

# The Dynamics of Low-lying Excited States of Benzene: the Biradicaloid Structure of the $S_2$ State

Matthias Meisl and Rudolf Janoschek\*

Institut für Theoretische Chemie, Karl-Franzens-Universität Graz, A-8010 Graz, Austria

An *ab initio* SCF–CI optimized biradicaloid structure of the  $S_2$  state of benzene shows  $C_s$  symmetry and allows a mechanism for the photochemical conversion into Dewar benzene to be proposed.

The excitation of benzene to its second excited singlet state ( $^1B_{1u}$ ) upon irradiation ( $\lambda_{\max}$ , 203 nm) leads directly to bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene).<sup>1</sup> This photochemical reaction is of particular interest in so far as it occurs from an excited singlet state which, though not the lowest, is non-dissociative.

The low-lying states of benzene have been the subject of numerous computational studies. These were concerned mainly with the vertical transition energies of  $S_0 \rightarrow S_n$ . In particular, that to  $S_2$  turned out to lie in the range 5.2–9.7 eV by the use of semi-empirical procedures as well as by *ab initio* SCF–CI treatments, whereas the experimental value is 6.3 eV.<sup>2</sup> Furthermore,  $D_{6h}$  structures of so-called spectroscopic minima were suggested for the states  $S_1$  and  $S_2$  where the C–C bond lengths are increased from 140 to 143–144 pm.<sup>2,3</sup>

A biradicaloid structure (1) is assumed for qualitative considerations of the photochemistry of benzene in its  $S_2$  state.<sup>4</sup>  $S_2$  ( $^1B_{1u}$ ) of benzene correlates with the  $^1B_2$  state of Dewar benzene. Simple valence-bond considerations rule out a  $C_{2v}$  structure of this state by the following arguments. The excitation of an olefinic double bond causes a torsion of the methylene fragments out of planarity so that a zwitterionic structure is achieved. If this behaviour is applied to Dewar benzene the hitherto assumed  $C_{2v}$  symmetry should be reduced to  $C_s$  (2).

This communication reports the results of an application of an *ab initio* SCF-limited CI (4-31G basis set) computation<sup>5</sup> on the  $S_0$ ,  $S_1$ ,  $S_2$ , and  $T_1$  energy hypersurfaces of  $C_6H_6$  in  $D_{6h}$ ,  $C_{2v}$ , and  $C_s$  symmetries. The optimized geometry and the electronic structure of the biradicaloid minimum of the  $S_2$  state allows a mechanism for photochemical conversion of benzene into Dewar benzene to be proposed.

The calculated low-lying singlet and triplet states of benzene, Dewar benzene, and the corresponding biradicaloid structure are presented in their energetic ordering in Figure 1. The biradicaloid structure of  $S_2$  is optimized in  $C_s$  symmetry; geometric data are presented in Table 1. The presence of a real minimum is proven by showing that it has only zero first derivatives and positive force constants. The symmetry

reduction  $C_{2v} \rightarrow C_s$  causes an avoided crossing of two  $^1A'$  states which correlate with  $^1E_{2g}$  and  $^1B_{1u}$  ( $S_2$ ), respectively, of benzene, according to the symmetry reduction scheme in Table 2.

Thus, the  $S_2$  state goes smoothly on to the  $S_1$  surface so that a non-adiabatic process can lead to ground-state Dewar benzene. The steep ascent of the  $S_1$  ( $^1B_{2u}$ ) state, which is  $^1A'$  in  $C_s$  symmetry, prevents its conversion into Dewar benzene. Thermal decomposition of Dewar benzene to benzene is accompanied by luminescence ( $T_1 \rightarrow S_0$ ).<sup>4d</sup> The necessary intersystem crossing,  $S_0 \rightarrow T_1$ , is energetically accessible at the transition structure. The symmetry reduction  $C_{2v} \rightarrow C_s$  also reduces the ground state energy barrier, which now corresponds to a saddle point, by 26 kJ/mol, in agreement with the qualitative prediction from an orbital symmetry analysis.<sup>8</sup> An improved picture of the biradical (1) rests on the elongation of the C–C double bonds from 132 to 137 pm and their twisting of  $5^\circ$ . Thus, the depiction of  $S_2$  as a fully localized biradical does not adequately describe its electronic structure, which retains some of the delocalization characteristic of benzene in its ground state.

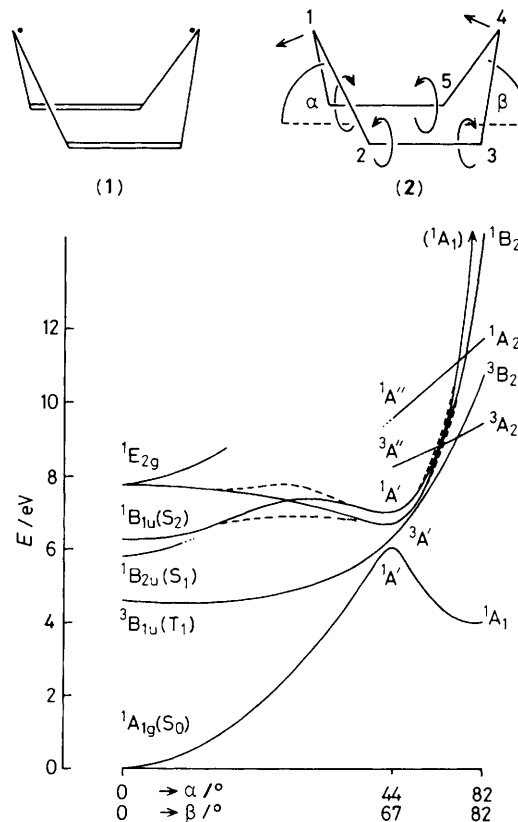


Figure 1. Calculated low-lying singlet and triplet states of benzene (ground state geometry;  $^1E_{2g}$  is taken from ref. 6), Dewar benzene (ground state geometry<sup>7</sup>), and the corresponding biradicaloid structure (optimization of  $S_2$  in  $C_s$  symmetry). The angles  $\alpha$  and  $\beta$  are defined in structure (2).

Table 1. Geometric data<sup>a</sup> of the biradicaloid structure of the  $S_2$  state of benzene ( $C_s$  symmetry).

Distances/pm				Angles/ $^\circ$			
1–2	3–4	2–3	1–4	$\alpha$	$\beta$	3–4–5	1–2–3–4 <sup>b</sup>
146	145	137	221	44	67	117	5

<sup>a</sup> Only data of the carbon skeleton are listed. <sup>b</sup> Dihedral angle.

Table 2. Symmetry reduction scheme.

$D_{6h}$	$\rightarrow$	$C_{2v}$	$\rightarrow$	$C_s$
$^1E_{2g}$	$\rightarrow$	$\begin{cases} ^1A_1 \\ ^1A_2 \end{cases}$	$\rightarrow$	$^1A'$
$^1B_{1u}$	$\rightarrow$	$^1B_2$	$\rightarrow$	$^1A'$

The authors are indebted to the Fonds zur Förderung der wissenschaftlichen Forschung, Austria, for financial support. The computer time made available by the Rechenzentrum der Universität Graz is gratefully acknowledged.

Received, 22nd April 1986; Com. 540

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