Semi-empirical Molecular Orbital Study of

Dicyclopentadienylberyllium, $(C_5H_5)_2Be$

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The molecule $(C_5H_5)_2Be$ has point group symmetry C_{5v}. A MO study of the twelve electron system with five electrons from each ring and two electrons from the Be atom is made for a number of Be positions on the fivefold rotation axis. The calculations are made in the zero differential overlap approximation with semiempirical choice of parameters. The energy and other properties of the system are investigated as a function of the position of the Be atom. The spectra of one-electron transitions are calculated.

I. INTRODUCTION AND SUMMARY

The molecular structure of gaseous $(C_5H_5)_2Be$ has been determined by electron diffraction by Almenningen *et al.* in 1963.[1] They reported the following data.

As in ferrocene the C_5H_5 rings are parallel and staggered. The ring-ring distance $h = 3.37 \pm 0.03$ Å, a value to be compared with the effective ring thickness of about 3.4 Å for aromatic molecules.[2] Thus there is a repulsion between the two rings. The beryllium atom may occupy two alternative positions on the fivefold rotation axis $h_1 = 1.485 \pm 0.005$ Å from one ring and $h_2 = 1.980 \pm 0.010$ Å from the other. Thus the molecule has point group symmetry C_{5v}. The discrepancy between the values found for h and $(h_1 + h_2)$ Almenningen *et al.* believed to be due to intramolecular motion.

The complex is diamagnetic.[3] $(C_5H_5)_2Be$ solved in benzene has a dipole moment of 2.46 ± 0.06 Debye, and solved in cyclohexane a dipole moment of 2.24 ± 0.09 Debye.[3]

The present investigation is a molecular orbital study of the complex with variation of the position of the Be atom on the axis, z. The semiempirical method used is described in Section II. In Section III explicit expressions are given for the semiempirical parameters used in the calculations. The total electric dipole moment, $\vec{\mu}(z)$, is treated in Section IV. The ground state energy, $E(z)$, is discussed in Section V. The results of the investigation are presented and discussed in Section VI.

The experimental value of z corresponds to a calculated value of $\mu(z_{exp}) = 2.7$ Debye (Table 6). For reasonable values of the parameters in the expression for $E(z)$, it is found that $E(z)$ has a minimum for $z = z_{exp}$ (Table 7 and Fig. 3). Table 8 shows that the theory predicts one band in the near UV for the symmetrical case but two well separated bands in the near UV for the asymmetrical case. Thus it would be of great interest to get experimental information of the UV spectra of the complex, as the spectral measurement might confirm the asymmetrical position of the Be atom found by Almenningen et al. The bands in the near UV can be classified as charge-transfer bands.

II. METHOD

Sandwich complexes with point group symmetry D_{5d}, and especially ferrocene $(C_5H_5)_2Fe$, have previously been treated by SCF MO-calculations.[4-6] A review of sandwich complexes may be found in Refs. 7, 8.

The present paper describes a calculation of the ground state of $(C_5H_5)_2Be$, using the LCAO-SCF approximation with assumed orthogonalized orbital basis and zero differential overlap (ZDO) introduced by Pariser and Parr[4] and Pople.[10] For a discussion of the choice of semiempirical parameters, see Fischer-Hjalmars.[11,12]

The electronic system is considered to be composed of the ten π-electrons of the rings and the two outer electrons of the Be atom. The nuclei and all remaining electrons are referred to as the "core".

The orbitals. In total fourteen AO's of the Slater type are used,

For C_μ: $\chi_\mu(2pz) = \left(\dfrac{\varrho^5}{\pi}\right)^{1/2} r \; e^{-\varrho r} \cos \vartheta; \; (\mu = 1, 2 \ldots 10)$

with $\varrho = 1.56$

For Be: $\chi_{11}(2s) = \left(\dfrac{\xi^5}{3\pi}\right)^{1/2} r \; e^{-\xi r}$

$\chi_{12}(2pz) = \left(\dfrac{\eta^5}{\pi}\right)^{1/2} r \; e^{-\eta r} \cos \vartheta$

$\chi_{13}(2px) = \left(\dfrac{\eta^5}{\pi}\right)^{1/2} r \; e^{-\eta r} \sin \vartheta \cos \varphi$

$\chi_{14}(2py) = \left(\dfrac{\eta^5}{\pi}\right)^{1/2} r \; e^{-\eta r} \sin \vartheta \sin \varphi$

where

$$\xi = 0.966 \text{ and } \eta = 0.858$$

are chosen as the arithmetic mean of the orbital exponents for the configurations $(2s)^2$, $(2s, 2p)$ and $(2p)^2$ as determined by Roothaan in 1955.[13] Roothaan determined a $2s$-orbital with node. Here ξ is chosen to give a corresponding nodeless $2s$-orbital.

The geometrical arrangement of the complex and the notations used for distances and angles are shown in Fig. 1.

In Table 1 are listed the real symmetry orbitals (SO's) of $(C_5H_5)_2Be$.
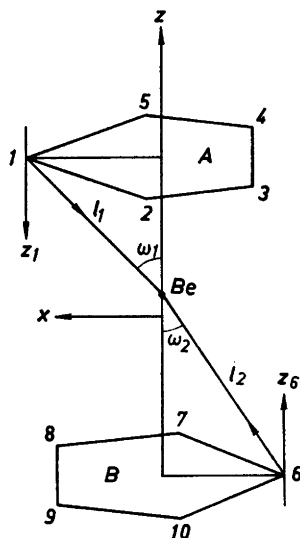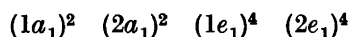
Fig. 1. The geometrical arrangement of the complex and the notations used for distances and angles.

As the complex is diamagnetic,[3] the ground state configuration must be of the form:

$$(1a_1)^2 \quad (2a_1)^2 \quad (1e_1)^4 \quad (2e_1)^4$$

where the MO's $(1\,a_1)$, $(2\,a_1)$, *etc.* are linear combinations of the SO's of the same symmetry, given in Table 1.

III. THE MATRIX ELEMENTS OF THE FOCK OPERATOR

The ground state of the molecule is described by a single determinant composed of doubly occupied molecular orbitals. In the LCAO approximation, where the MO's φ_i are expressed as

$$\varphi_i = \sum_\mu c_{i\mu}\, \chi_\mu \tag{1}$$

the SCF Hartree-Fock equations are expressed as a set of non-linear algebraic equations

$$\sum_\nu F_{\mu\nu}\, c_{i\nu} = \varepsilon_i \sum_\nu S_{\mu\nu}\, c_{i\nu} \tag{2}$$

where

$$S_{\mu\nu} = \langle \mu | \nu \rangle \tag{3}$$

$$F_{\mu\nu} = H_{\mu\nu}{}^c + \sum_\lambda \sum_\sigma P_{\lambda\sigma} \left\{ \langle \mu\lambda | \frac{1}{r_{12}} | \nu\sigma \rangle - \tfrac{1}{2}\langle \mu\lambda | \frac{1}{r_{12}} | \sigma\nu \rangle \right\} \tag{4}$$

$$H_{\mu\nu}{}^c = \langle \mu | T + U^c | \nu \rangle \tag{5}$$

Table 1. Symmetry orbitals of $(C_5H_5)_2Be$.

Symmetry	SO ($\alpha = 2\pi/5$)
a_1	$\sigma_1 = \chi_{11}$ $\sigma_2 = \chi_{12}$ $\sigma_3 = \dfrac{1}{\sqrt{5}}\,(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5)$ $\sigma_4 = \dfrac{1}{\sqrt{5}}\,(\chi_6 + \chi_7 + \chi_8 + \chi_9 + \chi_{10})$
e_1	$\sigma_5 = \chi_{13}$ $\sigma_6 = \chi_{14}$ $\sigma_7 = \dfrac{\sqrt{2}}{5}\,(\chi_1 + \chi_2\cos\alpha + \chi_3\cos2\alpha + \chi_4\cos2\alpha + \chi_5\cos\alpha)$ $\sigma_8 = \dfrac{\sqrt{2}}{5}\,(\chi_2\sin\alpha + \chi_3\sin2\alpha - \chi_4\sin2\alpha - \chi_5\sin\alpha)$ $\sigma_9 = \dfrac{\sqrt{2}}{5}\,(\chi_6 + \chi_7\cos\alpha + \chi_8\cos2\alpha + \chi_9\cos2\alpha + \chi_{10}\cos\alpha)$ $\sigma_{10} = \dfrac{\sqrt{2}}{5}\,(\chi_7\sin\alpha + \chi_8\sin2\alpha - \chi_9\sin2\alpha - \chi_{10}\sin\alpha)$
e_2	$\sigma_{11} = \dfrac{\sqrt{2}}{5}\,(\chi_1 + \chi_2\cos2\alpha + \chi_3\cos\alpha + \chi_4\cos\alpha + \chi_5\cos2\alpha)$ $\sigma_{12} = \dfrac{\sqrt{2}}{5}\,(\chi_2\sin2\alpha - \chi_3\sin\alpha + \chi_4\sin\alpha - \chi_5\sin2\alpha)$ $\sigma_{13} = \dfrac{\sqrt{2}}{5}\,(\chi_6 + \chi_7\cos2\alpha + \chi_8\cos\alpha + \chi_9\cos\alpha + \chi_{10}\cos2\alpha)$ $\sigma_{14} = \dfrac{\sqrt{2}}{5}\,(\chi_7\sin2\alpha - \chi_8\sin\alpha + \chi_9\sin\alpha - \chi_{10}\sin2\alpha)$

$$P_{\lambda\sigma} = 2 \sum_{\substack{i \\ \text{all} \\ \text{occupied} \\ \text{MO}}} c_{i\lambda}\, c_{i\sigma} \qquad (6)$$

$$\langle \mu\lambda | \frac{1}{r_{12}} | \nu\sigma \rangle = (\mu\nu | \lambda\sigma) \qquad (7)$$

The following approximations and assumptions are made in order to simplify the evaluation of matrix elements:

1) *ZDO approximation*

$$S_{\mu\nu} = \delta_{\mu\nu} \tag{8}$$

$$(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma} \ (\mu\mu|\lambda\lambda) = \delta_{\mu\nu}\delta_{\lambda\sigma}\gamma_{\mu\lambda} \tag{9}$$

As a check on the accuracy, calculations were also performed with non-zero values of the exchange integrals for AO's on Be. The results showed, that these exchange integrals could be safely neglected.

2) *Only one-center and two-center integrals are considered*

3) *Approximations of $\alpha_\mu = \langle\mu|H^c|\mu\rangle$*

a) For AO's localized on carbon atoms ($\mu = 1-10$):

$$\alpha_\mu = W(\mu) - \sum_{\substack{\nu=1 \\ \nu\neq\mu}}^{10} (\gamma_{\mu\nu}) + \langle\mu|U_{Be}{}^{++}|\mu\rangle \tag{10}$$

$$W(\mu) = \langle\mu|T + U_{C\mu}{}^{+}|\mu\rangle + \langle\mu|\sum_{\substack{\nu=1 \\ \nu\neq\mu}}^{10} U_{C\nu}{}^{\circ}|\mu\rangle \tag{11}$$

The value of $W(\mu)$ is chosen in accordance with calculations and estimations made by Fischer-Hjalmars [11]

$$W(\mu) = -0.3525 \text{ a.u.}$$

$\langle\mu|U_{Be}{}^{++}|\mu\rangle$ is calculated as $\langle\mu|-2/r_{Be}|\mu\rangle$

b) For AO's localized on the beryllium atom ($\mu = 11-14$):

$$\alpha_\mu = W(\mu) - \sum_{\nu=1}^{10} (\gamma_{\mu\nu}) \tag{12}$$

The values of $W(\mu)$ are obtained from atomic valence state ionization potentials.[14]

$$W(11) = \langle2s|T + U_{Be}{}^{++}|2s\rangle + \text{(neglected penetration terms)} \tag{13}$$

$$\langle2s|T + U_{Be}{}^{++}|2s\rangle = -\text{IP}\ (sx \to x)) - \gamma_{11,12} + \tfrac{1}{2}(11,12,|11,12) \tag{14}$$

In the same manner:

$$W(12) = W(13) = W(14) = -\text{IP}(sx \to s) - \gamma_{11,12} + \tfrac{1}{2}(11,12|11,12) \tag{15}$$

$$\text{IP}(sx \to x) = 0.3591 \text{ a.u.}$$
$$\text{IP}(sx \to s) = 0.2135 \text{ a.u.}$$

4) *Approximations of $\beta_{\mu\nu} = \langle\mu|H^c|\nu\rangle$; $\mu \neq \nu$*

All $\beta_{\mu\nu}$'s between nonadjacent carbon atoms are supposed to be zero in accordance with the ZDO approximation. In all other cases the simple Mulliken [15] assumption,

$$\beta_{\mu\nu} = k\ S_{\mu\nu} \tag{16}$$

is used, with $k = -0.326$ a.u., a value of k, that gives a value of $\beta_{CC} = -2.39$ eV for nearest neighbours in benzene. $S_{\mu\nu}$ are calculated; see appendix.

5) *One-center two-electron integrals*
For the carbon atoms, a value
$$\gamma_{\mu\mu} = 11.81 \text{ eV}^{11} \ (\mu = 1-10)$$
has been adopted.

For $\gamma_{11,11}$ and $\gamma_{12,12}$ the assumption of Pariser [16]

$$\gamma_{\mu\mu} = IP_\mu - A_\mu \tag{17}$$

has been applied. In (17) IP_μ is the valence state ionization potential and A_μ is the valence state electron affinity. The values of IP_μ and A_μ have been obtained from the tables of Pilcher and Skinner.[14]

For $\gamma_{11,12}$, the following assumption is used:

$$\frac{(\gamma_{11,12})_{exp}}{(\gamma_{11,12})_{theor}} = \tfrac{1}{2} \left[\frac{(\gamma_{11,11})_{exp}}{(\gamma_{11,11})_{theor}} + \frac{(\gamma_{12,12})_{exp}}{(\gamma_{12,12})_{theor}} \right] \tag{18}$$

$$\gamma_{12,13} = \frac{447}{501} \gamma_{12,12} \tag{19}$$

The value of $(11,12|11,12)$ has been obtained from Pilcher and Skinner's data [14]

$$(12,13|12,13) = \frac{27}{501} \gamma_{12.12} \tag{20}$$

The parameter values are collected in Table 2.
6) *Two-center two-electron integrals*
These integrals are chosen differently for different internuclear ranges.
Let R' be the distance between the two centers for which

$$\gamma_{\mu\nu}(R') = \tfrac{1}{2} \gamma_{\mu\nu}(0)$$

For $R \geq R'$, theoretical values, obtained from the tables of Sahni and Cooley,[17] have been used. For further details, see appendix. For $R \leq R'$, $\gamma_{\mu\nu}$ has been determined by a fourth degree approximation formula [18]

$$\gamma_{\mu\nu}(R) = \gamma_{\mu\nu}(0) + aR^2 + bR^3 + cR^4 \tag{21}$$

The parameter values $\gamma_{\mu\nu}(0)$, where μ belongs to a C-atom and ν to Be, are given in Table 3.

Table 2. Parameter values of one-center two-electron integrals. Section II, 5.

Parameter	Parameter value in a.u.
γ_{11}	0.4340
$\gamma_{11,11}$	0.2506
$\gamma_{12,12}$	0.2076
$\gamma_{11,12}$	0.2200
$\gamma_{12,13}$	0.1853
$(11,12|11,12)$	0.0529
$(12,13|12,13)$	0.0112

Table 3. Parameter values for two-center two-electron integrals. Section II, 6.

Parameter	Parameter value in a.u.
$\gamma_{1,11}(0) = \frac{1}{2}[(2s2s|2p2p)_{Be} + (2s2s|2p2p)_C]$	0.3141
$\gamma_{1,12}(0) = \frac{1}{2}[(2p2p|2p2p)_{Be} + (2p2p|2p2p)_C]$	0.3208
$\gamma_{1,13}(0) = \frac{1}{2}[(2p_z2p_z|2p_x2p_x)_{Be} + (2p_z2p_z|2p_xp_x)_C]$	0.2863

IV. THE DIPOLE MOMENT

The total electric dipole moment can be written as

$$\vec{\mu} = \vec{\mu}_{el} + 2\,e\,z_{Be}\hat{z} + \vec{\mu}_{core} \tag{22}$$

$$\vec{\mu}_{el} = -\,2\,e\,\Big\{ \sum_{\substack{i \\ all \\ filled \\ MO}} \sum_{\mu} c_{\mu i}^2 z_\mu + (c_{11,1}\,c_{12,1} + c_{11,2}\,c_{12,2})\,\langle 11|z|12\rangle \Big\}\,\hat{z} \tag{23}$$

$$\vec{\mu}_{core} = [5\,(\mu_{1z} + \mu_{6z}) + \mu_B]\,\hat{z} \tag{24}$$

$$\vec{\mu}_1 = \vec{\mu}_{C_1^+} = \alpha_1 \vec{E}_1$$

$$\vec{\mu}_6 = \vec{\mu}_{C_6^+} = \alpha_1 \vec{E}_6 \tag{25}$$

$$\vec{\mu}_B = \vec{\mu}_{Be^{++}} = \alpha_2\,\vec{E}_{Be}$$

α_1 and α_2 are the polarizabilities of the ions. A very rough estimate of α_1 is

$$\alpha_1 = \frac{1}{2}(\alpha_C + \alpha_{C^{++}}) = \frac{1}{2}(0.93 + 0.67)\,\text{Å}^3 = 0.80\,\text{Å}^3 \text{ (Ref. 19, 20)}$$

$$\alpha_2 = 0.00825\,\text{Å}^3 \text{ (Ref. 21)}$$

$\vec{E}_1$ is the electrostatic field at C_1^+ arising from the point charge $+\,2\,e$ of Be^{++} and the induced dipole moment, $\vec{\mu}_{Be^{++}}$.

V. THE GROUND STATE ENERGY

The part of the total energy of the system of interest in this case can be written as

$$E = E_{el} + E_{core} \tag{26}$$

where E_{el} is the electronic energy of the twelve outer electrons. E_{core} is the core-core repulsion energy. E_{core} is a "non-bonding" interaction between ions.

$$E_{core} = E_{el-stat} + E_{repuls} + E_{disp} \tag{27}$$

$E_{el\text{-}stat}$ is the purely electrostatic interaction between the ions.[22] E^r_{repuls} includes the repulsion terms of the exponential form, $A\, e^{-\varrho r}$. For $C^+ - Be^{++}$ the parameter ϱ has been chosen as 2.42 a.u.[23] E_{disp} is the London dispersion energy of the form $B\, r^{-6}$. The Slater-Kirkwood formula [23,24] is used.

$$B = -\frac{3\,\alpha_1\alpha_2}{2\,[(\alpha_1/N_1)^{\frac{1}{2}} + (\alpha_2/N_2)^{\frac{1}{2}}]} \qquad (28)$$

where N_1 and N_2 are effective numbers of outer-shell electrons.

For $C^\circ - Be^\circ$ a value of $A = 317$ a.u. is obtained by minimizing the non-bonded potential function, $A\, e^{-\varrho r} - B\, r^{-6}$ at $r = (r_{wC} + r_{wBe})$, where r_{wC} and r_{wBe} are the van der Waals radii for the atoms C and Be. For $C^+ - Be^{++}$ one can expect a value of $A > 317$, as this system has a more contracted electron cloud and thus a stronger repulsion. Since it is difficult to guess the correct value of A the calculations have been carried out for some reasonable values, i.e. $A = 317, 400, 500,$ and 600 a.u.

VI. RESULTS

The computations have been performed on the UNIVAC 1107 by means of a SCF-CI program written by Mr. Peter Eisenberger and Mr. Torbjörn Alm. Ten different values of the Be position, z, have been considered. ($z = 0, 0.1, 0.2 \ldots 0.9$ Å).

The calculations were started with a set of coefficients obtained from simple Hückel calculations.
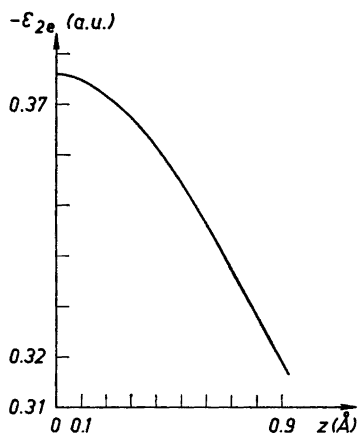

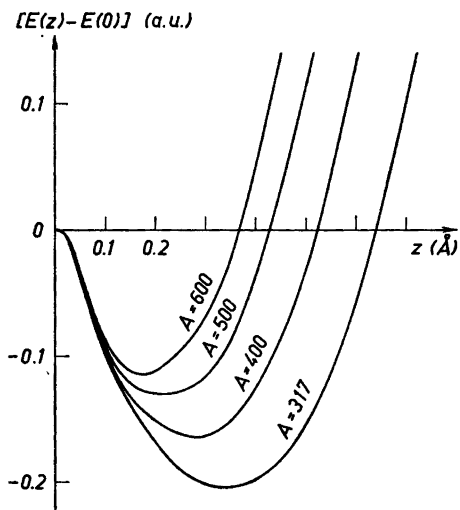Fig. 2. The energy of the highest filled MO as a function of z.

Fig. 3. $[E(z) - E(0)]$ for four different values of A.

Table 4. Molecular orbitals of $(C_5H_5)_2Be$ for four different values of the Be position, z. $z = 0$ is the symmetrical position (cf. Fig. 1).

Symmetry	MO, Form, Energy (a.u.)			
	$z = 0$	$z = 0.2$ Å	$z = 0.4$ Å	$z = 0.9$ Å
$1a_1$	$0.5387\sigma_1 + 0.5975(\sigma_3 + \sigma_4)$ $\varepsilon = -0.6806$	$0.5217\sigma_1 - 0.0213\sigma_2 +$ $+ 0.7233\sigma_3 + 0.4519\sigma_4$ -0.6881	$0.4769\sigma_1 - 0.0717\sigma_2 +$ $+ 0.8084\sigma_3 + 0.3376\sigma_4$ -0.7097	$0.2865\sigma_1 - 0.2752\sigma_2 +$ $+ 0.0934\sigma_3 + 0.1614\sigma_4$ -0.8129
$2a_1$	$0.3391\sigma_2 + 0.6652(\sigma_3 - \sigma_4)$ -0.5797	$-0.0737\sigma_1 + 0.3285\sigma_2 +$ $+ 0.5433\sigma_3 - 0.7690\sigma_4$ -0.5742	$-0.1196\sigma_1 + 0.2983\sigma^2 +$ $+ 0.4430\sigma_3 - + 0.8369\sigma_4$ -0.5592	$-0.2015\sigma_1 + 0.1717\sigma_2 +$ $+ 0.2809\sigma_3 - 0.9226\sigma_4$ -0.5017
$1e_1a$	$0.5303\sigma_5 + 0.5995(\sigma_7 - \sigma_9)$ -0.4914	$0.5084\sigma_5 + 0.7657\sigma_7 -$ $- 0.3941\sigma_9$ -0.5018	$0.4582\sigma_5 + 0.8522\sigma_7 -$ $- 0.2362\sigma_9$ -0.5282	$0.3348\sigma_5 + 0.9406\sigma_7 -$ $- 0.0562\sigma_9$ -0.6071
$2e_1a$	$0.7071(\sigma_7 + \sigma_9)$ -0.3758	$-0.1175\sigma_5 + 0.5151\sigma_7 +$ $+ 0.8491\sigma_9$ -0.3717	$-0.1878\sigma_5 + 0.3521\sigma_7 +$ $+ 0.9150\sigma_9$ -0.3615	$-0.2368\sigma_5 + 0.1525\sigma_7 +$ $+ 0.9595\sigma_9$ -0.3187
$3a_1$	$-0.8425\sigma_1 + 0.3809(\sigma_3 +$ $+ \sigma_4)$ $+0.0072$	$-0.6736\sigma_1 - 0.6082\sigma_2 +$ $+ 0.4093\sigma_3 + 0.0939\sigma_4$ -0.0113	$-0.7276\sigma_2 - 0.5881\sigma_2 +$ $+ 0.3444\sigma_3 + 0.0778\sigma_4$ -0.0351	$-0.8850\sigma_1 - 0.4215\sigma_2 +$ $+ 0.1250\sigma_3 + 0.1529\sigma_4$ -0.0920
$4a_1$	$-0.9407\sigma_2 + 0.2398(\sigma_3 -$ $- \sigma_4)$ $+0.0100$	$-0.5180\sigma_1 + 0.7226\sigma_2 +$ $+ 0.1189\sigma_3 + 0.4422\sigma_4$ $+0.0245$	$-0.4784\sigma_1 + 0.7483\sigma_2 +$ $+ 0.1699\sigma_3 + 0.4266\sigma_4$ $+0.0386$	$-0.3066\sigma_1 + 0.8468\sigma_2$ $+ 0.2987\sigma_3 + 0.3157$ $+0.0854$
$3e_1a$	$-0.8478\sigma_5 + 0.3750(\sigma_7 -$ $- \sigma_9)$ $+0.0729$	$-0.8531\sigma_5 + 0.3853\sigma_7 -$ $- 0.3518\sigma_9$ $+0.0718$	$-0.8665\sigma_5 + 0.3826\sigma_7 -$ $- 0.3203\sigma_9$ $+0.0683$	$-0.9124\sigma_5 + 0.3070\sigma_7$ $- 0.2707\sigma_9$ $+0.0419$
$1e_2a$	$0.7071(\sigma_{11} - \sigma_{13})$ $+0.0827$	$0.9997\sigma_{11} - 0.0241\sigma_{13}$ $+0.0551$	σ_{11} $+0.0183$	σ_{11} -0.0855
$2e_2a$	$0.7071(\sigma_{11} + \sigma_{13})$ $+0.0852$	$0.0241\sigma_{11} - 0.9997\sigma_{13}$ $+0.1053$	σ_{13} $+0.1221$	σ_{13} $+0.1652$

Table 5. The charge distribution in $(C_5H_5)_2Be$.

z (Å)	$(C_5H_5)_A$	$(C_5H_5)_B$	Be
0	-0.0323	-0.0323	$+0.0646$
0.1	-0.0264	-0.0552	$+0.0816$
0.2	-0.0428	-0.0963	$+0.1391$
0.3	-0.0765	-0.1472	$+0.2237$
0.4	-0.1275	-0.2065	$+0.3340$
0.5	-0.1883	-0.2677	$+0.4555$
0.6	-0.2502	-0.3250	$+0.5752$
0.7	-0.3210	-0.3846	$+0.7056$
0.8	-0.3740	-0.4299	$+0.8139$
0.9	-0.4131	-0.4596	$+0.8727$

Table 6. The values of $E_{el}(z)$ of eqn. 26 in a.u. and $\mu(z)$ of eqn. 22 in Debye units.

z (Å)	E_{el}	μ	μ_{core}
0	-20.3351	0	0
0.1	-20.3363	1.4	0.8
0.2	-20.3391	2.7	1.6
0.3	-20.3447	4.1	2.4
0.4	-20.3522	5.6	3.2
0.5	-20.3620	7.0	3.9
0.6	-20.3748	8.3	4.5
0.7	-20.3841	9.7	5.1
0.8	-20.3955	10.9	5.5
0.9	-20.4063	11.7	5.7

Table 7. The values of $[E(z) - E(0)]$ of Section V for four different values of A.

z (Å)	$[E(z) - E(0)]$ (a.u.)			
	$A = 317$	$A = 400$	$A = 500$	$A = 600$
0	0	0	0	0
0.1	-0.101	-0.097	-0.092	-0.087
0.2	-0.168	-0.151	-0.131	-0.111
0.3	-0.202	-0.163	-0.115	-0.068
0.4	-0.198	-0.125	-0.037	$+0.051$
0.5	-0.152	-0.031	$+0.115$	$+0.260$
0.6	-0.057	$+0.128$	$+0.351$	$+0.573$
0.7	$+0.100$	$+0.369$	$+0.692$	$+1.015$
0.8	$+0.319$	$+0.693$	$+1.143$	$+1.593$
0.9	$+0.605$	$+1.107$	$+1.712$	$+2.317$

Table 8. Calculated spectrum of $(C_5H_5)_2Be$. ($\perp$ means perpendicular to the five-fold axis of the molecule.)

Transition	z = 0			z = 0.1 Å			z = 0.2 Å (exp. value)			z = 0.3 Å			z = 0.4 Å		
	ν (cm⁻¹)	f	pol.	ν	f	pol.	ν	f	pol.	ν	f	pol.	ν	f	pol.
$^1A_1 - {}^1E_1$	32305	0.01	$\perp$	30893	0.005	$\perp$	28725	0.004	$\perp$	26060	0.002	$\perp$	23034	0.001	$\perp$
$^1A_1 - {}^1E_1$	33119	0		34116	0.004	$\perp$	35251	0.004	$\perp$	36232	0.004	$\perp$	37303	0.003	$\perp$
$^1A_1 - {}^1E_2$	46295	0		46254	0		45731	0		44826	0		42708	0	
$^1A_1 - {}^1E_2$	47418	0		47282	0		46862	0		46255	0		45722	0	
$^1A_1 - {}^1E_2$	48689	0		48722	0		48522	0		48278	0		47639	0	
$^1A_1 - {}^1A_2$	48728	0		48776	0		48534	0		48213	0		47731	0	
$^1A_1 - {}^1E_1$	56239	0.09	$\perp$	54923	0.049	$\perp$	53259	0.041	$\perp$	51385	0.045	$\perp$	48121	0.052	$\perp$

The final form of the MO's and the orbital energies are given in Table 4 for four values of z. The energies of the highest filled orbital are shown in Fig. 2 as a function of z. The charge distribution in the complex is given in Table 5. In Table 6 the values of $E_{el}(z)$ and $\mu(z)$ are given. $E_{el}(z)$ has a very flat maximum for $z = 0$. The experimental value of z corresponds to a value of $\mu(z) = 2.7$ Debye, in good agreement with the experimental values of $\mu(z) = 2.24 - 2.46$ Debye. In Table 7 and Fig. 3 the values of $[E(z) - E(0)]$ are given for four different values of the parameter A in E_{repuls}. In $[E(z) - E(0)]$ the dominant term is $[E_{core}(z) - E_{core}(0)]$ and thus the shape of the curve depends strongly on the values of the parameters A and α_1. For $A \sim 500$, there is a minimum of $E(z)$ at $z = z_{exp}$.

In order to find a more conclusive answer to the question which z-value will minimize the energy $E(z)$, a more refined model must be used. From the present calculation one can only draw the conclusion thet there might be a minimum of $E(z)$ for $z = z_{exp}$.

The energies of the excited states have been calculated with configurational interaction where all singly excited states have been included. The lowest singlet-singlet transitions of $(C_5H_5)_2Be$ are given in Table 8. The present investigation shows that there is one band in the near UV for the symmetrical case and two well separated bands in the near UV for the asymmetrical case. For these bands the theory predicts low but yet observable f-values. Thus it would be of great interest to know the measured UV-spectra of $(C_5H_5)_2Be$, but as far as is known to the author there are no published experimental data on the electronic spectra of this complex.

The theory further predicts several strongly allowed bands in the far UV. The excited states, $^1E_1$, corresponding to the bands in the near UV are essentially obtained by excitation of a $2e_1$-electron to the $3a_1$ and $4a_1$ orbitals. According to Tables 1 and 4, that means, that the electron goes over from an orbital almost completely localized on the rings to an orbital almost completely localized on the Be atom. Thus one may classify these bands as charge-transfer bands.

APPENDIX

The evaluation of $S_{\mu\nu}$ and two-center $\gamma_{\mu\nu}$, where μ and ν are not on the same ring, requires a transformation into a new coordinate system.[25] According to Fig. 4 one gets for instance
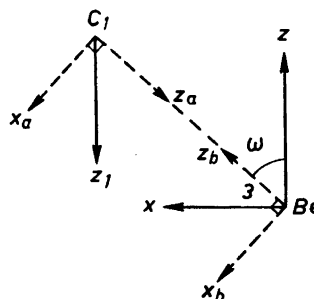

Fig. 4. The notations used for the evaluation of $S_{\mu\nu}$ and $\gamma_{\mu\nu}$.

$$\gamma_{1,11} = \cos^2\omega(z_a z_a | s_b s_b) + \sin^2\omega(x_a x_a | s_b s_b); \tag{29}$$

$$\gamma_{1,12} = \cos^4\omega(z_a z_a | z_b z_b) + \sin^4\omega(x_a x_a | x_b x_b) + \tag{30}$$
$$+ \sin^2\omega \cos^2\omega[(z_a z_a | x_b x_b) + (x_a x_a | z_b z_b)];$$

$$\gamma_{1,13} = \cos^2\omega \sin^2\omega[(z_a z_a | z_b z_b) + (x_a x_a | x_b x_b)] + \tag{31}$$
$$+ \cos^4\omega(z_a z_a | x_b x_b) + \sin^4\omega(x_a x_a | z_b z_b);$$

where s, x and z stands for $2s$, $2px$ and $2pz$. In the same manner:

$$\gamma_{1,6} = \cos^4\omega_1(z_a z_a | z_b z_b) + \sin^4\omega_1(x_a x_a | x_b x_b) + \tag{32}$$
$$+ 2 \sin^2\omega_1 \cos^2\omega_1(z_a z_a | x_b x_b);$$

where ω_1 is the angle between the z-axis and the C_1—C_6 direction.

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