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DOI
10.1021/ja00183a015

Publication date
1989

Published in
Journal of the American Chemical Society

Citation for published version (APA):

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

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Abstract: Experiments on the 3Blu state of benzene in the past have established that this state is conformationally unstable due to vibronic coupling with the 1Eg state and that this instability is critically dependent on the influence of a crystal field and substituents. For the 3Blu 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 3Blu state along the two-dimensional deformation coordinate S8 was calculated with large ab initio MRDCI calculations, including σ and σ 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 (3Blu) has received considerable attention since Moffit and Liehr pointed out that, in a static picture, the hexagonal conformation might be unstable because of vibronic coupling between the 3Blu and 2E1u states through 2σg modes. Low-temperature EPR experiments on benzene in a glassy matrix and subsequent EPR and ENDOR experiments on the C6H6 in C6D6 crystal established that in the solid state the electron spin distribution in the 3Blu state, indeed, is nonhexagonal. Spectroscopic observations supported these results; most remarkable amongst these was the strong doublet of spectroscopic and EPR results. Because of their semiempirical state have been made, which helped the qualitative interpretation of the spectroscopic and photochemical behavior of benzene, the 3Blu state along the two-dimensional deformation coordinate S8 was calculated with large ab initio MRDCI calculations, including σ and σ 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 calculation shows that in the 3Blu state the potential energy surface is depicted in Figure 1 for the two lowest roots. The resulting 3Blu 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 2E1u component to which 3Blu 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 below the deformations 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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in mind we can understand the dependence of the distortion on a crystal field and perturbing substituents since these will introduce a \( \varphi \) 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 \( \varphi \) 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

\[
x_{\ell J} = R_{\ell J}(\rho) \exp(i\varphi)
\]

The radical 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 \( \text{cm}^{-1} \), which compares very well with the experimental difference of 245 \( \text{cm}^{-1} \). The 245 \( \text{cm}^{-1} \) actually was measured in the presence of a crystal field as a doublet, which agrees with the degeneracy of the \( \varphi = 0^\circ \) and \( \varphi = 180^\circ \) correspond respectively to quinoid and antiquinoid conformations.

After completion of our manuscript, a paper was published by Osamura, 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 \( \pi \) electrons, and only the three energy extrema of the potential surface were considered which occur for the 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 \( \sigma-\sigma \) and \( \sigma-\pi \) correlation not only leads to a lowering of the relative energy minima by some 300 \( \text{cm}^{-1} \) 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.

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.

Acknowledgment. This work was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO).