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On the Molecular Structure of Beryllocene

Ning-Shih Chiu and Lothar Schäfer*

Contribution from the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. Received June 6, 1977

Abstract: A conformational analysis of beryllocene, $\text{Be}(\text{C}_5\text{H}_5)_2$, was executed based on ab initio standard single determinant MO theory with an STO-3G minimal basis. The study concentrated on two contradictory experimental models. One was the gas-phase electron diffraction model of $\text{Be}(\text{C}_5\text{H}_5)_2$, an asymmetrical sandwich structure in which the metal atom can occupy two alternate positions on the fivefold rotation axis, $h_1 = 1.472 \text{ \AA}$ from one ring and $h_2 = 1.903 \text{ \AA}$ from the other. The second model was the x-ray crystallographic slip-sandwich structure, in which one of the two parallel rings has slipped sideways by about 1.2 \AA , apparently producing a σ -bonded and a π -bonded ring system. The results of our calculations indicate that the gas-phase diffraction structure is 14–18 kcal/mol less stable in the STO-3G approximation than a symmetrical sandwich or a model which is similar to the x-ray structure, but has nonparallel rings. STO-3G calculations probably are too approximate to definitely rule out any conformation of a beryllium compound in a comparison of this kind. But it is possible to use these results as a basis for speculation that the vapors of $\text{Be}(\text{C}_5\text{H}_5)_2$ consist of a complicated conformational equilibrium with σ - π and σ - σ tautomerism which contains conformers in which the Be atom forms a π bond to one ring and a σ bond to the other. It is not unlikely that the radial distribution of this equilibrium is compatible with the experimental radial distribution observed by gas electron diffraction. This study points in a striking way to the usefulness of hybrid experimental and theoretical procedures in structural studies of gaseous molecules.

Introduction

The molecular structure which has been proposed for beryllocene (I), $\text{Be}(\text{C}_5\text{H}_5)_2$, in order to explain its vapor phase electron diffraction data^{1,2} is probably one of the most remarkable low-weight structural designs which are known. The Almenningen, Bastiansen, and Haaland (ABH) model of beryllocene^{1,2} describes the compound as a sandwich complex with two planar, symmetrical, parallel, and staggered C_5H_5 rings with a vertical ring-ring distance $h = 3.375 \text{ \AA}$. The CH skeleton of this model belongs to point group D_{5d} ; the complete molecule has the lower group C_{5v} , since the beryllium atom may occupy two alternative positions on the fivefold rotation axis, $h_1 = 1.472 \text{ \AA}$ from one ring and $h_2 = 1.903 \text{ \AA}$ from the other. Thus, the most characteristic feature of the ABH model for beryllocene is a double minimum potential energy curve for beryllium with the ability of the metal to tunnel between its two equilibrium positions.

In subsequent investigations Fritz and Sellmann³ claimed that the ABH structure was also found for I by analysis of its IR spectrum. Similar conclusions were reported by McVicker

and Morgan,⁴ who compared the IR condensed state spectrum of I to its vapor phase data. In direct contrast to this the earlier IR study of I by Fritz and Schneider⁵ seemed to favor an angular structure for this compound and inferred the presence of two equivalently bonded ligands. The semiempirical MO calculations by Sundbom⁶ indicated that the ABH structure might correspond to an energy minimum. But it was also warned⁶ that the shape of the energy curve depended strongly on the values chosen for some of the empirical parameters so that more refinements were needed to make a really conclusive statement. Lopatko, Klimenko, and Dyatkina⁷ used a somewhat more advanced semiempirical MO LCAO SCF procedure to calculate the electronic structure of I in a PNDO approximation taking into account all the valence electrons of beryllium and the $2p_z$ atomic orbitals of all the carbon atoms using a Slater-type basis set. The conclusion of these authors was that the asymmetrical conformation of I, C_{5v} , was energetically more favored than its symmetric form, D_{5d} .

In 1972 Wong, Lee, Chao, and Lee (WLCL)⁸ studied the crystal structure of I by x-ray diffraction at $-120 \text{ }^\circ\text{C}$ and

found, somewhat surprisingly, a model which was significantly different from the one proposed by ABH. The WLCL model of beryllocene is a "slip"-sandwich, with the Be atom π bonded to one and σ bonded to the other ring. Normal distance between the two rings is $h = 3.33 \text{ \AA}$, with $h_1 = 1.53 \text{ \AA}$ and $h_2 = 1.81 \text{ \AA}$. The most characteristic feature of the WLCL model is, therefore, a sandwich structure in which one of the two nearly parallel rings has slipped sideways in its plane by about 1.2 \AA , with the result that the shortest Be-C bond (the σ bond) is perpendicular to the plane of the five-membered ring. A reinvestigation of I at room temperature by x-ray diffraction⁹ confirmed the basic WLCL model, albeit with somewhat different parameters. A low-temperature ^1H NMR study¹⁰ was found to be consistent with both the ABH and the WLCL structures. Both were also interpreted to be at least in qualitative agreement with the surprisingly large dipole moment of I determined¹¹ from its solutions in benzene ($\mu_{25^\circ\text{C}} = 2.46 \text{ D}$) and in cyclohexane ($\mu_{25^\circ\text{C}} = 2.24 \text{ D}$). (In the following paragraphs we shall accept the notation " σ -bonded" and " π -bonded" ring to identify the two different systems without intending to make any inference concerning the true bonding state.)

In view of the conflicting results described above, it is now an interesting question whether the different structures reported for gaseous and crystalline $\text{Be}(\text{C}_5\text{H}_5)_2$ are the results of ambiguous experimental data which might be interpreted in several different ways, or whether the reported differences are the manifestations of true geometrical rearrangements which are induced in the system when it goes from the gaseous to the crystal state. McVicker and Morgan⁴ have shown that it is indeed possible to infer significant changes in the bonding properties of I by comparing its condensed-phase to its gas-phase IR spectra. Drew and Haaland have reported¹² that a static WLCL model, i.e., a single conformation with refined crystal parameters, was not compatible with the gas-phase diffraction data. A test to reproduce the gas-phase electron diffraction pattern by a dynamical model consisting of a mixture of many conformations with the rings in different states of rotation and slip has not been reported.

In this situation we found it promising to execute an ab initio analysis of $\text{Be}(\text{C}_5\text{H}_5)_2$. It was hoped that theoretical investigations might be able to further elucidate the conformational properties of this compound, when all experimental possibilities, for the time being, seemed to have been exhausted. As a result of our calculations, which will be described in the following paragraphs, we have to conclude that, in the space of the applied ab initio approximation, the ABH model is very unstable, while an energy minimum may be correlated to a WLCL structure with nonparallel rings.

During the final stage of this investigation Marynick¹³ reported the results of a molecular orbital study of I which employed the method of partial retention of diatomic differential overlap (PRDDO).¹³ This method is more than an order of magnitude faster than accurate ab initio minimum basis set calculations for molecules of this size. In general, however, its results compare favorably to those obtained by more advanced procedures.¹³ In the present case, too, there is good qualitative agreement between our STO-3G and the PRDDO results. Since these results contradict in a striking manner some experimental interpretations, and since the PRDDO calculations are also in disagreement with the earlier^{6,7} semiempirical studies, it is very useful to present, as a further confirmation, some details of our full ab initio treatment of $\text{Be}(\text{C}_5\text{H}_5)_2$.

Computational Procedures

For the ab initio calculations of this study, standard single determinant MO theory with the STO-3G minimal basis of Hehre, Stewart, and Pople¹⁴ was used. The computer program

was the "Gaussian 70" package by Hehre et al.¹⁵ Two versions of this program were used in this study. One is maintained in this department by N. S. Ostlund. The other was received from Professor B. Pullmann's group at IBPC in Paris. The two somewhat modified versions of the same parent program gave identical results for some test cases. These tests were made to exclude computing errors.

The standard molecular exponents for the Slater-type atomic orbitals of H, Be, and C were those of Hehre et al.¹⁶ It is well known that the STO-3G procedure is rather approximate and more extensive calculations would have been desirable for this study. However, a single-point calculation of beryllocene, even on the STO-3G level, required about 3–3.5 h of exclusive computing time on the University of Arkansas IBM 370/155. Since a theoretical analysis of I had a chance to be successful only if a somewhat extensive search of its energy surface was made, any more advanced procedure was beyond our means.

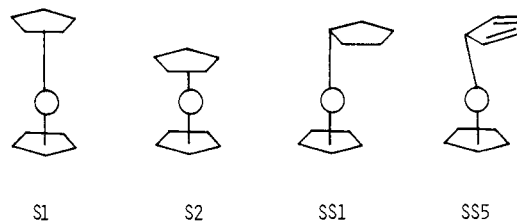
Geometry optimization made use of a gradient search method¹⁷ based on numerically derived first-order derivatives. This method was chosen because we have previously found it safe in many cases^{18,19} in which energy minimization had to start far from minimum.

The total energies of I obtained by our calculations are rather high (at about -394 au) compared to those of Marynick (about -398 au).¹³ This difference is probably caused by the different basis sets used in both studies. The beryllium valence shell exponent was optimized in the PRDDO calculations,¹³ while the standard exponents¹⁶ were used without change in our study. We have not attempted any optimization, because of the length of the calculations.

Results

The results of our calculations (total energies, dipole moments, and model parameters) are given in Table I.

Our calculations were started using the ABH model and its parameters² for beryllocene in its staggered and eclipsed form (models S1 and E1, respectively, Table I). The independent parameters of this model (C-C, C-H, h_1 , and h_2) were then refined in several cycles by optimizing the total energy of the C_{5v} system. Refinement was terminated when the change in total energy was less than 0.01 kcal/mol and the changes in bond distances were of the order of magnitude of 0.005 \AA for h_1 and h_2 and 0.001 \AA for C-C and C-H. During this optimization process, the Be atom moved from the asymmetrical ABH position to the center of the sandwich. The resulting symmetrical models, S2 and E2 (Table I), were about 18 kcal/mol more stable than the ABH conformations, S1 or E1. Differences between staggered and eclipsed forms were of the order of magnitude of a few tenths of a kcal/mol, favoring staggered. Calculations S3, S4, and S5 (Table I) showed that,



whenever the metal was moved out of the center of the sandwich, the total energy increased.

For the slip-sandwich forms (symbol $\text{SS}n$), it was not possible to perform a total energy optimization by relaxing all relevant parameters, because of their large number. The magnitude of the slip was, initially, set constant at 1.202 \AA , which brought the σ -bonded carbon atom perpendicular to the plane of the π -bonded ring on top of the metal as in the WLCL model.⁸

Table I. Calculated Energies (Total Energies in au, Relative Energies in kcal/mol), Dipole Moments (D), and Geometrical Parameters (Å) for Various Models of Beryllocene

Model ^a	C-C	C-H	h_1	h_2	h	$E(\text{tot})$	μ	$E(\text{rel})$
S1	1.425	1.103	1.472	1.903	3.375	-394.250 128	3.06	18.8
E1	1.425	1.103	1.472	1.903	3.375	-394.249 749	3.07	19.1
S2	1.412	1.078	1.619	1.619	3.239	-394.278 967	0.00	0.7
E2	1.412	1.078	1.619	1.619	3.239	-394.278 372	0.00	1.1
S3	1.412	1.078	1.413	1.826	3.239	-394.257 875	2.80	14.0
S4	1.412	1.078	1.343	1.896	3.239	-394.240 661	3.71	24.8
S5	1.412	1.078	1.609	1.629	3.239	-394.278 918	0.14	0.8
SS1	1.412	1.078	1.343	1.896	3.239	-394.245 309	5.26	21.8
SS2	1.412	1.078	1.413	1.826	3.239	-394.254 239	NC	16.2
SS3		1.078	1.452	1.823	3.275	-394.261 802	4.37	11.5
SS4		1.078	1.452	1.823		-394.276 568	4.80	2.2
SS5		1.078	1.452	1.823		-394.280 119	4.69	0.0

^a S1, E1, staggered and eclipsed conformations of beryllocene with parameters taken from ABH;² S2, E2, results of the geometry optimization of the staggered and eclipsed forms of I; S3, model with the h value of S₂ and with the h/h_1 and h/h_2 ratios of ABH;² S4, model with the h value of S₂ and with the h/h_1 and h/h_2 ratios of the WLCL structure;⁹ S5, intermediate step of the geometry optimization close to the minimum, S₂, with slightly different bonds h_1 and h_2 ; SS1, slip sandwich with h/h_1 , h/h_2 from WLCL⁹ and C-C, C-H, and h from the optimized structure, S₂ (the σ -bonded ring was slipped sideways by 1.202 Å); SS2, SS1 parameters with h_1 and h_2 as in S3 (dipole moment was not calculated since an unexpected number of iterations caused the program to run out of time); SS3, result of a one-step geometry optimization of SS2 refining h_1 , h_2 , and different C-C bonds in the σ -bonded ring (C(1')-C(2') = C(2')-C(3') = 1.461 Å; C(3')-C(4') = C(1')-C(5') = 1.352 Å; C(4')-C(5') = 1.413 Å. The Be-C(2') bond was perpendicular to the plane of the rings. All other parameters were kept constant as in SS2); SS4, model with SS3 parameters, but nonparallel rings (the angle between the Be-C bond and the plane of the σ -bonded ring was 126.4°); SS5, model with SS4 parameters, but the σ -bonded ring was slipped sideways by 0.963 Å.

The first slip-sandwich models which we calculated tested different values for h_1 and h_2 in connection with regular five-rings (models SS1 and SS2, Table I). The geometry of SS2 was then optimized for one cycle relaxing h_1 , h_2 , and three different C-C bonds in the σ -bonded ring keeping all other parameters constant. Model SS3 (Table I) was produced in this way.

At this point it was decided to release the σ -bonded ring out of its parallel relation to the π -bonded ring, retaining all the other parameters of SS3. This produced a considerable lowering of the total energy. The degree of inclination of the σ -ring plane was, therefore, optimized. Model SS4 resulted with an angle of 126.4° for this parameter. This conformation turned out to be about 16 kcal/mol more stable than the ABH model and 1.5 kcal/mol less stable than the optimized symmetrical staggered sandwich, S2. It is interesting to note that a similar model with nonparallel rings (structure III, with an angle of 117° between the two rings) was the most stable conformation of the PRDDO study.¹³

In comparing the energies of S2 and SS4 one must keep in mind that the structure of S2 is the result of several cycles of geometry optimization, whereas SS4 was found by rather crude guesses of individual parameter changes. We have, therefore, no doubt that the energy of SS4 could be further lowered by relaxing about 12 relevant parameters which determine its structural features. Indeed, even when only the magnitude of the slip was optimized in this conformation, model SS5 resulted, with a slip of 0.963 Å and the lowest total energy (Table I) of all the conformations of I which we tested.

The calculations had to be stopped at this point because they were very expensive and because they have already proved that conformations similar to WLCL conformations of beryllocene exist, which are much more stable in STO-3G calculations than the ABH structure and which do not contradict any experimental evidence. No further attempt was made to find details of the minimum of energy to which SS5 might belong. In view of the approximate nature of present quantum mechanical procedures (particularly of the STO-3G approximation), such details would probably not be very reliable. Moreover, they would be difficult to be related to experimental observations because of the essential differences in ab initio and observed parameters.

Discussion

The above calculations have shown that, in the realm of ab initio calculations (on the STO-3G level), the asymmetrical ABH model of beryllocene is highly unstable. It is 14–18 kcal/mol less stable than a symmetrical beryllocene sandwich or a σ - π -type system. This result can be interpreted in many different ways to speculate about the "true" conformational behavior of this compound.

It is possible, for example, that the used STO-3G procedure is too approximate to give meaningful results for beryllocene. The STO-3G minimal basis is well known to be particularly unreliable for beryllium-containing compounds, for which extended basis sets should be used.^{20,21} More advanced calculations than ours might, therefore, very well produce significantly changed energy differences for the various conformers. In addition this study is also affected by the usual uncertainties which complicate energy optimization on a multidimensional hypersphere.

On the other hand, our calculations are also relatively advanced and they should certainly overrule the contradicting conclusions of previous semiempirical studies. We are in essential agreement with the PRDDO investigation of I,¹³ even though our energy differences for ABH and WLCL type models are somewhat smaller (14–18 kcal/mol) than the PRDDO value (26 kcal/mol). It is, therefore, possible that this value can be further reduced by more advanced calculations based on improved wave functions. Our calculated energy differences are rather large, however, and seem to establish a clear trend. The refined or partially refined parameters are reasonable compared to experimental values. The ring-to-ring distance, $h = 3.239$ Å (r_e), may be somewhat small compared to the electron diffraction value, $h = 3.375$ Å (r_a). But then, this parameter seems to be very temperature dependent since it was found to be 3.33 Å at -120 °C, which is closer to our 0 K partially refined slip sandwich value of 3.275 Å.

We, therefore, want to use the results of our calculations as a basis to speculate that the electron diffraction data of I might possibly also be consistent with a different model than that proposed by ABH. If the molecule exists in the gaseous state in a conformation which is similar to that described by WLCL, then it must probably be described as a very dynamical conformational process. The two five-rings could be expected, for

example, to rotate independently around two different fivefold axes, at the same time slipping back and forth with respect to each other and to the metal, undergoing transitions from σ - to π -bonded states, bending some of the hydrogen atoms out of plane, and rearranging their C-C bond systems, while the metal changes its positions, at h_1 and h_2 , with respect to each ring. It is not unreasonable to expect that a complicated conformational equilibrium involving significant population of the many simultaneous intermediate states of this process might produce a radial distribution which, if it could be calculated and refined, would reproduce the experimental radial distribution found by electron diffraction for the vapors of I without making use of the ABH conformation.

The dipole moment calculated for SS5 is rather large (4.7 D) compared to the experimental value (2.2–2.5 D). This could again be an artifact of the applied approximation or it may be related to the fact that SS5 is not really an optimized model. On the other hand, this discrepancy could also be the result of solvent effects, or the experimental value might be an average involving many different conformations including less polar ones such as, for example, the symmetrical (D_{5d}) sandwich.

As far as the IR investigations of beryllocene are concerned, it must be noted that the vibrational spectrum of one compound can often be interpreted to be consistent with many different models. The claim by Fritz and Sellmann³ that, from the IR spectrum, a sandwich-type structure with asymmetrically placed Be atom is found in accordance with the result of the electron diffraction study is therefore probably somewhat unfounded in this specific and detailed formulation. The IR data are, therefore, probably not in real contrast to the present calculations.

Conformational analysis of molecules in the vapor phase is still a frontier of structural chemistry and very often our conclusions concerning the conformational behavior of undisturbed gaseous systems are uncertain. At present, hybrid theoretical and experimental techniques seem to offer the most powerful procedures in conformational studies of free molecules. The introduction of various expectation values into gas diffraction data analyses,^{18,19,22} for example, has often made

it possible to arrive at conclusions which could not have been obtained by applying individual techniques alone. The intimate connection and the complementarity of theory and experiment in studies of this kind seem to open a novel dimension in scientific research.

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Extreme Conformational Flexibility of the Furanose Ring in DNA and RNA

Michael Levitt*¹ and Arieh Warshel

Contribution from the Laboratory of Molecular Biology, Cambridge, CB2 2QH, England.
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Abstract: Consistent force field calculations have been used to calculate the variation of energy along the pseudorotational paths of ribose and deoxyribose rings. This energy changes by only 0.5 kcal/mol as the ring pucker changes from C3'-endo to C2'-endo. Therefore, the torsion angle ψ' of the sugar-phosphate backbone of nucleic acids is more flexible than a normal C-C single-bond torsion angle and cannot be frozen at a value corresponding to either of these puckers when other torsion angles are varied. An analytical expression for the variation of the ring energy and conformation as a function of ψ' is given to enable this extreme flexibility to be included in future calculations of nucleotide conformations. The finding that the furanose ring is so easily deformed has far-reaching implications about the structure of polynucleotides and the rigidity of DNA.

The furanose ring occupies a central position in the chemical structure of nucleic acids by linking phosphate groups into a backbone and providing attachment points for the bases. Any changes of conformation of this ring could have a profound effect on the possible conformation of DNA and RNA molecules. Previous calculations on nucleotide conformations²⁻⁸

have chosen to keep the furanose ring fixed at one or two conformations but have allowed the single bond torsion angles in the backbone to vary continuously. Rigidly fixing the conformation of a five-membered ring would seem too limiting when one considers that cyclopentane can freely change the ring pucker along a path known as pseudorotation.⁹⁻¹³ On the