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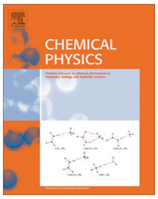

Measurement and analysis of the infrared absorption spectrum of the radical cation of $[3_4](1,2,4,5)$cyclophane: Observation of electron–molecular vibration interaction between two benzene moieties

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ABSTRACT

A high-quality infrared absorption spectrum has been observed for the radical cation of $[3_4]$(1,2,4,5)cyclophane in a dichloromethane solution by using a Fourier-transform infrared spectrometer contained in an inert gas glovebox system. The structures and vibrational properties (harmonic frequencies, vibrational modes, and infrared intensities) have been calculated for the neutral species and radical cation of $[3_4]$(1,2,4,5)cyclophane by density functional theory at the B3LYP/6-311+G(d,p) level. The observed infrared spectra of the neutral species and radical cation are in good agreement with those calculated. Some specific vibrational modes of the radical cation have large infrared absorption intensities. The origin of the large infrared absorption intensities characteristic of the radical cation is discussed in terms of electron–molecular vibration interaction (changes in electronic structure induced by specific normal vibrations) between two benzene moieties of $[3_4]$(1,2,4,5)cyclophane.

1. Introduction

In functional materials such as conducting charge-transfer complexes and conducting polymers, electronic devices based on organic materials, and some kinds of biological systems, electron transport is supported by ionic species of molecules. The molecular structures of such ionic species are different from those of neutral species. Since vibrational spectra are sensitive to changes in molecular structures, vibrational spectroscopy is considered to be useful for studying structural characteristics of ionic species and electron transport in these systems [1–4]. In addition, infrared spectral analysis of ionic species is one of the most promising methods for analyzing the change in electronic structure induced by molecular vibrations, namely the electron–molecular vibration interaction characteristic of the ionic species [5–7].

Efforts have been made to measure reliable and high-quality infrared absorption spectra of organic radical ions and divalent ions produced by various methods such as chemical reactions [5–12], electrochemical techniques [13], electron bombardments [14–20], vacuum ultraviolet photolyses [21–24], pulsed-glow discharge [25,26], X-ray irradiation [27], and low-temperature codeposits with alkali metals [28,29], etc. However, it is not easy to observe the infrared spectra of radical ions and divalent ions, because they are generally unstable at room temperature and in the air.

Recently, we developed a new approach to the spectral study of unstable radical and ionic species in solution by the use of an inert gas glovebox system, in which the oxygen and water concentrations are less than 0.1 ppm [7]. By this method, we obtained high-quality infrared absorption spectra of the radical anion and dianion of *p*-terphenyl by using a Fourier-transform infrared spectrometer contained in an inert gas glovebox system. The observed infrared spectra were analyzed on the basis of density functional theory calculations. The observed large infrared absorption intensities of some specific vibrational modes of the radical anion and dianion were associated with the charge fluxes [30] generated by the electron–molecular vibration interactions.

In the present study, we have measured and analyzed the infrared absorption spectrum of the radical cation of $[3_4]$(1,2,4,5)cyclophane (Fig. 1), one of the simplest dimeric molecules with the transannular π–π interaction [31], as a step to extend our studies on the *intramolecular* electron–molecular vibration interactions [5–7] to those on the *intermolecular* interactions. Since $[3_4]$(1,2,4,5)cyclophane has been reported to be oxidized to form the radical cation by cyclic voltammetry [32], we have planed to measure and analyze the infrared spectrum of this radical cation. The mechanism that gives rise to the large infrared absorption intensities for some specific vibrational modes of the radical cation is discussed in terms of the electron–molecular vibration interaction between two benzene moieties.

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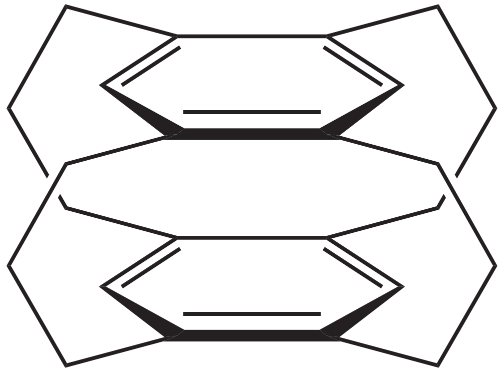

Fig. 1. Molecular structure of $[3_4](1,2,4,5)$cyclophane.

2. Experimental

The experimental setup for infrared and electronic absorption measurements in an inert gas glovebox system was basically the same as that reported previously [7]. Infrared spectra were recorded at room temperature on a Fourier-transform infrared spectrophotometer (JASCO FT-IR 4100) in the glovebox system (MBRAUN UNIlab). Interferograms were accumulated for 100 times and averaged to obtain a satisfactory signal-to-noise ratio. The wavenumber resolution was 2 cm^{-1}. Electronic absorption spectra were measured on an ultraviolet and visible spectrophotometer (JASCO V-530) in the glovebox system. The oxygen and water concentrations in the glovebox system were less than 0.1 ppm.

$[3_4](1,2,4,5)$Cyclophane (Fig. 1) was synthesized according to the method reported by Shinmyozu et al. [31]. The degassed and anhydrous deuterated dichloromethane (CD_2Cl_2) solutions of neutral $[3_4](1,2,4,5)$cyclophane and iron trichloride ($FeCl_3$) were prepared separately in the glovebox system. The radical cation of $[3_4](1,2,4,5)$cyclophane was generated by adding a CD_2Cl_2 solution of $FeCl_3$ (8.0×10^{-3} mol dm^{-3}) to a CD_2Cl_2 solution of $[3_4](1,2,4,5)$cyclophane (2.0×10^{-3} mol dm^{-3}) in the glovebox system. The ratio of the amount of substance of added $FeCl_3$ to that of neutral $[3_4](1,2,4,5)$cyclophane was 3. Since one-electron oxidation occurs by using two $FeCl_3$ molecules [33,34], this ratio of 3 means that the amount of substance of $FeCl_3$ is 1.5 times as many as the equivalent amount for oxidizing all neutral $[3_4](1,2,4,5)$cyclophane molecules.

The progress of the oxidative reaction was monitored by measuring electronic absorption spectra. A further oxidative reaction producing the dication of $[3_4](1,2,4,5)$cyclophane did not occur by addition of excess amounts of $FeCl_3$ in CD_2Cl_2. After the formation of the radical cation of $[3_4](1,2,4,5)$cyclophane was confirmed by its electronic absorption spectra, its CD_2Cl_2 solution was transferred to a CaF_2 cell (BioTools BioCell) with an optical pathlength of 123 μm. The infrared and electronic absorption spectra of the radical cation of $[3_4](1,2,4,5)$cyclophane were obtained from such CD_2Cl_2 solutions in a CaF_2 cell.

3. Theoretical calculations

The structures and vibrational properties (harmonic frequencies, vibrational modes, and infrared intensities) were calculated for the neutral species and radical cation (charge:+*e*, spin multiplicity: 2) of $[3_4](1,2,4,5)$cyclophane. Counter ions were not included in the calculations for the radical cation. Density functional theory calculations at the B3LYP (Becke's three-parameter hybrid method [35] using the Lee–Yang–Parr correlation functional [36]) level in combination with the 6-311+G(d,p) basis set were performed by using the GAUSSIAN 03 program [37]. The 'UltraFine' grid was used for numerical calculations of two-electron integrals.

Geometry optimizations for the neutral species and radical cation of $[3_4](1,2,4,5)$cyclophane were performed, and the results showed that both the species had D_{2h} symmetry, in which two benzene rings were equivalent to each other. No imaginary-frequency mode was found at the optimized structures of both the species. The calculated wavenumbers were multiplied by a single scale factor of 0.9738 for the neutral species and 0.9780 for the radical cation, each of which was determined to obtain the best fit between the calculated wavenumbers and the observed wavenumbers. Calculated atomic displacements in each vibrational mode were depicted with the VLX program [38].

4. Results and discussion

4.1. Molecular structures

The numbering of atoms in $[3_4](1,2,4,5)$cyclophane is shown in Fig. 2 with the Cartesian coordinate system. The structural parameters calculated at the B3LYP/6-311+G(d,p) level for the neutral species and radical cation of $[3_4](1,2,4,5)$cyclophane are listed in Table 1, together with those obtained by X-ray diffraction study for the neutral species [39]. As shown in Table 1, bond lengths, distances between the specific carbon atoms in the two equivalent upper and lower moieties including the benzene rings (for example C_1–$C_{4'}$, C_3–$C_{6'}$, C_7–$C_{9'}$), and bond angles calculated at the B3LYP/6-311+G(d,p) level for neutral $[3_4](1,2,4,5)$cyclophane are in good agreement with the experimental values.

The C_1–C_2 (C_4–C_5) bond of the benzene ring is lengthened and the C_2–C_3 (C_3–C_4, C_5–C_6, C_6–C_1) bond is slightly shortened on going from the neutral molecule to the radical cation. In the cross-linking carbon chains, the C_1–C_7 (C_2–C_8, C_4–C_9, C_5–C_{10}) bond is shortened and the C_7–C_{11} (C_8–C_{12}, C_9–$C_{11'}$, C_{10}–$C_{12'}$) bond is almost

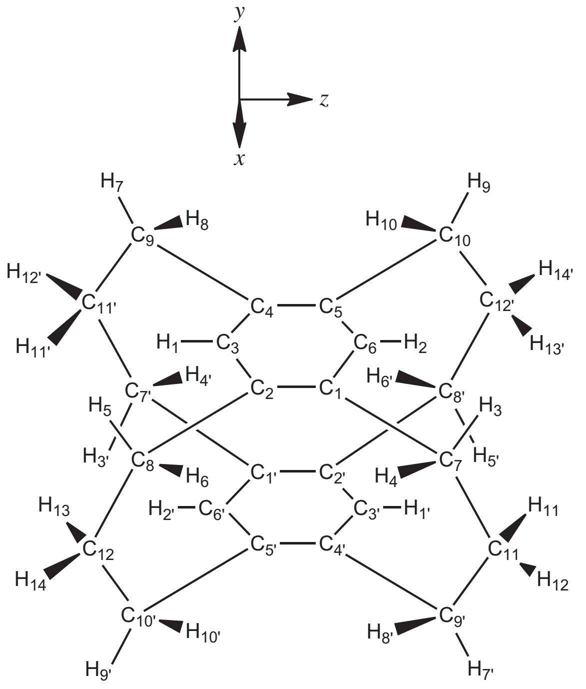

Fig. 2. Numbering of atoms and the Cartesian coordinate system for $[3_4](1,2,4,5)$cyclophane.