_2\text{Pb}$, and $(\text{C}_5\text{H}_5)_2\text{Mn}$ can be calculated to 0.01 Å by adding the radius of the dipositive ion to a carbon atom radius of 1.58 Å. (The M—C distances in $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ru}$ are about 0.3 Å shorter than predicted by this rule.) One might therefore predict a Be—C bond distance in $(\text{C}_5\text{H}_5)_2\text{Be}$ of 1.89 Å. The reason why Be—C6 is so much longer than this is probably that the attraction between the beryllium atom and the second ring is compensated by van der Waals repulsion between the π -electron clouds in the two ligands; the vertical distance between the two cyclopentadienyl rings, 3.375(0.010) Å, is of the order of the van der Waals thickness of an aromatic ring. It appears reasonable then that the ligand rings are staggered in the equilibrium conformation. In $(\text{C}_5\text{H}_5)_2\text{Mn}$ where the ring-to-ring distance is 4.101(0.008) Å the rings appear to undergo virtually non-hindered rotation.⁷ In $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ru}$ the equilibrium conformation is eclipsed,⁸ but this is probably an effect of the strong metal-to-ring bonding.

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Equilibrium Constants and Model Testing from Spectrophotometric Data, using LETAGROP

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Spectrophotometric measurements have often been used for studying chemical equilibria, and methods for treating data for systems with several consecutive reactions have been given by J. Bjerrum, Olerup, Fronæus and others. These methods are limited to systems with mononuclear complex species, and when many complexes are involved, there is a certain risk of the accumulation of errors during the calculations. Computer methods for a least-squares treatment of spectrophotometric data have hitherto mainly been limited to reactions of the type $A+B\rightleftharpoons AB$. (For literature references, we refer to Rossotti and Rossotti¹ and to a forthcoming paper²).

We have recently made a version of the general minimizing program LETAGROP that allows a generalized least-squares treatment of spectrophotometric data, assuming any set of mononuclear or polynuclear species. The first application was to Teder's measurements on polysulfide solutions (components $\text{H}^+ + \text{S}^{2-} + \text{S}^0$). The program treats absorbance data (either absorbance E or apparent molar extinction coefficient, ϵ_B of one component), for any number N_λ of wavelengths (bands), and any number N_{soln} of solutions. The present version is designed for the two cases that have hitherto been the most frequent in the literature: 1) two components, the total concentrations of both in each solution are known, (A, B), 2) three components, the free concentration of one, and the total concentration of the two others in each solution are known (a, B, C). We can easily extend the treatment to cases (A, B, C) and (a, B, C, L) as the need arises.

The error square sum to be minimized is either that of the absolute errors, $(E_{\text{calc}} - E_{\text{exp}})$, or that of the relative