

Probing Isomers of the Benzene Dication in a Low-Temperature Trap

Juraj Jašík,[†] Dieter Gerlich,^{†,‡} and Jana Roithová^{*,†}

[†]Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 12843 Prague 2, Czech Republic

[‡]Department of Physics, University of Technology, 09107 Chemnitz, Germany

S Supporting Information

ABSTRACT: The structure of doubly ionized benzene has been spectroscopically studied for the first time. Helium-tagged complexes were prepared at temperatures below 4 K and analyzed using infrared predissociation spectroscopy. Double ionization of benzene yields primarily high-energy dications with a six-membered-ring structure. Some of the dications undergo rearrangement to a more stable pyramidal isomer with a C₅H₅ base and CH at the apex. By means of isomer-selective heating by a CO₂ laser, infrared predissociation spectra of both the classical and pyramidal dications were obtained.

The six-membered ring of benzene is one of the few chemical structures that are well-known to the broad public. Verifying the structure of this molecule represented a big challenge for chemists in the late nineteenth and early twentieth centuries.¹ The first accepted and the best-known proposal is Kekule's model of six carbon atoms joined in a hexagonal arrangement with alternating double bonds.² Since the introduction and development of quantum theory, the resonance model for benzene with *D*_{6h} symmetry has been accepted, and this molecule was at the center of the development of valence bond theory³ and molecular orbital theory.⁴ Removal of one electron from benzene leads to a fluxional distortion of the six-membered ring toward *D*_{2h} symmetry. However, the energy barriers between the individual minima are very small, so the cation can also be viewed as having the *D*_{6h} symmetric structure.⁵

Determining the structure of doubly ionized benzene represents a challenge.^{6–8} The large concentration of positive charge leads to distortions, and the theoretically predicted structure of the singlet state of C₆H₆²⁺ is not planar (Scheme 1). Photoionization coincidence experiments revealed that the ground state is the triplet state (³1²⁺). However, the singlet state (1¹2⁺) is formed with a much larger cross section.⁹ The double photoionization spectrum also suggests that the singlet state of C₆H₆²⁺ immediately undergoes rearrangements to one or more of the more stable structures. Several possible

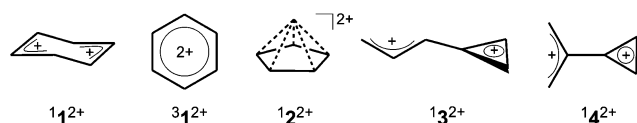
structures have been predicted by ab initio calculations (Scheme 1), and the pyramidal dication ¹2²⁺ has been highlighted as the most stable arrangement.^{10,11}

Benzene dication may be considered as a prototypical member of the nonclassical carbocation family.^{12–16} Doubly charged carbocations are formed under superacidic conditions. The permethylated analogue of C₆H₆²⁺, C₆(CH₃)₆²⁺, can be prepared in a “magic” acid solution from various precursors, and it has been shown to possess a pyramidal structure analogous to the suggested structure ¹2²⁺.¹⁷ Ionized hydrocarbons can be also viewed as analogues of boranes or carboranes.¹⁸

The structures of the C₆H₆²⁺ dications have never been experimentally addressed. This is because of the high reactivities of the dications and the small cross sections for their formation in photoionization experiments.^{12,19} Moreover, determining the structure of the dications formed by rearrangement of the initially formed isomer requires their direct probing. A possible approach stems from the use of infrared predissociation (IRPD) spectroscopy.^{20–22} The key requirement of this method is the formation of complexes between the ions of interest and an inert atom (e.g., argon)^{23–26} or molecule (e.g., H₂)^{27,28} that are assumed not to have a significant effect on the structure of the ions of interest.^{29,30} The complexes are irradiated by IR photons, and if the IR photons are in resonance with a vibrational transition of the complex, we can observe elimination of the tag. Hence, the dependence of the depletion of the tagged complexes on the photon wavenumber provides information similar to an IR absorption spectrum of the complex of interest.

Small hydrocarbon dications are very reactive, and they can form covalent bonds even with argon^{31,32} and certainly also with H₂ or other molecules.³³ The ideal tag is therefore helium.^{34–36} Generation of helium-tagged ions, however, requires very low temperatures. To this end, we have constructed a new instrument with a linear quadrupole ion trap, called ISORI, where temperatures below 4 K can be reached [Figure S1 in the Supporting Information (SI)].³⁷ Operating at high helium densities allows the mass-selected ions to form the required helium-tagged complexes (i.e., C₆H₆He²⁺) (Figure S2 in the SI). The C₆H₆²⁺ dications were generated by electron ionization, and therefore, we can expect that singlet-state dications were mainly formed.¹² The trapped ions were irradiated by photons with energies varying from

Scheme 1. Possible Structures of C₆H₆²⁺



Received: November 29, 2013

Published: February 14, 2014

2900 to 3200 cm^{-1} with a spectral resolution of 5 cm^{-1} , and the relative depletion of the number of the helium complexes was monitored with respect to the number of the nonirradiated complexes (the numbers of $\text{C}_6\text{H}_6\text{He}^{2+}$ complexes with and without IR irradiation are denoted as N_i and N_{i0} , respectively). More details about the instrument, the laser system, and the experimental procedures can be found in ref 37 and in the SI.

The IRPD spectrum of the $\text{C}_6\text{H}_6\text{He}^{2+}$ dications contains three pronounced peaks at about 2940, 3042, and 3060 cm^{-1} (Figure 1a). In order to disentangle the origins of the

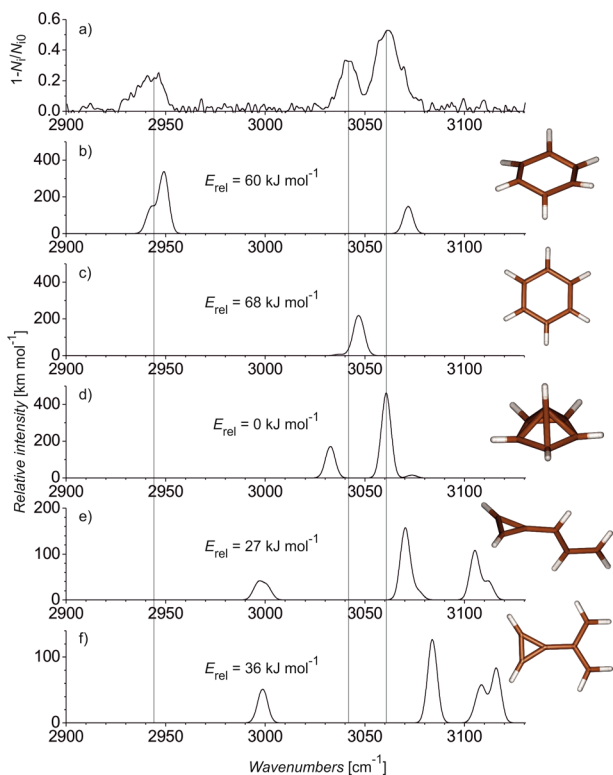


Figure 1. Comparison of (a) the IRPD spectrum of $\text{C}_6\text{H}_6\text{He}^{2+}$ ($\text{C}_6\text{H}_6^{2+}$ ions were generated from benzene) with the theoretical IR spectra of the $\text{C}_6\text{H}_6^{2+}$ isomers (b) ${}^11^{2+}$, (c) ${}^31^{2+}$, (d) ${}^12^{2+}$, (e) ${}^13^{2+}$, and (f) ${}^14^{2+}$ calculated at the MP2/aug-cc-pVTZ level of theory (using a scaling factor of 0.953). The relative energies were obtained at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory and include MP2/aug-cc-pVTZ zero-point vibrational energy corrections. More results at various levels of theory are provided in the SI.

experimental bands, we calculated IR spectra for all of the isomers shown in Scheme 1. Clearly, the only $\text{C}_6\text{H}_6^{2+}$ isomer that can account for the band at 2940 cm^{-1} is ${}^11^{2+}$. This isomer, however, cannot explain the whole IRPD spectrum, which therefore must originate from a mixture of isomers. If we consider just two isomers, the most probable combination appears to be a mixture of ${}^11^{2+}$ and ${}^12^{2+}$. We note in passing that the separation of the bands slightly depends on the level of theory (cf. Figures S5 and S6 in the SI) and that the calculated IR spectra of $\text{C}_6\text{H}_6\text{He}^{2+}$ differ only marginally from those of $\text{C}_6\text{H}_6^{2+}$ (cf. Figures S7–S9 in the SI). In order to experimentally modify the composition of the mixture of isomers, we can take two approaches: changing the ionization conditions or influencing the composition of the mixture in the ion trap. Changing the ionization conditions did not lead to significant changes or conclusive results, and thus, we concentrated on influencing the trapped ions. Our approach

involved “heating” of the trapped dications with a technical CO_2 laser. Depending on the power and the timing, this laser may be used to selectively impede complex formation or dissociate complexes.³⁸ Also, temporary heating of the trapped ions to high enough internal energies may also induce their isomerization. Here, the combination of CO_2 laser irradiation with measurement of IRPD spectra showed a gradual disappearance of the peak at 2940 cm^{-1} with increasing power of the CO_2 laser irradiation (Figure 2). When the laser

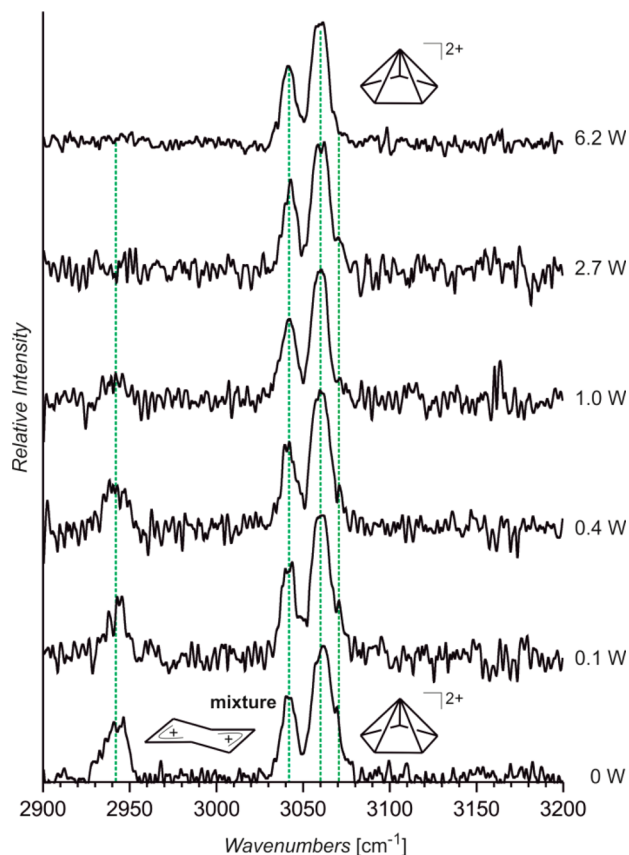


Figure 2. Dependence of the IRPD spectrum of the helium-tagged complexes of $\text{C}_6\text{H}_6^{2+}$ generated by double ionization of benzene on the power of the CO_2 laser (indicated at the right side of the spectra). The ion cloud was irradiated for 20 ms at a time delay of 55 ms with a trapping time 80 ms. All of the spectra have been normalized to the integral of the peak at 3042 cm^{-1} .

power was above 3 W, the peak at 2940 cm^{-1} disappeared completely. On the basis of a series of experiments (cf. Figures S10–S12 and the related discussion in the SI), we can conclude that the process corresponds to the selective destruction of one group of helium complexes by the CO_2 laser irradiation.

Finally, if we assume that one group of helium complexes is destroyed, whereas the other group is not influenced, we can separate the original IRPD spectrum into its two components. The first one corresponds to the spectrum obtained with CO_2 laser irradiation at a power of 6.2 W (this spectrum was accumulated for a longer time to achieve a better signal-to-noise ratio), and the second one is the difference between the first one and the original IRPD spectrum without CO_2 laser irradiation (Figure 3). Comparison of the separated spectra with the theoretical IR spectra of ${}^11^{2+}$ and ${}^12^{2+}$ (bars in Figure 3) shows very good agreement. We note in passing that all of the vibrational bands correspond to C–H stretching modes (cf.

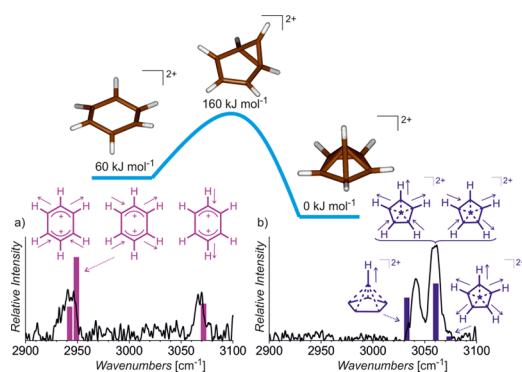


Figure 3. IRPD spectra of (a) 1^2+ and (b) 1^2+ separated by the selective destruction of the $[^1\text{He}]^{2+}$ complexes by CO_2 laser irradiation. The bar spectra correspond the theoretical IR spectra (MP2/aug-cc-pVTZ) of (a) 1^2+ and (b) 1^2+ (the corresponding C–H stretching modes are depicted by arrows using simplified structures). The potential energy surface for the rearrangement was obtained at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory and includes MP2/aug-cc-pVTZ zero-point vibrational energy.

Figure 3) and that the IRPD spectrum of $\text{C}_6\text{D}_6^{2+}$ as well as the theoretical spectra of $\text{D}_6\text{-}1^2+$ and $\text{D}_6\text{-}1^2+$ can be found in Figure S13 in the SI.

The selective depletion of the $[^1\text{He}]^{2+}$ complexes by the CO_2 laser can be easily understood if we compare the theoretically predicted IR spectra of the dications with the emission line of the CO_2 laser ($\sim 943\text{ cm}^{-1}$). While the 1^2+ (or $[^1\text{He}]^{2+}$) dication has three transitions in the emission range of the CO_2 laser, there is no band in this range in the spectrum of 1^2+ (or $[^2\text{He}]^{2+}$) (see Figure S12 in the SI). Hence, only the $[^1\text{He}]^{2+}$ dications can absorb photons produced by the CO_2 laser, which leads to the elimination of He from the complex (one photon delivers $\sim 11\text{ kJ mol}^{-1}$, while the binding energy of helium is about 2 kJ mol^{-1} ; cf. Table S2 in the SI). The mixture of $[^1\text{He}]^{2+}$ and $[^2\text{He}]^{2+}$ thus becomes depleted in $[^1\text{He}]^{2+}$, which is reflected in the IRPD spectra.

In conclusion, we have shown that the high-energy isomer 1^2+ with a six-membered ring, which is primarily formed upon double ionization of benzene, can be stabilized at low temperatures and characterized. As previously suggested, a large fraction of the 1^2+ dications undergo directly upon their generation a rearrangement to more stable isomers.⁹ By trapping and studying these ions, we have provided clear evidence that they correspond to 1^2+ dications with a pyramidal structure. Using selective heating and thus destruction of helium clusters of 1^2+ , we were able to obtain the pure IRPD spectrum of the helium-tagged 1^2+ pyramidal dications.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and computational details, Figures S1–S13, and Tables S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

roithova@natur.cuni.cz

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is dedicated to Helmut Schwarz on the occasion of his 70th birthday. The authors gratefully acknowledge financial support from the European Research Council (StG ISORI).

■ REFERENCES

- Brush, S. G. *Stud. Hist. Philos. Sci.* **1999**, *30*, 21.
- Kekulé, A. *Bull. Soc. Chim.* **1865**, *3*, 98.
- McWeeny, R. *Proc. R. Soc. London, Ser. A* **1955**, *227*, 288.
- Matsen, F. A. J. *Am. Chem. Soc.* **1950**, *72*, 5243.
- Lindner, R.; Müller Dethlefs, K.; Wedum, E.; Haber, K.; Grant, E. *R. Science* **1996**, *271*, 1698.
- Hogenvreen, H.; Kwant, P. S. *Acc. Chem. Res.* **1975**, *8*, 413.
- Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 1049.
- Dewar, M. J. S.; Holloway, M. K. *J. Am. Chem. Soc.* **1984**, *106*, 6619.
- Eland, J. H. D. *Chem. Phys.* **2008**, *345*, 82.
- Jonkman, H. T.; Nieuwpoort, W. C. *Tetrahedron Lett.* **1973**, *14*, 1671.
- Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1991**, *113*, 417.
- Olah, G. A. *J. Org. Chem.* **2001**, *66*, 5943.
- Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 991.
- Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321.
- Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; John Wiley & Sons: Hoboken, NJ, 2004.
- Aue, D. H. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 487.
- Hogenvreen, H.; Kwant, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 2208.
- Jemmis, E. D.; Jayasree, E. G. *Acc. Chem. Res.* **2003**, *36*, 816.
- Roithová, J.; Schröder, D.; Loos, J.; Schwarz, H.; Jankowiak, H. C.; Berger, R.; Thissen, R.; Dutuit, O. *J. Chem. Phys.* **2005**, *122*, No. 094306.
- Robertson, W. H.; Johnson, M. A. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173.
- Duncan, M. A. *Int. Rev. Phys. Chem.* **2003**, *22*, 407.
- Duncan, M. A. *J. Phys. Chem. A* **2012**, *116*, 11477.
- Solca, N.; Dopfer, O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3628.
- Douberly, G. E.; Ricks, A. M.; Schleyer, P. v. R.; Duncan, M. A. *J. Phys. Chem. A* **2008**, *112*, 4869.
- Mizuse, K.; Fujii, A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7129.
- Satink, R. G.; Piest, H.; von Helden, G.; Meijer, G. *J. Chem. Phys.* **1999**, *111*, 10750.
- Okumura, M.; Yeh, L. I.; Myers, J. D.; Lee, Y. T. *J. Chem. Phys.* **1986**, *85*, 2328.
- Garand, E.; Kamrath, M. Z.; Jordan, P. A.; Wolk, A. B.; Leavitt, C. M.; McCoy, A. B.; Miller, S. J.; Johnson, M. A. *Science* **2012**, *335*, 694.
- Bakker, J. M.; Satink, R. G.; von Helden, G.; Meijer, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 24.
- Cheng, T. C.; Bandyopadhyay, B.; Mosley, J. D.; Duncan, M. A. *J. Am. Chem. Soc.* **2012**, *134*, 13046.
- Ascenzi, D.; Tosi, P.; Roithová, J.; Schröder, D. *Chem. Commun.* **2008**, 4055.
- Roithová, J.; Schröder, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 8788.
- Roithová, J.; Schröder, D. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2341.
- Dopfer, O. *Int. Rev. Phys. Chem.* **2003**, *22*, 437.
- Olkhov, R. V.; Nizkorodov, S. A.; Dopfer, O. *J. Chem. Phys.* **1999**, *110*, 9627.
- Asmis, K. R.; Meijer, G.; Brummer, M.; Kaposta, C.; Santambrogio, G.; Woste, L.; Sauer, J. *J. Chem. Phys.* **2004**, *120*, 6461.
- Jašík, J.; Žabka, J.; Roithová, J.; Gerlich, D. *Int. J. Mass Spectrom.* **2013**, *354–355*, 204.
- Leavitt, C. M.; Wolk, A. B.; Fournier, J. A.; Kamrath, M. Z.; Garand, E.; Van Stipdonk, M. J.; Johnson, M. A. *J. Phys. Chem. Lett.* **2012**, *3*, 1099.