A New Type of Intramolecular Hydrogen Bonding: Hydroxyl−Methyl Interactions in the *o*-Cresol Cation

Asuka Fujii,* Eiji Fujimaki, Takayuki Ebata, and
Naohiko Mikami*

*Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578, Japan*

Hydrogen bonding concerning alkyl groups has been a controversial topic in chemistry.[1−3] Alkyl groups are generally considered to have no proton-donating and -accepting abilities and not to participate in hydrogen bonding, though very weak C−H- - - X hydrogen bonding has been suggested in some spectroscopic studies. In such hydrogen bonding, the alkyl group is expected to be a proton-donating site, because of the larger electronegativity of carbon than that of hydrogen.[1,2] On the other hand, C- - -H−X type hydrogen bonding was predicted in ab initio calculations, though its experimental evidence is scarce.[3]

In this Communication, we report an experimental evidence for a new type of intramolecular hydrogen bonding, in which a methyl group plays the role of a proton acceptor. Recently we developed a new technique for infrared (IR) spectroscopy of molecular cations in a supersonic jet.[4,5] Jet-cooled molecules are an ideal system for studies of intramolecular hydrogen bonding because intermolecular interactions are eliminated. IR spectroscopy of jet-cooled species is, therefore, a highly sensitive probe of intramolecular interactions. We measured IR spectra of rotational and structural isomers of jet-cooled cresol in both the neutral and cationic ground states. The OH stretching vibrational frequency only of the cis isomer of the *o*-cresol cation showed a substantial red-shift from those of other structural and rotational isomers, while the OH frequencies of all isomers are almost the same in the neutral ground state. These results demonstrate the presence of unconventional intramolecular hydrogen bonding between the hydroxyl and methyl group in the cis isomer of the *o*-cresol cation.

Details of experiments are described elsewhere.[4−7] Briefly, IR spectroscopy of jet-cooled molecules in the *neutral* ground state was performed by the infrared − ultraviolet (IR−UV) double resonance technique.[6,7] A pulsed UV laser, of which the wavelength is fixed at the S_1-S_0 transition of the molecule, is introduced, and the resonance-enhanced multiphoton ionization (REMPI) signal is observed as a measure of the ground-state population. Prior to the UV laser, an IR laser pulse was introduced, and its wavelength is scanned. When the IR wavelength is resonant on a vibrational transition of the molecule, the IR absorption is detected as a decrease of the REMPI signal intensity.

As for IR spectroscopy of *cations*, we applied autoionization-detected infrared (ADIR) spectroscopy, which we newly developed.[4,5] In this technique, we observe vibrational transitions of very high Rydberg states instead of the bare ion. Because of the extremely weak interaction between the ion core and the Rydberg electron, the ion core of the high Rydberg states is regarded to have the same structure as the bare ion. Two-color double-
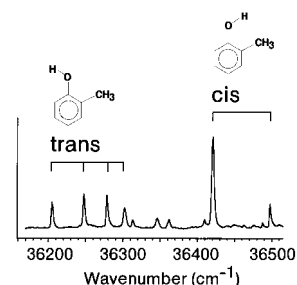

Figure 1. Resonance-enhanced multiphoton ionization (REMPI) spectrum of the S_1-S_0 transition of jet-cooled *o*-cresol in the origin band region. Two band groups correspond to the cis and trans rotational isomers of *o*-cresol. Their schematic structures are shown in the inset.

resonance excitation via the S_1 state is used to pump the molecule to the high Rydberg states just below the first ionization threshold (IP_0). When the ion core is vibrationally excited by the IR laser, the total energy of the Rydberg states exceeds IP_0 because of the vibrational energy. Then, vibrational autoionization (energy transfer from the vibration in the ion core to the Rydberg electron) occurs, and ions are produced. The high sensitivity in ion detection techniques allows us to measure the weak absorption of the ion core. An IR spectrum is obtained by monitoring the produced ion intensity as a function of the IR laser wavelength. Observed vibrational frequencies are practically regarded as those of the bare ion.

Figure 1 shows the REMPI spectrum of the S_1-S_0 transition of jet-cooled *o*-cresol. For *o*-cresol, two (cis and trans) rotational isomers, according to the orientation of the hydroxyl group, are present.[8] Each isomer shows different electronic transition energy and is easily distinguished in the electronic spectrum. The minimum energy configuration of the methyl group in the trans isomer rotates 60° with the electronic excitation, and the electronic spectrum of the trans isomer shows a long progression of the internal rotation of the methyl group.[8,9] On the other hand, the cis isomer has the same configuration in S_1 and S_0, resulting in the dominant intensity of the 0−0 band. These assignments of the spectrum have been confirmed by ab initio calculations [9] and by experiments on the cluster formation. [8]

Both in IR−UV spectroscopy for neutrals and in ADIR spectroscopy for cations, the different electronic energy of each isomer enables us to measure isomer-separated IR spectra, as is the case with *o*-cresol shown in Figure 1. The electronic transitions of *m*- and *p*-cresol have been studied by Oikawa et al.[10] and Tembreull et al.,[11] respectively. There are also two rotational isomers for *m*-cresol, while *p*-cresol has no rotational isomers.

Figure 2 shows IR spectra of rotational and structural isomers of jet-cooled *neutral* cresol observed by the IR−UV double-resonance technique. In each spectrum, the UV laser wavelength was fixed at the S_1-S_0 transition of each isomer, and the IR wavelength was scanned, monitoring the REMPI intensity due to the UV laser. Sharp dips in the spectra correspond to absorption due to the OH stretching vibration. Every OH stretch band in the spectrum appears in the same region, and the frequency difference among these five isomers is extremely small (within 3 cm^{-1}). Moreover, their OH frequencies are very close to that of free phenol (3657 cm^{-1}),[6] suggesting that the methyl substitution causes a negligible perturbation on the force field in the hydroxyl group.

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997, and references therein.
(2) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963,** *85,* 1715.
(3) Szczęśniak, M. M.; Chałasiński, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1993,** *98,* 3078.
(4) Fujii, A.; Iwasaki, A.; Ebata, T.; Mikami, N. *J. Phys. Chem.* **1997,** *101,* 5963.
(5) Fujii, A.; Iwasaki, A.; Mikami, N. *Chem. Lett.* **1997,** 1099.
(6) Watanabe, T.; Ebata, T.; Tanabe, S.; Mikami, N. *J. Chem. Phys.* **1996,** *105,* 408.
(7) Ebata, T.; Fujii, A.; Mikami, N. *Int. Rev. Phys. Chem.* **1998,** *17,* 331.

(8) Aota, T.; Ebata, T.; Ito, M. *J. Phys. Chem.* **1989,** *93,* 3519.
(9) Suzuki, T.; Iwata, S. Private communication.
(10) Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1984,** *88,* 5180.
(11) Tembreull, R.; Dunn, T. M.; Lubman, D. M. *Spectrochim. Acta* **1986,** *42A,* 899.

Communications to the Editor

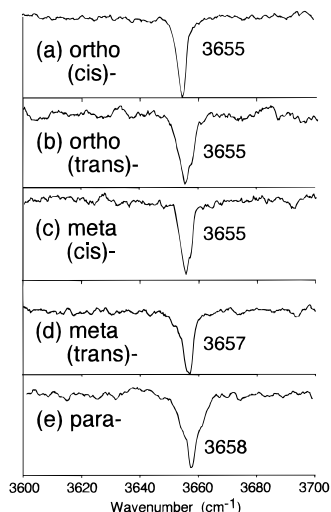*J. Am. Chem. Soc., Vol. 120, No. 50, 1998* 13257

Figure 2. Infrared spectra of isomer-separated *neutral* cresol in the OH stretching vibrational region. The IR−UV double-resonance technique is utilized to measure the spectra of jet-cooled molecules.

In the cis isomers of ortho-substituted phenols, intramolecular hydrogen bond formation is expected between the neighboring hydroxyl and substituent groups. On the other hand, it is clear that such an intramolecular hydrogen bond is forbidden in the trans isomers because of steric restriction. The cis and trans isomers of neutral *o*-cresol show the same OH frequency. These results indicate that intramolecular hydrogen bonding is negligible in neutral *o*-cresol.

IR spectra of the OH stretches of the cresol *cations* are shown in Figure 3. With ionization, the OH stretch frequencies shift to red over 100 cm^{-1}. A similar shift was observed for phenol, and the OH frequency of the phenol cation was found at 3534 cm^{-1}.[4] A significant feature in the spectra of the cations is the substantial red-shift of the OH band in the cis isomer of the *o*-cresol cation in comparison with those of all other isomers. The trans isomer of the *o*-cresol cation should give the same electronic substitution effects as the cis isomer to the hydroxyl group through the phenyl ring; however, its OH frequency is almost the same as those of meta and para isomers. Therefore, the origin of the characteristic red-shift of the cis isomer of the *o*-cresol cation is concluded to be due to local interactions between the hydroxyl and methyl groups, i.e., intramolecular hydrogen bonding. The steric configuration of the cis isomer and the red-shift of the OH frequency indicate that the methyl group should be the proton acceptor in this hydrogen bonding, while the hydroxyl group is the donor. Such intramolecular hydrogen bonding has not been known, and this report provides the first observation of the new interaction.

The OH frequency red-shift of the cis isomer from that of the trans is 25 cm^{-1} in the *o*-cresol cation, and this shift is as large
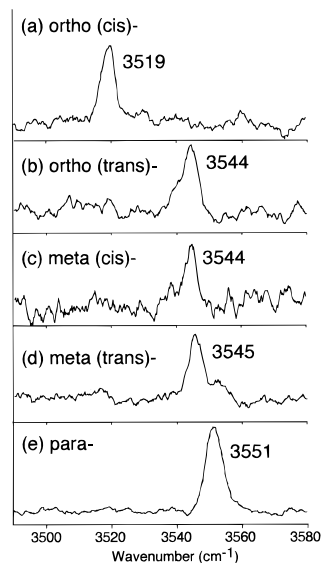

Figure 3. Infrared spectra of isomer-separated cresol *cations* in the OH stretching vibrational region. The autoionization-detected infrared (ADIR) spectroscopic technique is utilized to measure the spectra of the cold and isolated cations.

as the shift due to intramolecular hydrogen bonding in neutral *o*-fluorophenol,[12] suggesting the same order of the hydrogen bond strength. The very weak C- - -H−O type intermolecular hydrogen bonding was predicted in ab initio calculations of the CH$_4$−H$_2$O cluster.[3] The bonding energy was estimated to be extremely small (0.83 kcal/mol), and it is consistent with an undetectable red-shift of the OH stretch frequency observed for the *neutral* cis isomer of *o*-cresol. At present, it is difficult to give an unequivocal explanation for the appearance of the hydrogen bonding upon ionization; however, it is worthwhile to note that the carbon cation can be a five-coordinate site. The presence of this type of nonclassical cations, such as CH$_5^+$, has been confirmed.[13] The methyl group in cresol is positively charged because of its electron-donating ability to the phenyl ring, and the partial charge increases upon ionization. Such an increase of the charge distribution might induce mixing of such nonclassical character which contributes to the intramolecular hydrogen bonding.

(12) Omi, T.; Shitomi, H.; Sekiya, N.; Takazawa, K.; Fujii, M. *Chem. Phys. Lett*. **1996**, *252*, 287.

(13) For example, see Boo, D. W.; Lee, Y. T. *J. Chem. Phys*. **1995**, *103*, 520.