THE MOLECULAR STRUCTURE OF BERYLLOCENE, $(C_5H_5)_2Be$. A REINVESTIGATION BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The electron scattering pattern of gaseous dicyclopentadienylberyllium, Cp_2Be, has been recorded from $s = 2.00$ to 39.00 Å^{-1} with a nozzle temperature of about 120°C. Molecular models of D_{5d} symmetry or models containing one π-bonded and one σ-bonded Cp ring are not compatible with the data. The possibility that gaseous Cp_2Be consists fo a mixture of D_{5d} and π-Cp, σ-Cp conformers is considered and rejected. A model of C_{5v} symmetry can be brought into satisfactory agreement with the data. It is also found that a slip sandwich model obtained from the C_{5v} model by moving sideways the ring which is at the greatest distance from Be, while keeping the two rings essentially parallel is compatible with the electron diffraction data. The best fit between experimental and calculated intensity curves is obtained with a model with a sideways slip of 0.8(1) Å. This model is similar to that indicated by the X-ray diffraction investigations by Wong and coworkers [4,5]. It is suggested that the potential energy of the molecule does not change much as the magnitude of the slip changes and that the molecule thus undergoes large amplitude vibration.

Introduction

In 1964 Almenningen, Bastiansen and Haaland [1] published the result of a gas phase electron diffraction (GED) investigation of beryllocene, and concluded that the molecular symmetry is C_{5v} with two Cp (Cp = cyclopentadienyl) rings of fivefold symmetry lying one on top of the other. The Be atom was situated on the fivefold symmetry axis of the two rings, but closer to one ring than to the other, see model II in Fig. 1. Two other models that had been suggested at the time, a symmetric sandwich model of D_{5d} or D_{5h} symmetry (I)
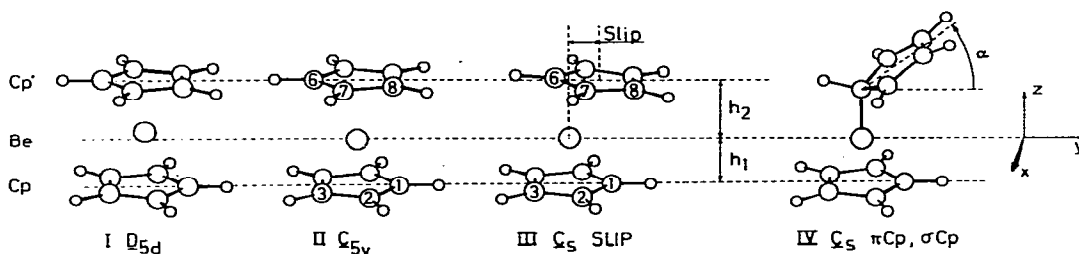
Fig. 1. Molecular models of Cp_2Be.

and a model with one π-bonded (η^5) and one σ-bonded (η^1) ring (IV), were implicitly rejected. The C_{5v} model succeeded in reconciling two earlier seemingly contradictory observations, namely (i) that beryllocene crystallizes with the same space group and with very similar unit cell parameters as ferrocene [2] and, unless there is disorder, this requires the space group to possess a molecular center of symmetry, and (ii) that the molecule has a dipole moment of 2.24 ± 0.09 Debye in cyclohexane [3].

In 1972 and 1973 Wong and coworkers published the results of X-ray diffraction investigations of beryllocene at —120°C [4] and at room temperature [5]. The crystals were disordered, but the molecular structure may be described as a slip sandwich which can be derived from the C_{5v} model by moving Cp' (the ring which is at the greatest distance from the Be atom) about 1.2 Å sideways. The Be atom is then directly below the edge of the ring. The electron density maps indicate that at —120°C the orientation of the Cp rings is such that the Be atom is below a carbon atom (see model III in Fig. 1), whereas at room temperature it appears to be below a C—C bond.

The slip sandwich model was not considered in the 1964 electron diffraction study. Drew and Haaland [6] therefore carried out refinements of the slip sandwich model using the old electron diffraction data. They concluded, wrongly as we shall show below, that the slip sandwich model was incompatible with the ED data. This conclusion received support from an earlier IR investigation [7], which revealed that while the vibrational spectrum of gaseous $BeCp_2$ consists of only the few lines expected for a C_{5v} model, the spectrum of the crystalline substance was much more complicated. It was therefore suggested that intermolecular forces were responsible for the sideways displacement of Cp' found in the crystal [6].

During the last few years molecular orbital calculations on the various models of beryllocene have been carried out within the PRDDO [8] and MNDO [9] approximations, and ab initio calculations have been carried out with an STO-3G basis [10,11]. In each set of calculations extensive structure optimization was carried out on each model. All these calculations suggest that a C_{5v} model has considerably higher energy than a symmetric D_{5d} or D_{5g} model, and that the most stable form of beryllocene would be one containing one π-bonded and one σ-bonded ring (model IV), and the validity of the C_{5v} and slip sandwich models were brought in question.

We therefore decided to carry out ab initio molecular orbital calculations with a double-ζ basis to see if similar results would be obtained with more

accurate calculations. Because of the size of the problem, calculations could be carried out only for a fixed, assumed geometry for each model [12]. The lowest energy (—398.6621 au) was obtained for the π-Cp, σ-Cp model (IV), followed by the D_{5d} model (I) (+9.2 kcal mol^{-1}), the slip sandwich model (III) with *Slip* = 1.2 Å, corresponding to the crystal structure at —120°C, (+12.4 kcal mol^{-1}) and finally the C_{5v} model (+16.3 kcal mol^{-1}).

Very recently Demuynck and Rohmer reported the result of ab initio calculations on a small number of fixed geometries with a minimal basis set for the inner shells and a double-ζ basis set for the valence shell [13]. Their calculations, which should be of an accuracy comparable to ours, yield the lowest energy for the D_{5h} model (—398.637 au), followed by the slip sandwich model with small differences between C—C bonds in the Cp′ ring (+7.5 kcal mol^{-1}), the C_{5v} model (+10.5 kcal mol^{-1}), and finally the π-Cp, σ-Cp model (+17.0 kcal mol^{-1}). Clearly the energy differences involved are so small that small differences in the bases and/or assumed geometries lead to contradictory results even at the double-ζ level.

In this present paper we wish to report the result of a reinvestigation of beryllocene by gas phase electron diffraction. In a subsequent paper [12] we deal with the result of our ab initio calculations and the photoelectron spectra recorded by Gleiter and coworkers.

Experimental and calculation procedure

Cp$_2$Be was synthesized from NaCp and BeCl$_2$ in diethyl ether [14] and purified by vacuum sublimation. The purity of the compound was checked by its melting point (59°C) and by its mass spectrum, which containing no peaks corresponding to possible impurities (CpBeCl or solvent). The crystalline, colorless samples were introduced into the Oslo electron diffraction unit [15] in closed ampules which were broken after the unit had been evacuated and the nozzle system heated to the appropriate temperature (reservoir, 105 to 110°C; nozzle tip, 120°C). The vapor pressure of Cp$_2$Be has been measured up to 190°C [16], so the substance is presumably thermally stable below this temperature. Exposures were made with nozzle to plate distances of about 48 and 20 cm. This study is based on the data obtained by photometer analysis of six plates from the first set and four from the second. The optical densities ranged from 0.10 to 0.55, which is in the region of linearity of plate response, and so no blackness correction was carried out. Otherwise the data were prosessed as described by Andersen et al. [17].

Each time a new model, or mixture of models, of Cp$_2$Be was considered, a new background was substracted using a program written by Gundersen and Samdal [18] modelled on a program described by Hedberg [19]. In this program the background on the levelled intensity curve is calculated as a polynominal of variable degree. The coefficients are determined by a least-squares procedure using the experimental levelled intensity data and a theoretical intensity curve calculated for the model under consideration. After a few trials the degree of the polynominal was selected as equal to five for both 48 and 20 cm data, in the final refinements the degree was increased to eight for the 48 cm data.
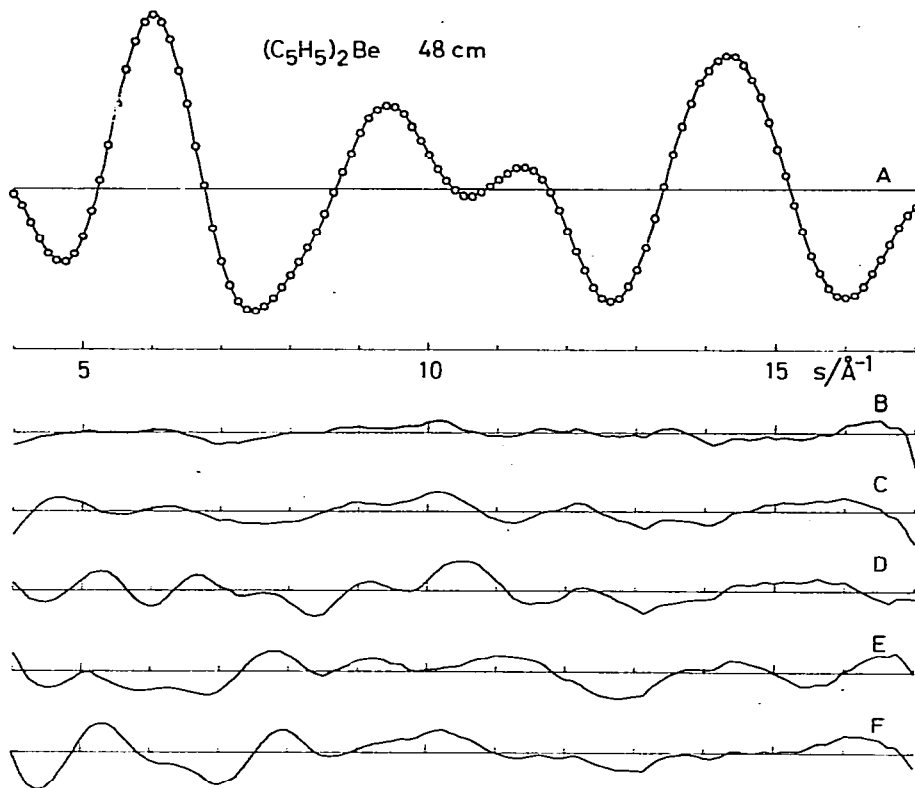
Fig. 2. A: Experimental modified molecular intensity values from $s = 4.00$ to 17.00 Å^{-1}, obtained by subtraction of a background calculated for a C_{5v} model (Refinement 9, Table 1). Below the difference between the experimental and calculated intensities of various models: B: C_{5v} model, Refinement 9; C: C_{5v} model, Refinement 5; D: π-Cp, σ-Cp model, Refinement 6; E: D_{5d} model, Refinement 10; F: D_{5d}/π-Cp, σ-Cp mixture, Refinement 11.

After backgrounds had been subtracted, the data obtained from each nozzle to plate distance were averaged and converted into modified molecular intensities (eq. 10 in ref. 17), The modified molecular intensity curves obtained by subtraction of backgrounds calculated for a C_{5v} model are shown in Fig. 2A and Fig. 3A. It should be emphasized that the backgrounds calculated for the various models were very similar; the resulting modified molecular intensity curves could hardly be distinguished when plotted on the scale of Fig. 2 and Fig. 3.

Finally the scale factor of each average curve and structure parameters were refined using a least-squares program written by Seip [20]. Most refinements were carried out with a diagonal, but the final refinements were carried out with a non-diagonal weight matrix.

A few refinements were also carried out on the intensity data of Cp$_2$Be recorded in 1963 [1]. The intensity data had then been corrected for non-linearity of plate response and averaged for each nozzle to plate distance. The average curves were now processed anew as described above.

Radial distribution curves were calculated by Fourier inversion of experimental or calculated intensity curves after multiplication with the artificial damp-
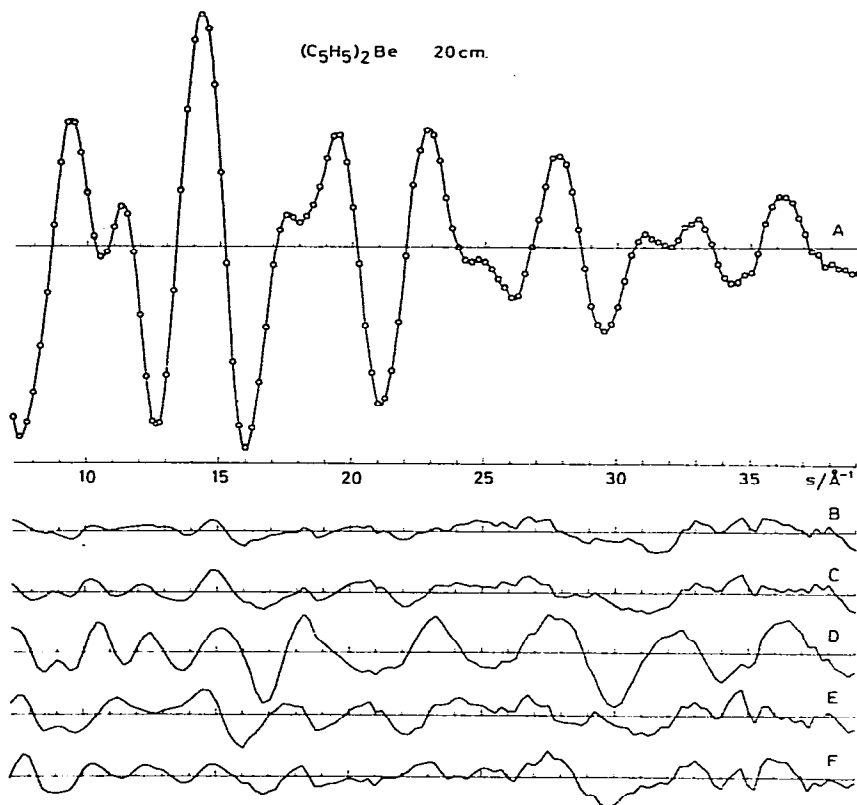
Fig. 3. A: Experimental modified molecular intensity values from $s = 7.25$ and 39.00 Å^{-1} obtained by subtraction of a background calculated for a C_{5v} model. (Refinement 9, Table 1). Below the difference between the experimental and calculated intensities of various models: B: C_{5v} model, Refinement 9; C: C_{5v} model, Refinement 5; D: π-Cp, σ-Cp model, Refinement 6; E: D_{5d} model, Refinement 10; F: D_{5d}/π-Cp, σ-Cp mixture, Refinement 11.

ing function $\exp(-ks^2)$. The experimental intensity curves were then first joined to a theoretical curve calculated for the model under consideration in the inner non-observed s-range, 0 to 2 or 0 to 4 Å^{-1}.

Results and discussion

Since most of the molecular orbital calculations mentioned in the introduction yielded lower energies for the π-Cp, σ-Cp model and the D_{5d} model than for the C_{5v} model or the slip sandwich model, we first investigated whether the π, σ or D_{5d} models, or a mixture of the two, could be brought into agreement with the electron diffraction data.

Calculations on the 1963 data [1]. C_{5v} is a subgroup of D_{5d}. Therefore, if the molecular symmetry is in fact D_{5d}, least-squares refinement of a model of C_{5v} symmetry should, in the absence of systematic errors. converge to parameter values which do not deviate significantly from those of a D_{5d} model. In fact least-squares refeinments [21] led to a model in which the distances from

TABLE 1

LEAST-SQUARES REFINEMENTS OF VARIOUS MODELS OF Cp₂Be

Refinement number	Model	Parameters refined[a]	Reference	s-range	$R_2(R_3)$[b]	s-range	$R_2(R_3)$[b]	$R_2(R_3)$[b] total
1	II C_{5v}	0	1	2.00—18.00	12.2	10.00—44.00	12.8	12.4
2	IV π, σ	0	1	2.00—18.00	13.1	10.00—44.00	23.8	17.3
3	II C_{5v}[c]	0	1	2.00—18.00	15.7	10.00—44.00	13.1	14.9
4	IV π, σ	$l(C-C)_{mean}$	1	2.00—18.00	13.5	10.00—44.00	15.9	14.4
5	II C_{5v}	0	this work	4.00—17.00	6.2	7.25—39.00	11.3	8.5
6	IV π, σ	0	this work	4.00—17.00	7.6	7.25—39.00	25.5	16.8
7	II C_{5v}[c]	0	this work	4.00—17.00	7.9	7.25—39.00	11.2	9.3
8	IV π, σ	$l(C-C)_{mean}$	this work	4.00—17.00	8.3	7.25—39.00	15.5	11.5
9	II C_{5v}	14[d]	this work	4.00—17.00	3.7	7.25—39.00	9.5	6.5
10	I D_{5d}	11[d]	this work	4.00—17.00	8.2	7.25—39.00	14.1	10.9
11	$D_{5d}/\pi, \sigma$	7[d]	this work	4.00—17.00	9.6	7.25—39.00	13.2	11.1
12	II C_{5v}	16[d]	this work	2.00—17.00	5.9(8.6)	7.25—39.00	9.6(13.0)	7.0(11.5)
13	III Slip	17[d]	this work	2.00—17.00	5.4(7.8)	7.25—39.00	9.5(12.8)	6.6(11.1)
14	III Slip	15[d,c]	this work	2.00—17.00	5.5(8.3)	7.25—39.00	9.7(13.1)	6.7(11.5)

[a] Parameters refined in addition to the two scale factors. [b] $R_2 = 100[\sum_k p_{kk} V_{kk}^2 / \sum_k p_{kk} I_k^2]^{1/2}$ and $R_3 = 100[\sum_k \sum_l p_{kl} V_k V_l / \sum_k \sum_l p_{kl} I_k I_l]^{1/2}$, see ref. 20. [c] These refinements were carried out on molecular intensity curves obtained by subtraction of a background calculated for a π, σ model, as in Refinement 2 and 6, respectively. [d] See text for details. [e] Slip = 1.20 Å was not refined.

the Be atom to the centra of the two rings were significantly different: $h_1 = 1.472(6)$ Å and $h_2 = 1.903(8)$ Å.

When the structure parameters listed in ref. 21 were used to calculate the theoretical intensity for a C_{5v} model, backgrounds corresponding to fifth degree polynominals subtracted, and the scale factors of the two average modified molecular intensity curves refined by least-squares calculations with a diagonal weight matrix, the resulting R-factors [20] were 12.2 for the 48 cm data and 12.8 for the 19 cm data. See Table 1, Refinement 1.

A π-Cp, σ-Cp model of Cp_2Be was constructed in the following way: The π-CpBe fragment was assumed to have C_{5v} symmetry, the H atoms were assumed to lie in the plane of the C atoms, and the bond distances C—C = 1.423 Å, C—H = 1.100 Å and Be—C = 1.920 Å selected by comparison with the known structures of π-CpBeCH$_3$ [22] and π-CpBeH [23]. The structure of the σ-Cp ring was taken from the recent microwave study of cyclopentadiene by Damiani and coworkers [24]. The ring was joined to Be by removing one H atom on the saturated C atom and replacing it with the Be atom at a bond distance, Be—C_α = 1.698 Å, equal to the Ce—C(Me) bond distances in monomeric Be(CH$_3$)$_2$ [25] and π-CpBeCH$_3$ [22], and without changing the valence angles around the C_α atom. The Be—C_α bond was assumed to lie along the fivefold symmetry axis of the π-CpBe fragment. The angle between the two Cp ring planes is then $\alpha = 36.9°$. The vibrational amplitudes of the CC bond distances were selected as follows:

π-Cp, C—C = 1.423 Å, l = 0.045 Å (5 ✕)
σ-Cp, C—C = 1.468 Å, l = 0.048 Å (1 ✕)
σ-Cp, C—C = 1.506 Å, l = 0.048 Å (2 ✕)
σ-Cp, C=C = 1.345 Å, l = 0.040 Å (2 ✕).

Other vibrational amplitudes were selected by comparison with CpBe compounds studied in this laboratory.

A theoretical intensity curve was calculated and after the background had been subtracted, the two scale factors were refined as for the C_{5v} model. The resulting R-factors are listed in Table 1 (Refinement 2). It is seen that the π-Cp, σ-Cp model gives considerably poorer agreement between experimental and calculated intensity data over the range s = 10.00 to 44.00 Å^{-1}. This region carries more information about the bond distances and their vibrational amplitudes than the region from s = 2.00 to 18.00 Å^{-1}. Comparison of radial distribution curves showed that the CC bond distance peak at 1.42 Å in the calculated RD curve was lower and broader than the corresponding peak in the experimental curve. On the other hand a refinement of the C_{5v} model against the intensity curves obtained by background subtraction for the π, σ model, shows good agreement in the outer region, $R_2 = 13.1\%$, (Refinement 3).

Finally we held the difference between the various CC bond distance vibrational amplitudes constant, but refined the mean value along with the scale factors. (Refinement 4). As was to be expected, the fit in the outer region improved considerably, $R_2 = 15.9\%$, but the resulting mean amplitude, $l = 0.022(3)$ Å, is clearly unacceptable. Thus, barring systematic errors, the π, σ model must be considered incompatible with the experimental data.

It is well known that a faulty blackness correction may introduce considerable systematic errors into the vibrational amplitudes determined by electron diffrac-

tion, so at this point it was decided to record a new set of data. As described in the experimental section, the range of optical densities of the new plates is such as to eliminate non-linearity of plate response as a source of error, or at least to reduce it considerably.

Calculations on the new data. When backgrounds were calculated, it was found difficult to obtain satisfactory backgrounds in the region below $s = 4.00$ Å^{-1} for both the C_{5v} model and the π-Cp, σ-Cp models. In this region the background may indeed be less smooth than at higher s-values, and so we did not wish to rule out any model because of disagreement between experimental and calculated intensity curves in this region, and the data below $s = 4.00$ Å^{-1} were disregarded for the time being.

Backgrounds were calculated for both the C_{5v} model and the π, σ model and refinements carried out as already described for the 1963 data. The R-factors obtained are listed in Table 1. Curves showing the differences between experimental and calculated intensity data are shown in Fig. 2C and D, and in Fig. 3C and D. Again it is seen that with reasonable values for the vibrational amplitudes of CC bond distances, the π, σ model leads to serious disagreement between experimental and calculated intensities in the higher s-range. When a mean CC vibrational amplitude is refined, the fit is improved (Table 1, Refinement 8), but the resulting mean amplitude, 0.014(3) Å, is far outside the acceptable range. We conclude that the π-Cp, σ-Cp model, or any other model containing localized CC single and double bonds in one or both rings, is incompatible with both the 1963 and the new electron diffraction data.

We now turn our attention to the D_{5d} model. When the four independent structure parameters of the C_{5v} model (the C—H and C—C bond distances and the perpendicular distances from Be to each of the two rings, h_1 and h_2) were refined along with the ten most important vibrational amplitudes, the agreement between experimental and calculated intensities improved considerably (Table 1, Refinement 9, Fig. 2B and Fig. 3B). The structure parameters obtained were very similar to those obtained previously by least-squares refinement on the 1963 data [21]. In particular the two perpendicular Be—Cp distances were $h_1 = 1.472(5)$ Å and $h_2 = 1.898(8)$ Å. We conclude that the D_{5d} model is incompatible with the electron diffraction data.

On the basis of the similar energies obtained for the σ, π and D_{5d} models by molecular orbital calculations, several workers have suggested that gaseous Cp_2Be may consist of a mixture of π, σ and D_{5d} conformers [8,10]. In order to investigate this possibility we need an estimate for the perpendicular BeCp distance in the D_{5d} model. Attempts to refine a D_{5d} model gave a distance of 1.49 Å, very close to the value obtained for h_1 in the C_{5v} model, while several vibrational amplitudes diverged. The BeCp distance was therefore fixed at 1.62 Å, equal to the value obtained by optimization of the D_{5d} model by ab initio calculations with STO 3G basis [10,11], but somewhat shorter than the average of the two BeCp distances obtained by refinement of the C_{5v} model, 1.68 Å. Refinement of the C—C and C—H bond distances and the same vibrational amplitudes as for the C_{5v} model (except l (Be···H)), yielded the R factors listed in Table 1, Refinement 10, and the difference curves displayed in Fig. 2E and Fig. 3E. The amplitude obtained for the ten equal Be—C bond distances was 0.25 Å. As was to be expected, the D_{5d} model gave much poorer agreement

TABLE 2

INTERNUCLEAR DISTANCES AND ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES OBTAINED BY LEAST-SQUARES REFINEMENTS OF DIFFERENT MODELS OF $(C_5H_5)_2Be$. (Estimated standard deviations in parentheses) [a]

Model:	II C_{5v}		III Slip (best model)		III ($Slip$ = 1.21 Å)	
	r_a (Å)	l (Å)	r_a (Å)	l (Å)	r_a (Å)	l (Å)
C—C	1.423(2)	0.051(1)	1.423(2)	0.051(1)	1.423(2)	0.051(1)
C—H	1.098(4)	0.080(5)	1.104(4)	0.085(6)	1.104(4)	0.081(5)
C(1)···C(3)	2.303(3)	0.054(1)	2.303(3)	0.055(1)	2.303(3)	0.054(1)
C(1)···H(2)	2.251(4)	0.107(8)	2.256(4)	0.097(8)	2.253(4)	0.108(8)
C(1)···H(3)	3.364(5)	0.087(5)	3.369(5)	0.094(6)	3.366(5)	0.086(5)
Be—C(1)	1.904(6)	0.085(4)	1.903(8)	0.093(6)	1.904(6)	0.085(4)
Be—C(6)	2.27(2)	0.40(6)	1.99(7)	0.12 [b]	1.90(4)	0.25 (ass.)
Be—C(7)			2.25(4)	0.25 (ass.)	2.33(2)	0.25 (ass.)
Be—C(8)			2.62(5)	0.12 [b]	2.89(6)	0.25 (ass.)
Be···H(1)	2.737(5)	0.09(3)	2.741(7)	0.16(11)	2.739(6)	0.11(4)
Be···H(6)	3.01(2)	0.11(4)				
C(1)···C(8)	3.48(1)	0.22(1)	3.35—3.6	0.16(1)	3.35—3.6	0.20(2)
C(1)···C(7)	3.92(1)	0.60(6)	3.6—4.0	0.67(7)	3.6—4.0	0.69(14)
C(1)···C(6)	4.17(1)	0.21(2)	4.0—4.5	0.28(4)	4.0—4.7	0.23(2)
h_1	1.470(7)		1.468(10)		1.470(7)	
h_2	1.92(2)		1.86(2)		1.82(4)	
$Slip$	0		0.79(10)		1.21(ass.)	
α	0		—4(3)°		—4(3)°	

[a] For numbering of the atoms consult Fig. 1. The H atoms are numbered as the C atoms to which they are bonded. [b] These amplitudes were assumed equal.

than the C_{5v} model, particularly in the lower s-region.

Refinement of scale factors was now carried out on π, σ/D_{5d} mixtures with the concentration of D_{5d} conformers increasing from 10 to 90% in 10% increments. Only one least-squares minimum near 50% was found. The background was recalculated and the mole fraction $x(D_{5d})$ was refined along with the following structure parameters of the D_{5d} conformer: The BeCp distance, the C—C and C—H bond distances and the vibrational amplitudes l(Be—C), l(C(1)···C(3)), l(C(1)···C(7)), and l(C(1)···H(3)). Attempts to refine more parameters led to divergence. The mole fraction obtained was $x(D_{5d})$ = 0.47, h(BeCp) = 1.48 Å and l(Be—C) = 0.15 Å. The R-factors are listed in Table 1, Refinement 11, and the difference curves displayed in Fig. 2E and 3E. They are so much higher than the R-factors obtained by refinements of the C_{5v} model, Refinements 5 and 9, that a mixture of π, σ and D_{5d} conformers can be ruled out.

The C_{5v} and slip sandwich models. At this point the low angle data from s = 2.00 to 4.00 Å^{-1} were included in the refinements, and the degree of the polynominal subtracted as a background to the 48 cm data increased from five to eight. Least-squares refinement with a non-diagonal weight matrix of the four independent structure parameters of the C_{5v} model along with the twelve most important vibrational amplitudes yielded the R-factors found in Table 1, Refinement 12, and the parameter values lusted in the first two columns of Table 2. An experimental radial distribution (RD) curve, and the difference between this curve and a theoretical curve calculated for the best C_{5v} model is shown in Fig. 4. The low R-factors obtained and the good fit between experi-
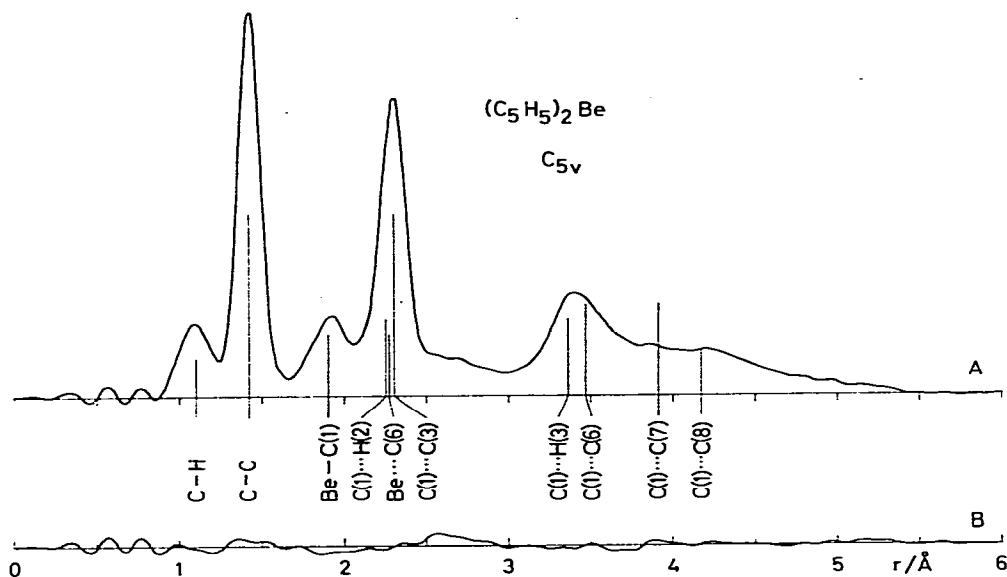
Fig. 4. A: Experimental radial distribution curve for Cp$_2$Be calculated by Fourier inversion of intensity curves. The intensity data from $s = 0.000$ to 1.875 Å^{-1} have been calculated for a C_{5v} model. Artificial damping constant, $k = 0.001$ Å^2. B: Difference between the experimental curve (A) and a theoretical curve for best C_{5v} model (Table 2).

mental and calculated RD curves show that the C_{5v} model is in satisfactory agreement with the new electron-diffraction data as well as with the 1963 data, though close inspection of the RD curves reveals a minor disagreement in the region around 2.6 Å.

All parameters obtained by refinement of the C_{5v} model lie in the expected range, except the vibrational amplitude of the long Be—C distance, $l(Be—C(Cp'))$ = 0.40(6) Å. This value is much larger than the amplitude of the short Be—C bond, 0.085(4) Å, the Be—C(Cp) amplitude in CpBeMe, 0.075(3) Å [22], or the Mg—C amplitude in Cp$_2$Mg, $l(Mg—C) = 0.103(3)$ Å [26].

Inspection of the radial distribution curve in Fig. 4 shows that while the geometry of the π-CpBe fragment and of the Cp' ring is clearly defined by resolved peaks (C—H, C—C and Be—C(Cp)), the curve contains no features yielding similarly precise information about the position of the Cp' ring relative to the π-CpBe fragment. One reason for this may be that though the equilibrium structure is C_{5v}, the molecule undergoes large amplitude motion leading to the large value obtained for $l(Be—C(Cp'))$. This large amplitude motion could be a Be—Cp' stretching mode, a Cp' ring tilt mode, or a Cp' slip mode.

An alternative explanation for the absence of a clearly defined Be—C(Cp') peak in the RD curve may be that the equilibrium geometry has lower symmetry than C_{5v}; i.e., that Cp' is tilted or slipped in such a way that the five Be—C(Cp') distances no longer are exactly equal.

In addition to the structure parameters of the C_{5v} model we therefore define two new structure parameters, *Slip*, equal to the distance from the center of the Cp' ring to the fivefold symmetry axis of the π-CpBe fragment, and α, equal

to the angle between the planes of the two rings. The sign of α is defined as positive when Cp$'$ has been rotated counterclockwise about the x-axis, see Fig. 1. In order to fix the position of all atoms unambiguously, one must also define two angles describing the angle of rotation of the two rings about their (approximate) fivefold symmetry axes. In the following we shall, however, confine ourselves to model III in Fig. 1, in which the rings are oriented in such a way that both C(1) and C(6) are in the y—z plane. This model corresponds to the crystal structure at −120°C [4]. The problem of the structure of Cp$_2$Be may now be restated as the problem of determining how the potential energy of the molecule varies with *Slip*; if the potential energy surface has a minimum at *Slip* = 0 and α = 0, the equilibrium structure is C_{5v}, if the minimum is found at some value of *Slip* $\neq$ 0, the equilibrium structure is a slip sandwich.

Before proceeding we note that in a slip sandwich model, the Cp$'$ ring is no longer required to retain its fivefold symmetry. However, the vibrational amplitudes obtained by refinement of a C_{5v} model l(C—C) = 0.051(1) Å and l(C(1)$\cdots$ C(3)) = 0.054(1) Å are very similar to the corresponding amplitudes obtained for CpBeCH$_3$, 0.051(1) and 0.057(2) Å, demonstrating that at least the carbon atom skeleton of the two Cp rings show no perceptible deviation from fivefold symmetry, though differences between individual C—C bonds of the order of four or five hundredths of an Å unit cannot be ruled out.

The *Slip* parameter was refined by least-squares calculations with diagonal weight matrix with a C_{5v} start model (*Slip* = 0.0) and a start model corresponding to the crystal structure at −120°C; *Slip* = 1.21 Å. Both refinements converged to a model with *Slip* = 0.8 Å. The background was readjusted and the refine-
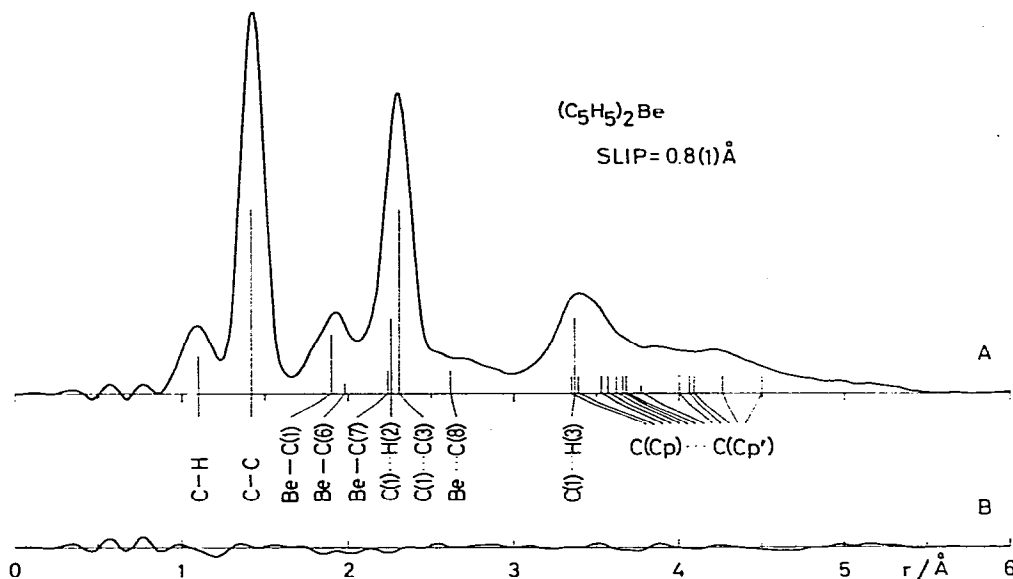

Fig. 5. A: Experimental radial distribution curve for Cp$_2$Be calculated by Fourier inversion of intensity curves. The intensity data from s = 0.000 to 1.875 Å^{-1} have been calculated for the best SLIP model. Artificial damping constant k = 0.001 Å^2. B: Difference between the experimental curve (A) and a theoretical curve for best slip model (Table 2).

ments continued with a non-diagonal weight matrix. All the vibrational amplitudes that had been refined for the C_{5v} model could be refined without divergence except the amplitudes of the three Be—C(Cp') distances. Somewhat arbitrarily the amplitude of the intermediate distance was fixed at 0.25 Å, while the two other amplitudes were assumed equal. Under these conditions refinements gave the R-factors listed in Table 1, Refinement 13, and the structure parameters listed in Table 2.

Comparison of the R-factors show that the slip sandwich model gives a slightly better fit between experimental and calculated intensity curves than the C_{5v} model, and comparison between RD curves show that the disagreement around 2.6 Å has been largely eliminated. See Fig. 5.

Finally similar refinements were carried out on a model with *Slip* fixed at 1.21 Å. Initially the same assumptions as before were made regarding the three l(Be—C(Cp')), but after l(Be—C(6)) and l(Be—C(8)) had refined to values well above 1 Å, they too were fixed at 0.25 Å. The resulting R-factors are listed in Table 1, Refinement 14, and parameter values are listed in the last two columns of Table 2. It is seen that the agreement is about as good as that obtained with the C_{5v} model and comparison of RD curves show that some disagreement has been reintroduced in the region around 2.6 Å.

Concluding remarks

The best agreement between calculated and experimental intensities is obtained with a slip sandwich model and the structure parameters listed in Table 2. The value obtained for *Slip*, 0.79(10) Å, would seem to rule out both the C_{5v} and the *Slip* = 1.21 Å models. However, since the standard deviation has been obtained for a fixed background, it cannot be taken at face value. In our view the fit obtained with the C_{5v} and *Slip* = 1.21 Å models is so good that the C_{5v} model as well as slip sandwich models with *Slip* between 0 and 1.2 Å must be considered compatible with the electron diffraction data.

This conclusion is at variance with that drawn by Drew and Haaland who concluded after refinements on the 1963 data, that models with *Slip* >0.6 Å could be ruled out. However, their refinements were carried out with a single fixed background drawn by hand for a C_{5v} model and with a slip model with exactly parallel rings.

Ab initio molecular orbital calculations on the slip sandwich model yield orbital energies in satisfactory agreement with the vertical ionization potentials obtained by PE spectroscopy, while a model of C_{5v} symmetry is only compatible with the PE spectrum if the Jahn—Teller splitting of the lowest ^2E state of the molecular ion is exceptionally large [12]. The microwave spectrum of Cp_2Be is more complicated than expected for a symmetric top [27], indicating that the equilibrium structure has lower symmetry than C_{5v}.

As mentioned in the introduction the molecular structure in the crystalline phase is that of a slip sandwich [4,5] and the Raman spectra offer strong indications that this conformation is retained in the melt [28].

Though a C_{5v} equilibrium structure of Cp_2Be cannot be ruled out, the experimental evidence seems to favor a slip sandwich equilibrium geometry for the gas phase. Perhaps the most reasonable hypothesis at this time is that the poten-

tial energy of the molecule varies slowly with the magnitude of the slip. The potential energy surface would have fivefold symmetry around the z-axis. The minimum energy, and consequently the equilibrium structure, is found at a distance of about *Slip* = 1 Å from the z-axis. The height of the mound at *Slip* = 0 (i.e. the relative energy of the C_{5v} conformation) is unknown, but probably not very large. The molecule consequently undergoes large amplitude vibrations.

The 'H NMR spectrum of Cp_2Be in CF_2Cl_2 consists of a single sharp peak down to —135°C [29]. Equivalence of all protons is probably achieved by rapid rotation of the two rings about their (approximate) fivefold symmetry axes and by motion of the Be atom between two potential energy minima each on the fivefold axis of one of the rings h_1 = 1.49 Å above (below) the ring center. The energy barrier between the two minima is clearly low enough to allow the alteration of the Be atom between the minima to be rapid on the 'H NMR timescale even at —135°C, but the sharpness of the peak at 1.92 Å in the RD-curve of Cp_2Be shows that the barrier height must be significantly greater than the thermal energy available under our experimental conditions, RT = 0.8 kcal mol^{-1}.

In model III the Be—C(6) distance is shorter than the Be—C(7) and Be—C(8) distances. Probably for this reason some workers have described the model as containing one *pentahapto* and one *monohapto* ring or even as a π-Cp, σ-Cp model. We believe that these descriptions may be misleading and prefer to describe it as a slip sandwich model or a *pentahapto, trihapto* model for the following reasons:

(i) The gas phase electron-diffraction data and IR spectrum [7] and the Raman spectrum of the melt [28] show that the Cp' ring does not deviate much from fivefold symmetry. This indicates that the π-system of the ring remains delocalized.

(ii) The angle between the Cp and Cp' ring planes, α = —4(3)°, is significantly different from the angle expected if Be is bonded to C(6) through a single covalent σ-bond, +36.9° [24].

(iii) The Be—C(6) distance is significantly longer than the Be—C(Me) distance in CpBeMe, 1.706(3) [22], while the Be—C(7) distance is so short as to indicate a bonding interaction between the two atoms.

Acknowledgements

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