CHEMISTRY LETTERS, pp. 311-314, 1993.

Observation of the Infrared and Raman Spectra of *p*-Benzoquinodimethane in Low-Temperature Ar Matrices

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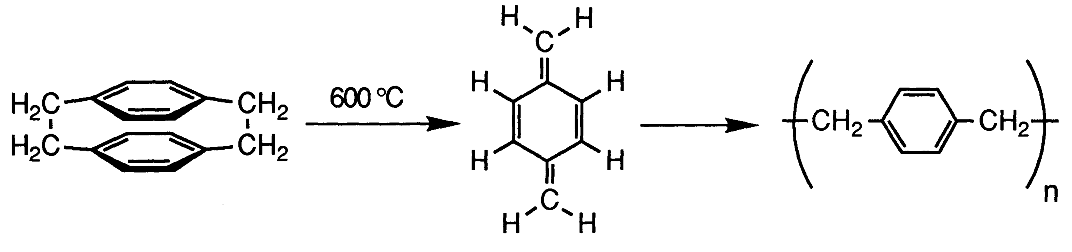
The infrared and Raman spectra of *p*-benzoquinodimethane have been observed in low-temperature Ar matrices. The infrared spectrum obtained has proved to be more reliable and useful than the existing numerical data on the absorption wavenumbers and qualitative intensities. The Raman spectrum has been observed for the first time. Vibrational assignments of bands characteristic of this quinoid molecule are discussed on an experimental basis.

p-Benzoquinodimethane (*p*-BQM, **1**) is the smallest of quinoid molecules consisting of only the carbon and hydrogen atoms. Its molecular and electronic structures are interesting in view of the importance of quinoid structures in studies dealing with organic conductors[1)] including various conjugated polymers.[2)] *p*-BQM is also closely related to *p*-benzoquinone and related quinones, which are known to play an important role in electron transfer in biological systems.[3)] Thus, detailed characterization of *p*-BQM is essential for understanding the mechanism of electron transport in both organic and biological systems.

The existence of *p*-BQM was first predicted from a theoretical viewpoint,[4)] and it was in fact found in the pyrolyzates of *p*-xylene.[5)] Later, an efficient method of preparing *p*-BQM by pyrolysis of [2,2]-paracyclophane (**2**) was established.[6)] Since then, structural and spectroscopic studies have been reported on *p*-BQM by using nuclear magnetic resonance,[7)] He (I) photoelectron spectroscopy,[8)] ultraviolet-visible absorption,[9)] electron diffraction,[10)] and infrared absorption.[11)] However, no Raman spectrum of *p*-BQM has been reported so far, probably because *p*-BQM is highly reactive and polymerizes to form poly(1,4-phenylene-1,2-ethanediyl) (**3**). This paper reports the observation of reliable infrared and Raman spectra of *p*-BQM.



2 **1** **3**

Scheme 1. Preparation of **1** from **2** and polymerization of **1** into **3**.

p-BQM was generated from [2,2]-paracyclophane in the same way as reported in Refs. 6 and 11 using the apparatus shown in Fig. 1, which was a modification of the ones employed in Refs. 12 and 13. A reaction tube (15 mm in diameter) made of quartz was placed through the cylindrical cavity (300 mm in length, 40 mm in diameter) in a furnace (Isuzu Seisakusho Co., Ltd.). Metal components (a needle valve, a flange, and fittings) connecting the reaction tube with the other parts of the apparatus were purchased from Swagelok Co. The temperature of the reaction tube inside the furnace was maintained at 600 °C, and the part of the reaction tube outside the furnace was also heated to 100 °C with ribbon heaters, to prevent the polymerization of the generated *p*-BQM at this part of the tube. A small amount (50 mg) of [2,2]-paracyclophane (Aldrich Chemical Co., Inc.) placed in the reaction tube outside the furnace was sublimed under a flow of Ar gas (99.999999%), which carried the sublimed [2,2]-paracyclophane into the furnace. This flow of Ar gas, which was characteristic of the present method, efficiently accelerated the sublimation and pyrolysis processes.

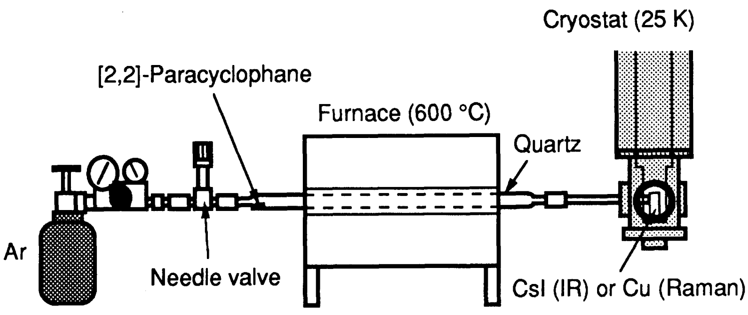


Fig. 1. Apparatus for pyrolysis.

The *p*-BQM generated inside the furnace was slowly sprayed through a stainless tube onto either a CsI plate (for infrared measurements) or a silver-plated copper block (for Raman), which was attached to the cold head of a cryostat (evacuated to a pressure $<10^{-2}$ Pa before cooling), and maintained at 25 K by a closed-cycle He cryocooler (Osaka Sanso Kogyo Ltd. CRYOMINI D). The Ar/*p*-BQM ratio was estimated to be in the ranges of 3–10 and 1–2 in the infrared and Raman measurements, respectively, although it was difficult to determine this ratio accurately. The matrix/sample ratios in the present measurements were therefore much smaller than those usually employed in matrix-isolation spectroscopy.

Infrared spectra were measured on a Fourier-transform infrared spectrophotometer (JEOL JIR-100) under 1 $\mathrm{cm^{-1}}$ resolution. Raman measurements were performed on a triple polychromator (SPEX 1877 TRIPLEMATE) with a multichannel detector (EG & G PARC 1421). The 514.5-nm line of an Ar ion laser (NEC GLG 3300, 48 mW at the sample position) and the 632.8-nm line of a He-Ne laser (NEC GLG 108, 26 mW) were used for Raman excitation. For 514.5- and 632.8-nm excitations, the slit width of the polychromator was fixed, respectively, at 40 µm (2 $\mathrm{cm^{-1}}$ resolution) and 100 µm (3 $\mathrm{cm^{-1}}$ resolution).

The infrared spectrum of *p*-BQM is shown in Fig. 2 (a). The observed bands are sharp (full widths at half maximum being about 1 $\mathrm{cm^{-1}}$ for bands in the region below 2000 $\mathrm{cm^{-1}}$ and about 5 $\mathrm{cm^{-1}}$ for bands in the region above 3000 $\mathrm{cm^{-1}}$), indicating that the *p*-BQM molecules are well isolated in the Ar matrix.

Since the *p*-BQM molecule has D_{2h} symmetry, four CH stretching modes are expected to be infrared-active. In fact, only four bands are clearly observed in the 3110–3030-$\mathrm{cm^{-1}}$ region, indicating that the amount of polymerized aromatic hydrocarbons, which might coexist, does not reach an appreciable level. The infrared wavenumber and intensity data reported by Chapman et al.11) are consistent with the spectrum in Fig. 2 (a), except that information on an important band at 1591 $\mathrm{cm^{-1}}$ (see below) is lacking in their data. This omission might have been caused by the difficulty in discerning bands of *p*-BQM in the 1750–1550-$\mathrm{cm^{-1}}$ region from those of H_2O coexisting in the matrix. Pearson et al.14) have also reported the infrared spectrum of *p*-BQM in the solid state. However, their spectrum seems to contain many bands due to impurities.

The medium-intensity band at 1605 cm^{-1} is assignable to the out-of-phase stretch of the wing double bonds, and the weak band at 1591 cm^{-1} is considered to arise from the out-of-phase stretch of the ring double bonds, which is probably mixed with the ring CH bend. The wavenumber of the latter band is considerably higher than either of the two infrared-active ring stretches of *p*-xylene at 1529 and 1421 cm^{-1},[15] reflecting the difference between the quinoid and benzenoid structures.

Chapman et al.[11] have suggested that the medium-intensity 1735-cm^{-1} band may be assigned to the first overtone of the very intense band at 867 cm^{-1}, which is undoubtedly assigned to the CH_2 wag. However, the first overtone of this mode is forbidden in the infrared absorption. We therefore assign the 1735-cm^{-1} band to a combination of the 867-cm^{-1} CH_2 wag and a mode giving rise to a Raman band at 863 cm^{-1} (see below). Another medium-intensity band at 465 cm^{-1} may be assigned to an out-of-plane ring mode, which deforms the molecule toward the boat form of a six-membered ring.

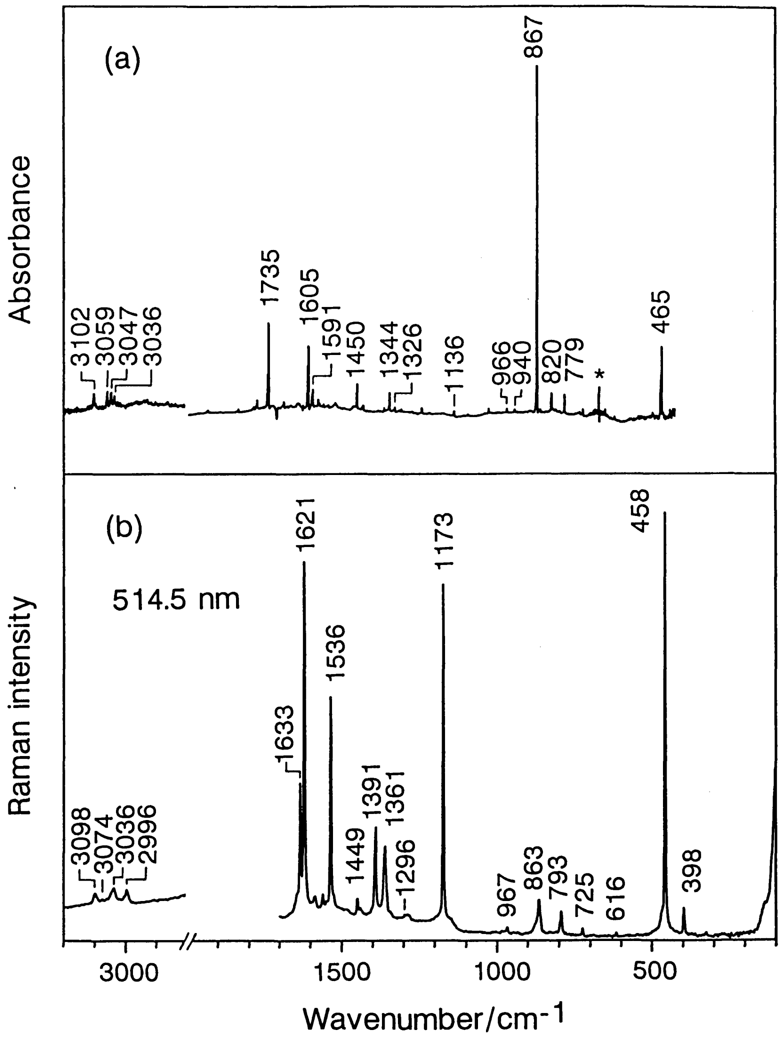


Fig. 2. Infrared (a) and Raman (b) spectra of *p*-BQM in low-temperature Ar matrices.

The 514.5-nm-excited Raman spectrum of *p*-BQM is shown in Fig. 2 (b). Essentially the same spectrum has been obtained with 632.8-nm excitation. This means that Raman excitations at these wavelengths correspond to off-resonant conditions. The widths of the Raman bands in Fig. 2 (b) (about 7–4 cm^{-1} for bands in the region below 2000 cm^{-1} and about 17 cm^{-1} for bands in the 3100–2990-cm^{-1} region) are much larger than those of the infrared bands in Fig. 2 (a), reflecting the above-mentioned difference in the matrix/sample ratios used in these two kinds of measurements.

In the double-bond stretching region of the Raman spectrum, three bands at 1633, 1621, and 1536 cm^{-1} are prominent. The 1621- and 1536-cm^{-1} bands are assignable, respectively, to the in-phase stretches of the two double bonds in the wing and those in the ring. The 1536-cm^{-1} band is lower in position than the corresponding band of *p*-xylene at 1616 cm^{-1}.[15,16] This is probably due to mixing of the ring and wing double-bond stretches. The 1633-cm^{-1} band most probably arises from a combination of the modes giving rise to the intense Raman bands at 1173 and 458 cm^{-1}. The 1173-cm^{-1} band is assignable to the totally symmetric ring CH bend.

In the Raman spectrum of *p*-xylene, a very strong, polarized band is observed at 828 cm^{-1},[15,16] which has been assigned to a substituent-sensitive ring mode[15] or the ring breathing.[17] Although the detailed assignment of this band should be studied further, the existence of the 828-cm^{-1} band itself is beyond question. It is therefore noted that no such band is found in the 900–800-cm^{-1} region in Fig. 2 (b) and, instead, the most intense band is observed at 458 cm^{-1}. This band must be due to a totally symmetric in-plane ring deformation significantly different from the ring breathing. A more detailed vibrational analysis of *p*-BQM based on *ab initio* molecular orbital and normal coordinate calculations is now under way, and will be reported elsewhere.

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(Received October 29, 1992)