

Conformational Instability of the Lowest Triplet State of Benzene: The Result of ab Initio Calculations

W. J. Buma,^{*,†} J. H. van der Waals,[†] and M. C. van Hemert[†]

Contribution from the Center for the Study of Excited States of Molecules, Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands, and Department of Chemistry, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. Received June 14, 1988

Abstract: Experiments on the $^3B_{1u}$ state of benzene in the past have established that this state is conformationally unstable due to vibronic coupling with the $^3E_{1u}$ state and that this instability is critically dependent on the influence of a crystal field and substituents. For the $^3B_{1u}$ state of the free molecule, however, the energy differences and sizes of distortion are not known. Since these quantities are of importance for the interpretation of the spectroscopic and photochemical behavior of benzene, the potential energy surface of the $^3B_{1u}$ state along the two-dimensional deformation coordinate S_8 was calculated with large ab initio MRDCI calculations, including σ - σ and σ - π correlation. The results show the hexagonal conformation to be unstable and to lie 800 cm^{-1} above an almost cylindrical trough. Calculation of spectroscopic observables yields good agreement with the experimentally observed vibrational spacing and Franck-Condon factors.

The geometry of benzene in its lowest triplet state ($^3B_{1u}$) has received considerable attention since Moffitt and Liehr pointed out that, in a static picture, the hexagonal conformation might be unstable because of vibronic coupling between the $^3B_{1u}$ and $^3E_{1u}$ states through e_{2g} modes.¹ Low-temperature EPR experiments on benzene in a glassy matrix^{2a} and subsequent EPR^{2b} and ENDOR^{2c} experiments on the C_6H_6 in C_6D_6 crystal established that in the solid state the electron spin distribution in the $^3B_{1u}$ state, indeed, is nonhexagonal. Spectroscopic observations³ supported this result; most remarkable amongst these was the strong doublet, $245 \pm 6\text{ cm}^{-1}$ above the 0-0 in the $^3B_{1u} \leftarrow A_{1g}$ absorption spectrum of the C_6H_6 in C_6D_6 crystal.^{3f} The idea that this feature corresponds to ν_8 , at 1584 cm^{-1} in the ground state, was corroborated by Zeeman studies.^{3h,3i} The EPR experiments further revealed that the size and even the kind of distortion are critically dependent on the nature of the environment into which benzene is incorporated.⁴

A large number of calculations on vibronic coupling in the $^3B_{1u}$ state have been made, which helped the qualitative interpretation of spectroscopic and EPR results.⁵ Because of their semiempirical nature, however, no clear picture exists of the energy differences and sizes of distortion involved in the deformation of the free molecule in the $^3B_{1u}$ state.

In view of its importance for the interpretation of the spectroscopic and photochemical behavior of benzene, we have performed ab initio configuration interaction (CI) calculations to determine the $^3B_{1u}$ potential energy surface as a function of the S_8 coordinate. A detailed account of these calculations and of the effects of a crystal field and substituents will be given elsewhere. Here, we report the principal conclusions regarding the free molecule. The calculation shows that in the $^3B_{1u}$ state the hexagonal conformation corresponds to an energy maximum, about 800 cm^{-1} above a flat, almost cylindrical trough. When the first vibrational excitation for the $^3B_{1u}$ potential surface is calculated, the low-frequency doublet of Burland et al.^{3f} is nicely recovered, indicating that even for large molecules as benzene accurate energy surfaces are calculable.

The nuclear coordinate chosen is S_8 , dominant in the $Q_8(\rho, \varphi)$ normal coordinate⁶ (see Figure 1). For the hexagonal conformation the experimental ground-state C-H distance of 2.0539 bohr is taken, and a C-C distance of 2.722 bohr, optimized for the triplet state. The atomic orbital basis set is a slightly modified (9s5p|5s)-[4s2p|2s] set of Fischer-Hjalmaris,⁷ which in view of recent results of Matos et al. and Kitao al.⁸ should be adequate for the description of the lowest triplet state. The molecular orbitals used in the CI are the SCF orbitals for a state in which

the π electrons are coupled to the quintet $(1a_{2u})^2(1e_{1g})^2(1e_{2u})^2$ ($^5A_{1g}$). The CI calculations have been performed with the CRAY XMP version of the Wuppertal-Bonn MRDCI programs,⁹ in which the energy corresponding to the full-CI space within the AO basis is estimated with a formula given in ref 10. The correlation of 20 electrons and use of 15 reference configurations leads to MRDCI spaces of 300 000-800 000 configurations of B_{1u} symmetry, of which 3000-8000 are selected using a threshold of $15\text{ }\mu\text{H}$ and selection on the two lowest roots.

The resulting $^3B_{1u}$ energy surface is depicted in Figure 1 for three values of the parameter φ . For comparison, this figure also contains the surface calculated for the $^3E_{1u}$ component to which $^3B_{1u}$ is coupled. It is clear from this figure that the surface for the lowest triplet state is extremely flat and that the hexagonal conformation is unstable, lying 800 cm^{-1} above the conformations of minimal energy. The dependence on φ , if it exists at all, is very small and much smaller than the stabilization energy. With this

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[†]Huygens Laboratory.
[‡]Gorlaeus Laboratories.

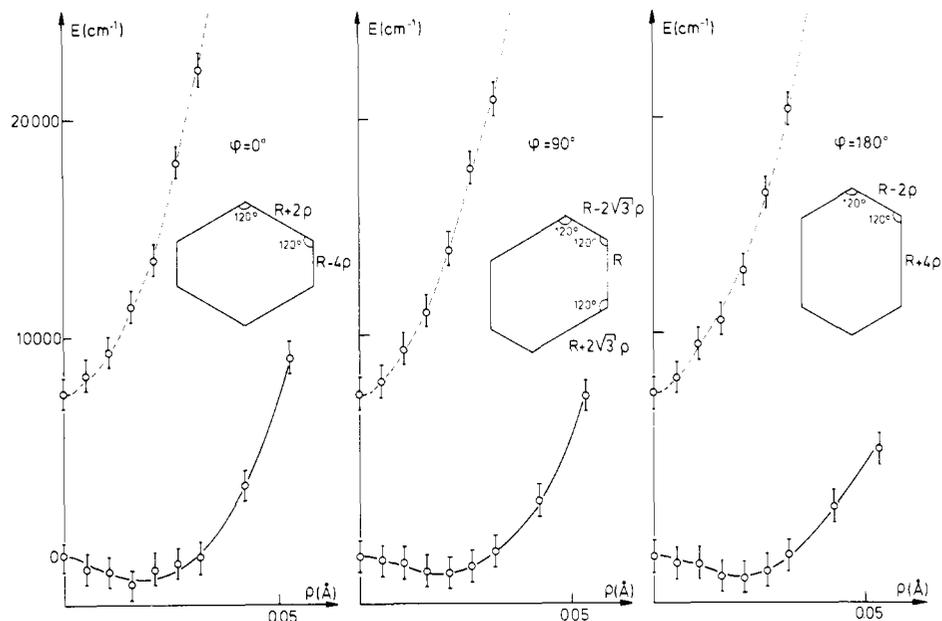


Figure 1. Potential energy curves for the ${}^3B_{1u}$ state (—) and the component of the ${}^3E_{1u}$ state (---) to which the ${}^3B_{1u}$ state is vibronically coupled as a function of the $S_8(\rho, \varphi)$ symmetry coordinate. Energy 0.0 corresponds to the energy of the ${}^3B_{1u}$ state in the hexagonal conformation. $\varphi = 0^\circ$ and $\varphi = 180^\circ$ correspond respectively to quinoid and antiquinoid conformations.

in mind we can understand the dependence of the distortion on a crystal field and perturbing substituents^{4,11} since these will introduce a φ dependence of the energy that could easily be larger than for the free molecule.

In order to calculate spectroscopic observables, we have to solve a two-dimensional nuclear Schrödinger equation. When the φ dependence of the potential is neglected, which seems justified by our results, the problem is reduced to a one-dimensional differential equation. The vibrational eigenfunctions then are

$$\chi_{v,l} = R_{v,l}(\rho) \exp(il\varphi) \quad (1)$$

The radial part of this function was solved variationally.

In Figure 2 the first six calculated vibrational levels are depicted. The energy difference between the two lower levels is 220 cm^{-1} , which compares very well with the experimental difference of 245 cm^{-1} . The 245 cm^{-1} actually was measured in the presence of a crystal field as a doublet,^{3f} which agrees with the degeneracy of the $v = 1; l = \pm 1$ level.

One of the remarkable features in the phosphorescence is the strong intensity of the 8_3^0 emission relative to the 8_1^0 emission. Using Franck-Condon factors, we derive a ratio of 0.25 in accordance with the experimentally found ratio of 0.16.^{3e}

In summary, we have been able to calculate a potential energy surface for the distortion of the ${}^3B_{1u}$ state of benzene. The accord of calculated spectroscopic observables with measured ones gives us reason to believe that this surface is a good starting point for the interpretation of the spectroscopy and photochemistry of benzene in its lowest triplet state.

After completion of our manuscript, a paper was published by Osamura,¹² who also investigated the deformation of the lowest triplet state of benzene with results somewhat similar to ours. His work, however, differs from ours in two respects: the correlation was restricted to the π electrons, and only the three energy extrema of the potential surface were considered which occur for the

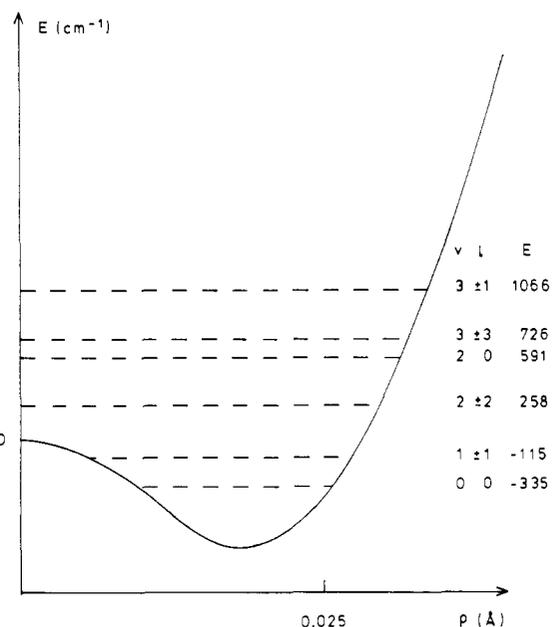


Figure 2. Energy levels of the first six vibronic levels in the ρ dependent part of the potential energy surface of the ${}^3B_{1u}$ state. Quantum numbers ν and l are defined in eq 1.

hexagonal, quinoid, and antiquinoid conformations. When the results of ref 12 (which agree with similar, unpublished, calculations made by us) are compared with the results presented here, it appears that the inclusion of σ - σ and σ - π correlation not only leads to a lowering of the relative energy minima by some 300 cm^{-1} but, more importantly, also causes the energy difference between the quinoidal and antiquinoidal forms to vanish, in agreement with the evidence provided by EPR experiments.⁴ Because of the anharmonicity of the potential surface and its two-dimensional nature, the frequencies inferred from the second derivatives at the extrema determined in ref 12 express certain trends but cannot be compared with spectroscopic observables.

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