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Infrared and Raman spectra and theoretical calculations for benzocyclobutane in its electronic ground state

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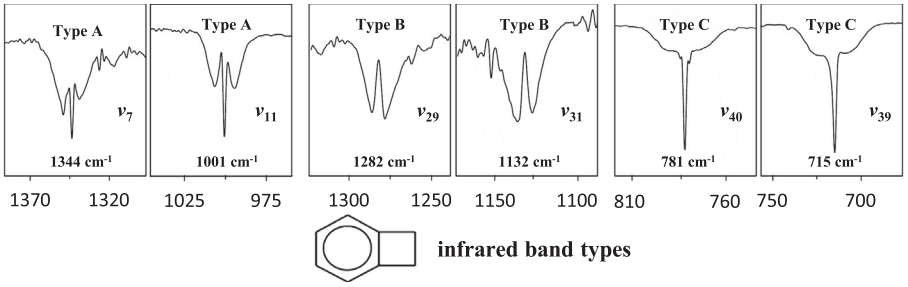
HIGHLIGHTS

- The infrared and Raman spectra of bicyclobutane vapor and liquid have been recorded and assigned.
- The computed spectra from DFT calculations match the experimental spectra very well.
- *Ab initio* calculations were used to obtain the structure of the molecule and this was compared to related bicyclic molecules.
- Very distinct infrared band types were observed.
- The low-frequency skeletal modes are a reflection of the ring rigidity.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared and Raman spectra of vapor-phase and liquid-phase benzocyclobutane (BCB) have been recorded and assigned. The structure of the molecule was calculated using the MP2/cc-pVTZ basis set and the vibrational frequencies and spectral intensities were calculated using the B3LYP/cc-pVTZ level of theory. The agreement between experimental and calculated spectra is excellent. In order to allow comparisons with related molecules, *ab initio* and DFT calculations were also carried out for indan (IND), tetralin (TET), 1,4-benzodioxan (14BZD), 1,3-benzodioxan (13BZD) and 1,4-dihydronaphthalene (14DHN). The ring-puckering, ring-twisting, and ring-flapping vibrations were of particular interest as these reflect the rigidity of the bicyclic ring system. The infrared spectra of BCB show very nice examples of vapor-phase band types and combination bands.

Introduction

In recent years we have investigated the structures, conformations, and molecular vibrations of a number of bicyclic molecules in their ground and excited electronic states. Among these are indan (IND) [1], tetralin (TET) [2], 1,4-benzodioxan (14BZD) [3–5], 1,3-benzodioxan (13BZD) [6], and 1,4-dihydronaphthalene (14DHN) [7]. In the present study we report the infrared and Raman spectra and theoretical calculations for benzocyclobutane (BCB). Except for 14DHN, each of the other bicyclic molecules has a non-planar structure. The five-membered ring of IND is puckered, while the six-membered rings of TET, 14BZD, and 13BZD all have twisted structures. The BCB molecule investigated here is expected to be totally planar. Nonetheless, the investigation of its structure and vibrations in its ground and excited states and their comparison to the related molecules will be of considerable interest. In the present paper we present the results for the electronic ground state. The spectroscopic and theoretical calculations for the $S_1(\pi,\pi^*)$ electronic excited state will be presented elsewhere [8].

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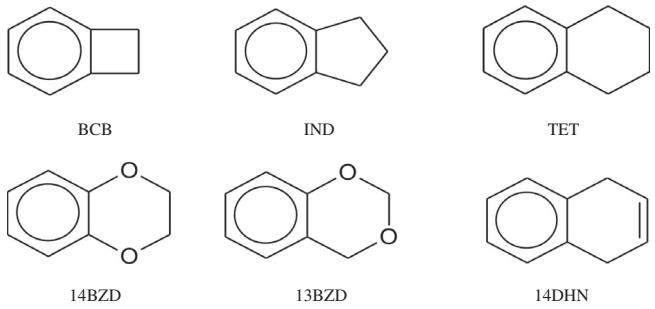

Experimental

The BCB sample (98% purity) was purchased from Aldrich Chemical Company and further purified by vacuum distillation. The infrared spectra were recorded using a Brucker Vertex 70 instrument which was purged by a stream of nitrogen gas at room temperature. Vapor-phase infrared spectra of 3 Torr of sample in 10 cm glass cells were recorded at 0.5 cm^{-1} resolution. KBr windows were used for the mid-infrared region (4000–400 cm^{-1}) and polyethylene windows were used for the far-infrared (600–50 cm^{-1}). Four thousand scans were typically averaged. Liquid-phase mid- and far-infrared spectra were recorded at 1 cm^{-1} and 2 cm^{-1} resolution, respectively, and up to four thousand scans were typically averaged. Spectra of a drop of sample as a capillary film contained between either KBr or CsI windows were recorded.

The Raman spectra were recorded using a Jobin–Yvon U-1000 spectrometer equipped with a Coherent Verdi V10 laser operating at 532 nm and with a liquid-nitrogen cooled, charge-coupled device (CCD) detector producing a resolution of 0.7 cm^{-1}. Vapor-phase Raman spectra of approximately 0.5 atm of sample were recorded at 150 °C using a laser power of 5 W. The sample was contained in a special heatable Raman cell which has been previously

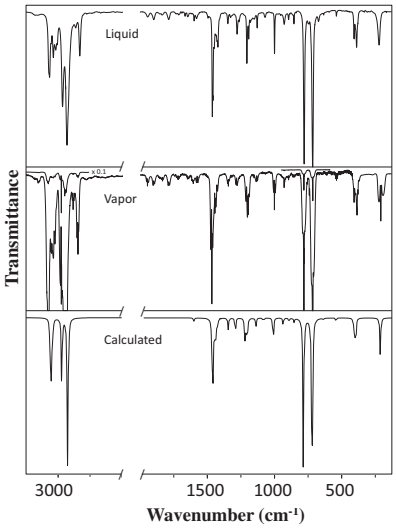

Fig. 2. Experimental and calculated infrared spectra of BCB.

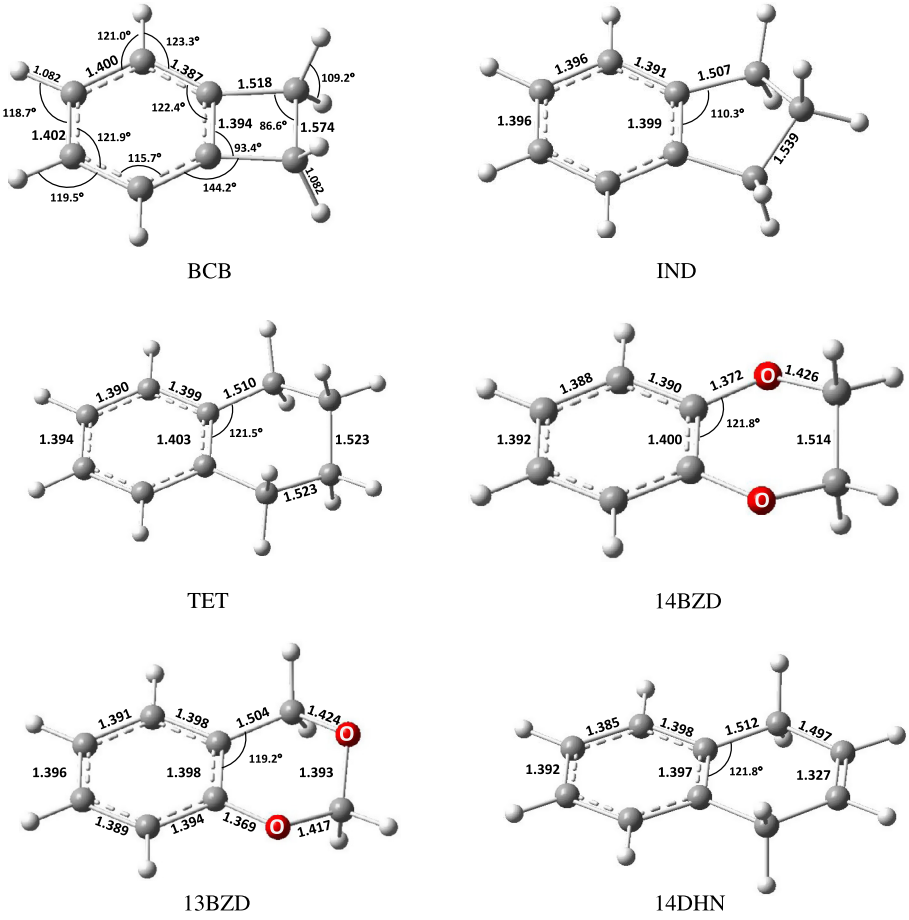

Fig. 1. Calculated structures of BCB and related molecules utilizing the MP2/cc-pVTZ level of theory.