is suggested that metal coordination to the five-membered ring would distort the electronic distribution of the arene rings with concurrent loss of aromatic stabilization.[2] Simple calculations on the fluorenide ion charge distribution place a substantial negative charge on C(9), −0.4 e; the remaining negative charge is distributed more or less evenly at carbons 1, 3, 6, 8, 11, and 12.[23] There is less negative charge on the five-membered ring of the fluorenyl anion, and this group should be a poorer donor than the cyclopentadienide anion to a metal. Similarly, the LUMO orbitals for the fluorenide anion are substantially on the six-membered rings, and only in small part on the five-membered ring. Thus there should be a poorer overlap between LUMO and filled metal orbitals resulting in less back-donation to the metal. In effect, the η^5-fluorenide anion is a poorer acceptor than the cyclopentadienide anion, and should bond to a metal more weakly.

There are no qualitative bonding arguments against a η^6-fluorenyl structure, except possibly a reservation concerning charge separation. This concern is minimal, though, due to the extent to which the cyclohexadienyl–metal structure is assumed. The negative charge formally assigned on C(9) is expected to be partly delocalized over metal and ligand systems. This delocalization probably accounts for the stabilization of the anionic intermediates in the reactions described by Jaouen[24] and others. This does not speak fully to the question of relative stabilization of the two possible structures, of course; perhaps the problem is really too complex to address directly. Nonetheless a qualitative observation can be suggested. By assuming the observed structure rather than the alternative η^5-fluorenyl structure, the iron atom retains some measure of positive charge; in contrast electron density at the metal in the η^5-fluorenyl complex would be higher. The actual metal electron density would be determined by the ligands' ability to remove charge from the metal. Neither ligand is particularly adept in this regard. On the other hand fluorenyl complexes of other metals with good acceptor ligands might behave differently, and a η^5-structure preferred. Indeed, this is the result for the manganese tricarbonyl system.[6]

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Supplementary Material Available: A listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(10) All crystallographic programs used in structure determination and refinement were written by J. C. Calabrese, with the exception of the direct methods program MULTAN (Main, Woolfson, and Germain). The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP2 (C. K. Johnson).
(11) $R_1 = [\Sigma||F_o|-|F_c||/\Sigma|F_o|] \times 100\%$ and $R_2 = \Sigma\omega_i//|F_o|-|F_c||^2/\Sigma\omega_i|F_o|^2] \times 100\%$ where $\omega_i = [\sigma(F)]^{-2}$. Refinement was based on R_2.
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Studies of the Molecular and Electronic Structure of Dicyclopentadienylberyllium

Dennis S. Marynick

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received June 14, 1976*

Abstract: The molecular and electronic structure of dicyclopentadienylberyllium is investigated by the method of partial retention of diatomic differential overlap. Six possible structures are considered, and the most stable structure is calculated to be one in which the beryllium is π bonded to one ring and σ bonded to the other, although the structure analogous to ferrocene appears to be only ~6 kcal/mol less stable. No evidence is found for a stable structure of C_{5v} symmetry. Several different mechanisms of intramolecular tautomerism are explored, and the bonding is analyzed in terms of localized molecular orbitals and population analyses.

Since the discovery of ferrocene[1] in 1951, a large number of dicyclopentadienyl–metal complexes have been synthesized. The smallest of these is dicyclopentadienylberyllium, $(C_5H_5)_2Be$.

Dicyclopentadienylberyllium was first synthesized by Fischer and Hofmann[2] in 1959 via the reaction of cyclopentadienyl sodium and beryllium chloride. The compound was found to be extremely reactive, polar in benzene and cyclohexane solutions, and diamagnetic. In 1964, Almenningen, Bastiansen, and Haaland[3] showed that the electron diffraction pattern of $(C_5H_5)_2Be$ was most consistent with a structure of C_{5v} symmetry (structure I, Figure 1), rather than a ferrocene like D_{5d} structure (structure II, Figure 1). The C_{5v} structure, although highly unusual, provided a nice explanation of the dipole moment of this molecule. Later, Haaland[4] presented a re-refinement of the 1964 electron diffraction data and estimated the ring-ring distance to be 3.375 Å, with the beryllium occupying a position 0.43 Å closer to one ring than the other. Fritz and Sellmann[5] interpreted the infrared spectra as favoring the C_{5v} model for the solid and for solutions in benzene and cyclohexane; however, the molecular structure in the crystalline phase is now known not to closely resemble the C_{5v} structure (see below), and there is strong evidence[6] that $(C_5H_5)_2Be$ associates with aromatic solvents and possibly even with nonaromatics such as methylcyclohexane. An examination of the gas phase infrared spectrum led McVicker and Morgan[7] to conclude that the structure in the gas phase involves essentially completely ionic ring-metal bonding, since only fundamental frequencies of the planar cyclopentadienyl anion were observable. Finally, the microwave spectrum has been recorded but not solved,[8] but the microwave data are apparently not consistent with a symmetric top molecule.

The crystal structure of $(C_5H_5)_2Be$ has been solved at −120 °C[9] and at room temperature.[10] At low temperatures (Figure 1, structure V) the molecule assumes a slip sandwich structure with the two cyclopentadienyl rings parallel and the beryllium π bonded to one ring and σ bonded to the other. At room temperature (Figure 1, structure VI) the structure is even more complex, although the large thermal parameters prevent a precise determination of structural parameters. In both cases the crystal structure is disordered, with the beryllium assuming one of two possible positions related by a center of symmetry.

The ^1H NMR spectrum of $(C_5H_5)_2Be$ consists[11] of only a sharp singlet as low as −135 °C, and the temperature independence of the spectrum makes it impossible to assign a barrier height for a probable beryllium tautomerism without making drastic assumptions concerning the shape of the potential energy surface or the preexponential factor for the rate process.

Two theoretical studies[12,13] of $(C_5H_5)_2Be$ have also appeared. While these studies considered only the C_{5v} and D_{5d} structures and employed semiempirical molecular orbital theory, they both found the C_{5v} structure to be more stable. However, no accurate ab initio or nonempirical theoretical studies of this molecule have yet appeared. In this paper we present a nonempirical molecular orbital study of $(C_5H_5)_2Be$. We employ the method of partial retention of diatomic differential overlap (PRDDO) developed by Halgren and Lipscomb.[14] This method, although more than an order of magnitude faster than the most rapid available ab initio methods for a molecule this size, yields results which compare very favorably to accurate ab initio minimum basis set calculations on similar systems.[15] We present optimized or partially optimized geometries, population analyses, calculated relative energies for four possible gas phase structures, and energetics for several possible pathways of intramolecular tautomerism. Localized molecular orbitals (LMO's) are obtained for two of the possible structures by employing the Boys criteria[16] as implemented by the Edmiston and Ruedenberg procedure,[17] and the bonding is analyzed in terms of the LMO's and the population analyses.[18]

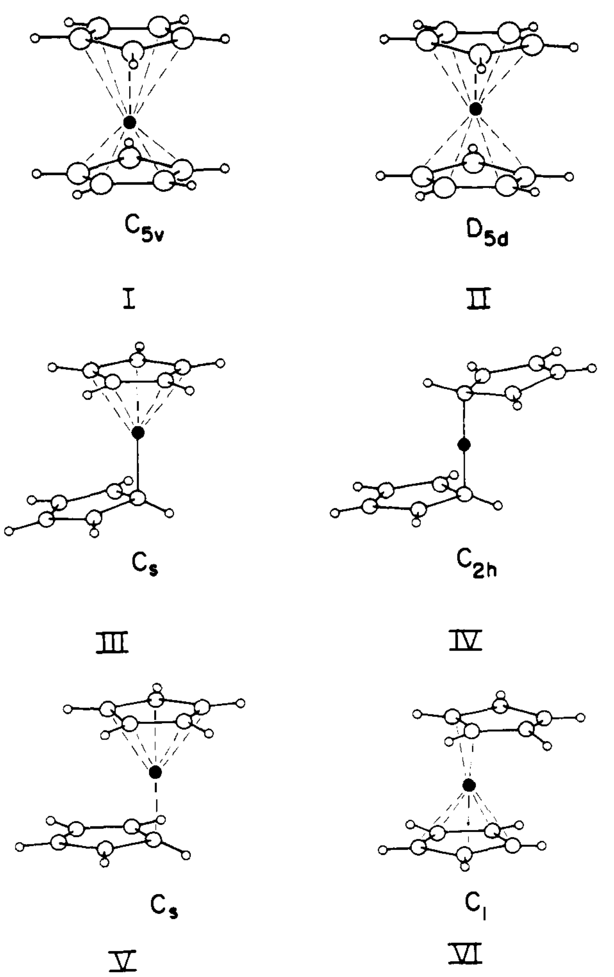


Figure 1. Some possible structures for $(C_5H_5)_2Be$. I, II, III, and IV are possible gas-phase structures; V and VI are the structures in the crystalline phase at −120 °C and room temperature, respectively.

Calculations

Each calculation took approximately 1 min on an IBM 360/91. Most exponents were held constant at the standard values given by Hehre et al.,[19] however, the beryllium valence shell exponent was usually optimized. Geometry optimizations were carried out as follows. Structure II was completely optimized except for the C–H bond distance, held constant at 1.10 Å. For structure III the initial geometrical parameters of the top ring were taken from structure II, those of the bottom ring from cyclopentadiene,[20] and each beryllium-ring distance, the ring-ring angle, and the Be-C_σ-H angle (C_σ denotes a σ-bonded carbon) were fully optimized. The beryllium was assumed to bind the top ring symmetrically only after preliminary calculations failed to locate an unsymmetrical (off center) bonding arrangement. Parameters for structure IV were taken from the appropriate fragment of structure III. Coordinates for structures II, III, and IV are given in Table I.

Potential surfaces for the interconversion of structures II and III (σ–π tautomerism) and for the rotation of the bottom ring of structure III (σ–σ tautomerism) were calculated as follows. Initial estimates of the geometrical parameters of the transition states were made by the techniques of linear and quadratic syncronous transits.[21] The geometry was then partially optimized subject to the constraint that the path coordinate did not change (for the details of this procedure see ref 21). Finally, the valence shell exponent on beryllium was optimized. Our pathways for the σ–π and σ–σ tautomerisms are not fully optimized and represent upper bounds for the exact

Table I. Coordinates[a]

Structure	Atom	x	y	z
II	Be	0.0	0.0	0.0
	C_1	−2.2472	0.0	−3.0425
	C_2	−0.6944	2.1373	−3.0425
	C_3	1.8180	1.3209	−3.0425
	C_4	1.8180	−1.3209	−3.0425
	C_5	−0.6944	−2.1373	−3.0425
	C_6	2.2472	0.0	3.0425
	C_7	0.6944	−2.1373	3.0425
	C_8	−1.8180	−1.3209	3.0425
	C_9	−1.8180	1.3209	3.0425
	C_{10}	0.6944	2.1373	3.0425
	H_1	−4.3316	0.0	−3.0425
	H_2	−1.3385	4.1196	−3.0425
	H_3	3.5043	2.5460	−3.0425
	H_4	3.5043	−2.5460	−3.0425
	H_5	−1.3385	−4.1196	−3.0425
	H_6	4.3316	0.0	3.0425
	H_7	1.3385	−4.1196	3.0425
	H_8	−3.5043	−2.5460	3.0425
	H_9	−3.5043	2.5460	3.0425
	H_{10}	1.3385	4.1196	3.0425
III	Be	0.0	0.0	−0.1846
	C_1	−2.2908	0.0	−2.8781
	C_2	−0.7079	2.1787	−2.8781
	C_3	1.8533	1.3465	−2.8781
	C_4	1.8533	−1.3465	−2.8781
	C_5	−0.7079	−2.1787	−2.8781
	C_6	0.0	0.0	3.0714
	C_7	−1.6496	−2.2456	3.9118
	C_8	−3.7709	−1.3795	4.9932
	C_9	−3.7709	1.3795	4.9932
	C_{10}	−1.6494	2.2456	3.9118
	H_1	−4.3752	0.0	−2.8781
	H_2	−1.3519	4.1610	−2.8781
	H_3	3.5395	2.5716	−2.8781
	H_4	3.5395	−2.5716	−2.8781
	H_5	−1.3519	−4.1610	−2.8781
	H_6	1.9767	0.0	3.7327
	H_7	−1.1686	−4.2544	3.6668
	H_8	−5.2870	−2.5729	5.7655
	H_9	−5.2870	2.5729	5.7655
	H_{10}	−1.1686	4.2544	3.6668
IV	Be	0.0	0.0	0.0
	C_1	0.0	0.0	−3.2560
	C_2	1.6494	2.2456	−4.0964
	C_3	3.7709	1.3795	−5.1779
	C_4	3.7709	−1.3795	−5.1779
	C_5	1.6494	−2.2456	−4.0964
	C_6	0.0	0.0	3.2560
	C_7	−1.6494	−2.2456	4.0964
	C_8	−3.7709	−1.3795	5.1779
	C_9	−3.7709	1.3795	5.1779
	C_{10}	−1.6494	2.2456	4.0964
	H_1	−1.9767	0.0	−3.9174
	H_2	1.1686	4.2544	−3.8515
	H_3	5.2870	2.5729	−5.9501
	H_4	5.2870	−2.5729	−5.9501
	H_5	1.1686	−4.2544	−3.8515
	H_6	1.9767	0.0	3.9174
	H_7	−1.1686	−4.2544	3.8515
	H_8	−5.2870	−2.5729	5.9501
	H_9	−5.2870	2.5729	5.9501
	H_{10}	−1.1686	4.2544	3.8515

[a] Atomic units.

PRDDO barrier heights. Localized orbitals were obtained by applying a unitary transformation to the occupied molecular orbitals which maximizes D, the sum of squares of displacements of the orbital centroids from an arbitrarily defined molecular origin. D is defined as

$$D = \sum_{i=1}^{n} \langle \phi_i | \bar{r} | \phi_i \rangle \langle \phi_i | \bar{r} | \phi_i \rangle$$

where the summation extends over n occupied molecular orbitals. A typical localization calculation required 20 s of 360/91 time. In all cases the localized orbitals converged to a true maximum on the LMO hypersurface.

Results

Geometries and Energetics. Structure I. Our calculations suggest that this structure of C_{5v} symmetry is not a minimum on the SCF potential surface. Calculations using the geometrical parameters derived from the electron diffraction work[4] indicate that the C_{5v} structure is ~26 kcal/mol less stable than the structure of D_{5d} symmetry. A detailed examination of the asymmetric stretching mode of the D_{5d} structure gave no evidence for an unsymmetrical structure of C_{5v} symmetry. Since the possible existence of an unsymmetrical C_{5v} minimum has been rationalized on the basis of highly ionic bonding,[3] these calculations were repeated with the valence shell of the beryllium removed; however, the D_{5d} structure was still found to be ~5 kcal/mol more stable without geometry optimization.

Structure II. The optimized geometrical parameters are Be-C = 2.00 Å and C-C = 1.40 Å, and the ring-ring distance is 3.22 Å. Using standard exponents this structure is calculated to be 15.0 kcal/mol less stable than structure III. Optimization of the valence shell exponent on beryllium for both structures reduced this energy difference to 6.4 kcal/mol. The optimized valence shell exponent is ~0.85, unusually small for beryllium in a molecular environment.

Since structures II and III are apparently close in energy and are related by a possible pathway for intramolecular tautomerism (see below), an examination of some of the normal modes of structure II was undertaken to see if this structure represents a minimum on the PRDDO energy surface. Examination of the symmetric and asymmetric stretches, symmetric and asymmetric tilts, and the ring-Be-ring deformation mode indicated that, within the PRDDO approximation, structure II is a minimum on the surface.

The calculated barrier to internal rotation is only ~0.4 kcal/mol without reoptimization of the geometry. Interestingly, the highest energy rotational conformer appears to be midway between the D_{5d} and D_{5h} structures, although the energy differences may be too small to be meaningful.

Structure III. The optimized geometrical parameters are Be-C_σ = 1.72 Å, Be-C_π = 1.87 Å, Be-C_σ-H = 108.5° and the angle between the two rings is 117°, although the energy is very weakly coupled to this angle within 15° of the minimum. This structure is calculated to be more stable than any other we have studied. The barrier to internal rotation is calculated to be 0.3 kcal/mol without reoptimization of the geometry.

Structure IV. This structure is calculated to be ~45 kcal/mol less stable than III. No geometry optimizations were attempted.

Structure V. Coordinates for this structure, which is the probable structure in the crystalline phase at low temperature,[8] were estimated by rotating the bottom ring of structure III 27° to make the two rings parallel and reoptimizing the Be-C_σ-H angle. The calculated energy is 13.9 kcal/mol higher than III. If the ring-ring distance is constrained at exactly the value found in the solid state, the calculated energy is 21.3 kcal/mol higher than III.

Structure VI. A trial calculation employing the ring-ring distance, displacement, and orientation from the x-ray diffraction work[9] yielded a calculated energy 31 kcal/mol higher than III. No further geometry optimizations were attempted because of the complete lack of symmetry in this molecule.

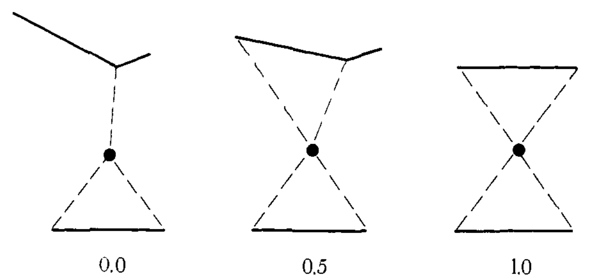


Figure 2. The relative ring orientations for three points on the σ-π tautomerism pathway.

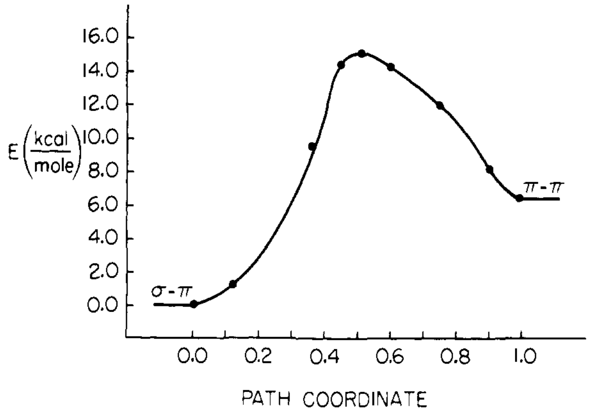


Figure 3. Energy as a function of path coordinate along the σ-π tautomerism pathway. The path coordinate corresponds roughly to the degree of displacement of the two rings.

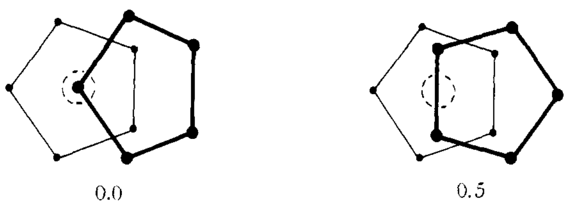


Figure 4. The relative ring orientations for two points on the σ-σ tautomerism pathway.

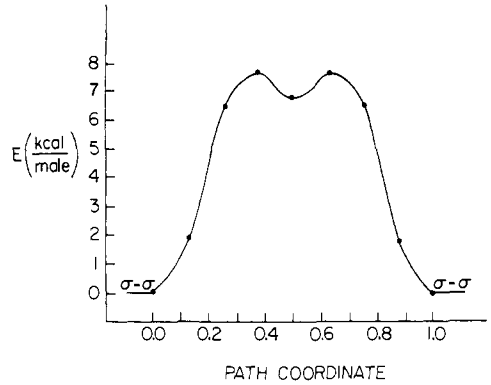


Figure 5. Energy as a function of path coordinate along the σ-σ tautomerism pathway. The path coordinate corresponds roughly to the degree of rotation of one ring with respect to the other ring.

Table II. Energetics

Structure	Total energy[a]	ΔE[b]
I[c]	−398.6155	26.3
II[d]	−398.6472	6.4
III[e]	−398.6574	0.0
IV[e]	−398.5864	44.6
V[e]	−398.6353	13.9[f]

[a] Atomic units. [b] Kcal/mol relative to structure III. [c] The electron diffraction geometry was employed with an optimized valence shell exponent (0.80) for beryllium. [d] The optimized valence shell exponent for beryllium is 0.85. [e] The valence shell exponent for beryllium is 1.10. [f] Readjustment of the ring-ring distance to correspond exactly with the distance found in the solid state yields a calculated energy of −390.6235 and a ΔE of +21.3 kcal/mol.

Intramolecular Tautomerism. Since the ^{1}H NMR results indicate that $(C_5H_5)_2Be$ probably undergoes an intramolecular tautomerism in solution making all protons equivalent on the NMR time scale, we have investigated several possible pathways for intramolecular tautomerism in this molecule.

The first pathway interconverts structures II and III and is denoted σ-π tautomerism. The relative ring displacements for path coordinates of 0.0, 0.5, and 1.0 are shown in Figure 2. The highest energy point on the surface corresponds to a path coordinate of 0.5 and an energy 15.0 kcal/mol higher than structure III and 8.6 kcal/mol higher than structure II (Figure 3). This barrier is probably within 5 kcal/mol of the fully optimized PRDDO limit.

The second pathway corresponds to the transfer of the Be-C σ bond from one carbon atom to a nearest neighbor carbon atom in the same ring and is denoted σ-σ tautomerism. The relative ring displacements for path coordinates of 0.0 and 0.5 are shown in Figure 4. The double maximum shape of the energy profile (Figure 5) may be an artifact of incomplete geometry optimization, but further optimizations will only lower the already low barrier (7.6 kcal/mol). Of course, the σ-σ pathway does not lead to complete equivalence of all hydrogens, but the relatively low energy barrier does suggest that such a tautomerism may be important in this system.

A third possible pathway for intramolecular tautomerism in structure III can be described as a direct transfer of the metal-ring π bonds from one ring to the other (and a similar switch of σ bonds). Such a tautomerism could be particularly important because it *may* be dominated by motions of the relatively light beryllium atom, rather than the cyclopentadiene rings (although the rings must change their relative orientation and undergo some displacement). In fact, a detailed analysis by the technique of linear synchronous transits clearly demonstrated that substantial ring movement is energetically strongly favored and that an intermediate in this motion is the D_{5d} structure. Thus, this tautomerism is best described as a two-step process σ-π → π-π → π-σ, both steps being identical with the σ-π tautomerism discussed above.

It has also been suggested[10] that a similar process may be important in the solid state (structure V), where presumably the rings are fixed and the motion would involve only a beryllium exchange between the two equivalent positions and small readjustments in the cyclopentadiene ring bond lengths and angles. Linear synchronous transit studies on this motion indicate a barrier of 24-31 kcal/mol, but uncertainties in the bond lengths and degree of mobility of the cyclopentadiene rings in the solid state preclude a precise estimate of this barrier. It is, however, unlikely that the barrier is lower than that for σ-π tautomerism in the gas phase because of restriction of movement of the cyclopentadiene rings in the solid.

Population Analysis and Localized Orbitals. Mulliken charges and overlap populations for structures II and III are given in Table III.

To the extent that covalent effects are important in structure II, bonding occurs primarily via overlap of the degenerate p_x and p_y orbitals on beryllium and the $p_z(\pi)$ orbitals on the cyclopentadienyl rings. The p_z orbital on beryllium (of A_{2u} symmetry) is relatively less important for metal-ring bonding

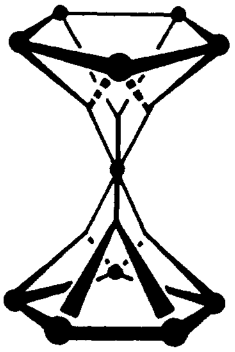
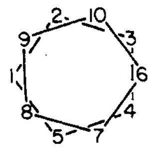


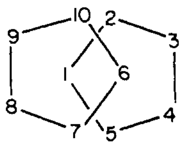
Figure 6. The localized molecular orbitals for structure II.

Table III. Mulliken Charges and Overlap Populations

Structure	Atom[a]	Charge[b]	Bond	Distance, Å	Overlap population[b]
II	Be	−0.09 (+0.17)	Be−C	2.00	0.03 (0.14)
	C_1	−0.07 (−0.09)	C−C	1.40	0.99 (0.97)
	H_1	+0.08 (+0.07)	C−H	1.10	0.79 (0.78)
III	Be	+0.05	Be−C_1	1.87	0.17
	C_1	−0.07	Be−C_2	1.87	0.17
	C_2	−0.07	Be−C_6	1.72	0.68
	C_3	−0.08	Be−C_3	1.87	0.17
	C_6	−0.05	C_1−C_2	1.42	0.94
	C_7	−0.05	C_2−C_3	1.42	0.95
	C_8	−0.09	C_3−C_4	1.42	0.94
	H_1	+0.10	C_6−C_7	1.54	0.77
	H_2	+0.10	C_7−C_8	1.34	1.16
	H_3	+0.09	C_8−C_9	1.46	0.87
	H_6	+0.04			
	H_7	+0.03			
	H_8	+0.03			

[a] The numbering systems are:





[b] The numbers in parentheses are obtained from a population analysis using standard exponents.

because of weak overlap and because there are only two occupied molecular orbitals of the appropriate symmetry in the valence shell. The identical situation prevents significant contributions from the beryllium 2s orbital (of A_{1g} symmetry). It is interesting to note that the formal charge on beryllium in this structure is *negative*. This rather unusual result is directly attributable to the diffuse valence shell orbitals on beryllium, and a population analysis using standard exponents yields a more realistic formal charge of +0.14 on beryllium.

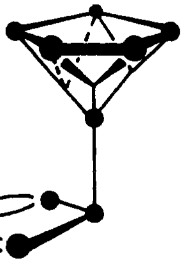


Figure 7. The localized molecular orbitals for structure III.

Localized orbitals for structures II and III are presented in Figures 6 and 7 respectively and summarized in Table IV.

The LMO description of the bonding in the D_{5d} structure (Figure 6) consists of six central three-center C-C-Be orbitals, with one fractional center[21] on each ring. In Figure 6 the fractional centers (denoted by dashed lines) are trans; however, the localization is not unique and other orientations of the two fractional centers can be found when the localization is initiated with a different random unitary matrix.[23] The nonuniqueness of the LMO's and the existence of fractional centers are both expected on the basis of symmetry arguments previously applied to carboranes.[22b] The average hybridization of the six hybrids on beryllium is $sp^{3.19}$, while the average hydridization of carbon orbitals for the LMO's involved in bonding to the central atom is $sp^{15.4}$ (nearly pure p). Hybridizations were calculated by truncating nonlocal contributions, renormalizing, and determining the percent s character in each hybrid orbital.[23]

The LMO analysis of the bonding in structure III indicates that one ring is bound to the beryllium by a reasonably well localized Be-C two-center σ bond and can be described as σ-bonded cyclopentadiene. The second ring is bound by two C-C-Be central three-center bonds and a very delocalized Be-C two-center bond (the delocalization is indicated by the dashed lines). Again, the bonding of this ring to the central atom is primarily through carbon p_z and beryllium p_x and p_y orbitals.

Discussion

The σ-π structure (III) is calculated to be the most stable, followed closely by the structure of D_{5d} symmetry (II); however, the relative energies are too close to allow a definitive determination of the gas-phase structure. Indeed, it seems possible that the gas phase could consist of a mixture of these two structures. Appreciable amounts of II would account for the infrared spectrum, while small amounts of III would account for the dipole moment and the fact that the microwave spectrum is apparently not consistent with a symmetric top molecule. It seems clear that further experimental work is needed to resolve this problem. The molecule may well also be

Table IV. Localized Molecular Orbitals[a]

Structure	Orbital	Populations			Hybridizations[b,c]			Percent delocalization[b]
		Be	C	C	Be	C	C	
II	Be-C_1-C_5	0.42	0.82	0.69	3.02	11.8	10.6	22.3
	Be-C_2-C_3	0.43	0.89	0.56	3.17	14.4	12.2	24.3
	Be-C_3-C_4	0.44	0.35	0.95	3.39	27.6	19.4	28.6
	Be-C_6-C_7	0.43	0.91	0.51	3.20	15.4	12.3	25.1
	Be-C_7-C_8	0.44	0.39	0.95	3.37	20.3	18.6	27.6
	Be-C_9-C_{10}	0.42	0.72	0.80	3.00	10.6	11.3	22.0
III	Be-C_2-C_3	0.41	0.61	0.88	4.05	8.01	9.53	18.1
	Be-C_4-C_5	0.41	0.85	0.66	3.90	8.80	7.77	17.2
	Be-C_6	0.84	1.13		1.27	4.43		16.1
	Be-C_1	0.44	0.95		4.03	12.3		

[a] Only the LMO's involved in ring-beryllium bonding are listed. [b] Reference 24. [c] Hybridizations are given as sp^x.

fluctional. If structure III exists in the gas phase, σ–σ tautomerism probably occurs, and σ–π tautomerism, which results in complete equivalence of all hydrogens, may also be important.

Structure IV is calculated to be 45 kcal/mol less stable than III and can be eliminated as a possible gas-phase structure. The relative energies of structures II, III, and IV can be rationalized in an intuitively simple way. Structure III, the most stable, uses the degenerate $2p_x$ and $2p_y$ orbitals on beryllium for bonding to the π orbitals of one ring and the $2p_z$ and 2s orbitals for σ bonding to the second ring. Structure II, with no σ bonds, makes relatively less use of the beryllium 2s and $2p_z$ orbitals, and structure IV, with 2 σ bonds, makes almost no use of the $2p_x$ and $2p_y$ orbitals. Thus, the stability of structure III is probably associated with the fact that *all* of the atomic orbitals on beryllium are involved in the bonding, while the relative instability of structure IV is attributable to the fact that two of the four valence orbitals are not used at all. Structure II represents an intermediate case in which all orbitals are used, but the $2p_z$ and 2s orbitals contribute considerably less to the bonding than the $2p_x$ and $2p_y$ orbitals (see Results).

The structure of C_{5v} symmetry is not a minimum on the PRDDO energy surface, but using the geometry consistent with the electron diffraction work[4] we estimate this structure to be ~26 kcal/mol less stable than II. Our calculations suggest that this structure is not probable in the gas phase. The relative instability of structure V may be understood in the following way. If the bonding is assumed to be completely ionic, a simple point charge model suggests that the C_{5v} structure defined by the electron diffraction work would be ~3.5 kcal/mol more stable than the D_{5d} structure. However, the height of the D_{5d} "barrier" decreases as the *square* of the charge separation in a simple point charge model, and therefore even small amounts of charge transfer from the rings to the beryllium will substantially lower this "barrier". Certainly some charge transfer is expected solely on the basis of electronegativity differences. Furthermore, the simple point charge model does not take electron repulsion into account, but the electron repulsion term strongly favors the D_{5d} structure and probably dominates any barrier due to charge separation. The failure to explicitly include electron repulsion probably accounts for the earlier theoretical predictions[12,13] that the C_{5v} structure is more stable.

The suggested[9] slipped sandwich structure for the solid state (structure V) appears to be ~14–21 kcal/mol less stable than III (Table II). Geometry optimization will probably substantially lower this value, and intermolecular effects found only in the crystalline phase are almost certainly important.[24] Finally, a LMO analysis of structure V indicates that the molecule contains one π bound and one σ bound ring, rather than two π bound rings as previously suggested.[25]

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