J. Phys. Chem. A **2004,** *108,* 721−726 **721**

Experimental and Computational Studies of the Infrared Spectra of 3,4-Benzotropone and Naphtho[2,3-*c*]tropone: Medium Effects on the Molecular Structures of the Tropones

Tadatake Sato,*,† Hiroyuki Niino,† and Masakazu Ohkita‡

Photoreaction Control Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan, and Department of Applied Chemistry, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Received: June 10, 2003; In Final Form: November 26, 2003

The IR spectra of 3,4-benzotropone (**2**) and naphtho[2,3-*c*]tropone (**3**) isolated in nitrogen matrices at 13 K were directly observed. These tropones were generated in the matrices by the photoisomerization of 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (**4**) and naphtho[2,3-*f*]bicyclo[3.2.0]hepta-3,6-dien-2-one (**5**), respectively. The observed IR bands of the photoproducts were in good agreement with the theoretically predicted bands. The intense $\mathrm{C{=}O/C{=}C}$ bands of **2** were observed at 1607 and 1615 $\mathrm{cm^{-1}}$, and the corresponding band of **3** was observed at 1605 $\mathrm{cm^{-1}}$ with shoulder peaks. The fact that the $\mathrm{C{=}O/C{=}C}$ band of **3** was observed at a slightly lower wavenumber than the corresponding bands of **2** indicates that benzo-annelation enhanced the contribution of the polarized resonance form to **3**. The observed IR spectra of **2** in the nitrogen matrix differed significantly from the spectra observed previously in a $\mathrm{CFCl_3{-}CF_2BrCF_2Br{-}CHCl_3}$ matrix. Self-consistent reaction field calculations on **2** using the Onsager dipolar-sphere model revealed that the observed differences in the spectra reflect structural changes induced in the tropones by the surrounding media.

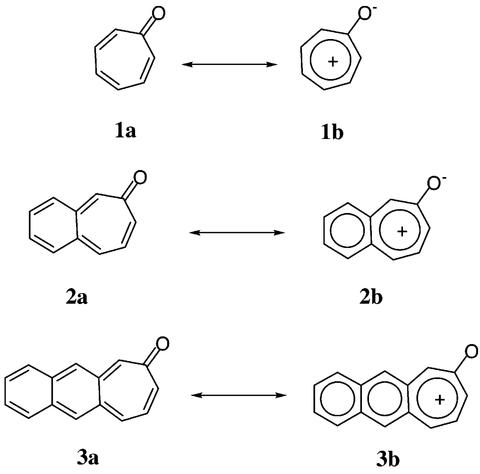
Introduction

Tropone (**1**) has generally been considered to be a representative nonbenzenoid aromatic compound. However, structural studies—such as X-ray crystallographic studies,[1] electron diffraction studies,[2] and microwave studies on the free monomer[3]—as well as theoretical studies[4−7] have suggested that **1** has a predominantly triene character with little aromaticity. The level of aromaticity is considered to depend on the contribution of electronically polarized form **1b**[4,5] (Scheme 1), which should stabilize the planar geometry.

The IR spectra of tropones have been used to probe the contribution of the polarized resonance form.[8−11] Although strong mixing between the $\mathrm{C{=}O}$ and $\mathrm{C{=}C}$ stretching often complicates the assignment of the $\mathrm{C{=}O/C{=}C}$ bands, the IR bands of tropones have been reasonably well assigned by means of IR studies using various media and ^{18}O isotopomers[9−11] and by means of theoretical studies.[6] However, complex spectral changes induced by the surrounding media are not sufficiently understood.

Recently, one of the authors (M. O.) reported that in a $\mathrm{CFCl_3{-}CF_2BrCF_2Br{-}CHCl_3}$ matrix, 3,4-benzotropone (**2**) showed multiple $\mathrm{C{=}O/C{=}C}$ IR bands. On the basis of an isotopic shift induced by ^{18}O labeling, an IR band at a significantly lower wavenumber (1506 $\mathrm{cm^{-1}}$) was assigned to a vibration involving primarily $\mathrm{C{=}O}$ stretching.[12] This result indicated that the contribution of polarized resonance form **2b** was enhanced and, consequently, that the $\mathrm{C{=}O}$ bond was elongated in **2**, even though **2** was predicted to be only weakly stabilized relative to its valence isomers, 2,3-benzotropone and 4,5-benzotropone.[13] Because **2** is an *o*-quinoidal species, it is a highly reactive, kinetically unstable molecule and easily dimerizes in fluid media even at −78 °C. Moreover, recent theoretical studies on benzo-annelated tropones indicate that aromaticity may be further enhanced in naphtho[2,3-*c*]tropone (**3**).[14]

SCHEME 1



Prompted by these results, we conducted detailed studies of the IR spectra of benzo-annelated tropones **2** and **3** by means of the matrix-isolation technique using solid nitrogen as a matrix medium. This technique enabled us to study these labile species by directly observing their IR spectra. Tropones **2** and **3** were generated in nitrogen matrices by the photoinduced rearrangement of the corresponding precursors, **4** and **5** (Scheme 2). The observed IR spectra were analyzed with the aid of density functional theory (DFT) calculations. Because polarized resonance forms such as **1b** have larger dipole moments than do nonpolarized forms such as **1a**, the contribution of the polarized

---

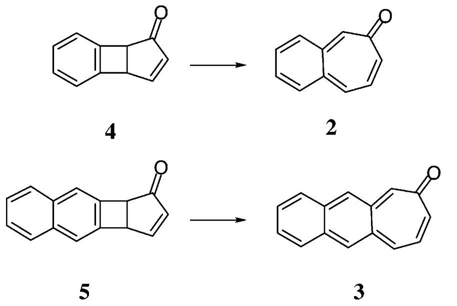
* Corresponding author. E-mail: sato-tadatake@aist.go.jp.

† National Institute of Advanced Industrial Science and Technology (AIST).

‡ Nagoya Institute of Technology.

10.1021/jp035650e CCC: $27.50

SCHEME 2



resonance form may increase in polar media. Accordingly, the molecular structures of the tropones may depend on the medium. This medium effect has been discussed on the basis of results obtained by means of self-consistent reaction field (SCRF) calculations using the Onsager dipole-sphere model.[15−17]

Experimental Section

Chemicals. The preparation of 6,7-benzobicyclo[3.2.0]hepta-3,6-diene-2-one (**4**) and naphtho[2,3-*f*]bicyclo[3.2.0]hepta-3,6-diene-2-one (**5**) has been reported in previous articles.[12,14]

Matrix Isolation. Matrix-isolation experiments were performed with a closed-cycle helium cryostat (Air Products Displex CS-202). The pressure in the sample chamber was maintained at 10^{-4}−10^{-5} Pa during the experiments. A CsI or BaF_2 plate cooled to 13 K was used as a substrate, on which vaporized **4** or **5** was co-deposited with nitrogen (99.9999%). The cryostat had two pairs of windows: one pair of KBr windows for FT-IR measurements and one pair of quartz windows for UV−vis absorption measurements. The two sets of windows allowed for the measurement of both the UV−vis and FT-IR spectra of each sample. The matrix-isolated precursors were photoirradiated with light from a high-pressure mercury lamp (Ushio, 500 W) with a 20-cm water filter and a glass UV-cut filter. The precursors could also be photolyzed with a XeCl excimer laser ($\lambda = 308$ nm; Lambda Physik) whose repetition rate and laser fluence were set at 5 Hz and 1 $mJ \cdot cm^{-2} \cdot pulse^{-1}$, respectively. FT-IR spectra were measured on a Perkin-Elmer Spectrum-GXI spectrometer with a resolution of 1 cm^{-1}, and UV−vis spectra were measured with a Shimadzu UV-3100 spectrometer.

Computational Methods

All DFT calculations were performed with the Gaussian 98 program package.[18] Geometries were optimized using the B3LYP method[19,20] and the 6-31G* basis set. The obtained geometries were identical to those used previously to calculate the nucleus-independent chemical shift (NICS) values.[14] The nature of the stationary points was assessed by means of vibrational frequency analysis. A value of 0.9510 was used as a scaling factor for the calculated vibrational frequencies; this value was determined from the observed and calculated frequencies of seven C═O bands in **2**, **3**, **4**, and **5**. The medium effect on the tropones was confirmed by means of SCRF calculations at the B3LYP/6-31+G* level by using the Onsager dipole-sphere model.[15−17] This model permits full structural optimizations and vibrational frequency calculations. Vibrational frequencies obtained by these calculations were scaled by a value of 0.9614. All of the calculations were made on the IBM RS/6000-SP system at the Tsukuba Advanced Computing Center (TACC) of AIST.

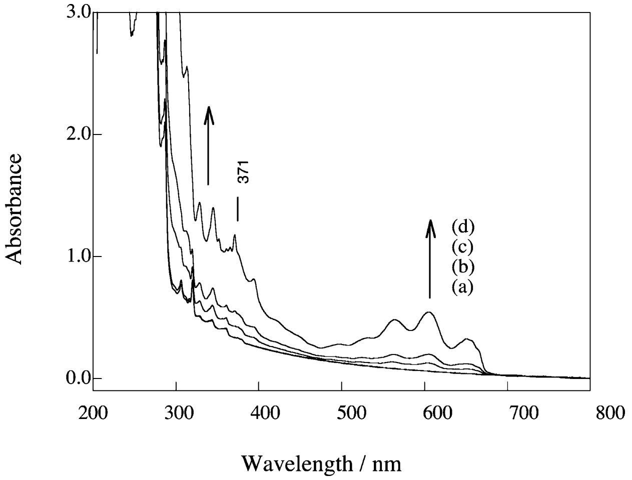


Figure 1. UV−vis absorption spectra observed upon irradiation of **5** in a nitrogen matrix at 13 K with a XeCl excimer laser ($\lambda = 308$ nm, 5 Hz, 2.5 $mJ \cdot cm^{-2} \cdot pulse^{-1}$): (a) 60, (b) 1560, and (c) 6060 pulses and (d) subsequent irradiation with a high-pressure mercury lamp ($\lambda > 290$ nm) for 1 h.

Results and Discussion

Matrix Spectra of Naphthotropone. To generate **3**, we photolyzed precursor **5** isolated in a nitrogen matrix at 13 K by monochromatic irradiation with a XeCl excimer laser. The photolysis was monitored by UV−vis and FT-IR absorption spectroscopy (Figure 1). The changes in the spectra were similar to those previously observed in EPA glass at 77 K.[14] Precursor **5** could be photolyzed further with a high-pressure mercury lamp equipped with a UV-cut filter ($\lambda > 290$ nm).

During the photolysis, new IR bands ascribed to the photoproducts appeared in the FT-IR spectra while the IR bands of **5** decreased in intensity. The changes in the IR spectra corresponded to those observed in the UV−vis spectra. The difference IR spectrum before and after irradiation is shown in Figure 2, together with the theoretical IR spectra of **3** and **5**. The most intense C═O/C═C band of the photoproducts was observed at 1605 cm^{-1}. We expected that the benzo-annelation of **2** would enhance the contribution of the polarized resonance form in **3** and, accordingly, that the prominent C═O/C═C bands of **3** would appear at lower wavenumbers than the band of **2**. However, the most intense band of **3** was located at a higher wavenumber than the previously observed C═O band of **2** (1506 cm^{-1}).[12] Despite the prominent C═O/C═C band that appears at an unexpectedly higher wavenumber, the fact that the IR bands of the photoproducts—not only the prominent C═O/C═C band but also the weak skeletal vibrational bands—corresponded fairly well to the theoretical IR bands of **3** (except for the IR band at 2128 cm^{-1}) proved that **3** was generated. (The assignment of the IR band at 2128 cm^{-1} will be discussed later.) The intense C═O/C═C band of **3** (1605 cm^{-1}) was observed at a lower wavenumber than the C═O bands of **5**, which appeared at 1721 and 1731 cm^{-1} (Table 1). This difference indicates that the bond in **3** was elongated relative to that in **5**; that is, the polarized resonance form contributed to **3**.

It is worth mentioning that DFT calculations predicted only one C═O band, at 1724.8 cm^{-1}, for **5** and two intense C═O/C═C bands for **3** (1605.1 and 1609.7 cm^{-1}) (Table 1). The splitting observed for the C═O band of **5** was probably due to Fermi resonance.[10,21] The intense C═O/C═C band of **3** at 1605 cm^{-1} was accompanied by shoulder peaks at 1585, 1589, and 1614 cm^{-1}. Although some of these shoulder peaks could also

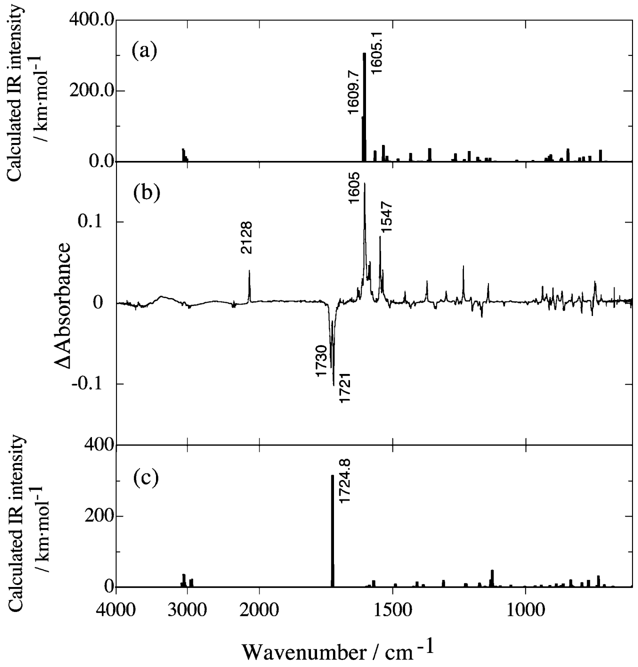


Figure 2. (a) IR spectrum of **3** calculated at the B3LYP/6-31G* level. (b) Difference IR spectrum before and after irradiation of a nitrogen matrix containing **5** with a XeCl excimer laser and a high-pressure mercury lamp. (Peaks pointing up correspond to the product, and peaks pointing down correspond to the decomposed precursor.). (c) IR spectrum of **5** calculated at the B3LYP/6-31G* level.

TABLE 1: Observed and Calculated Vibrational Frequencies (cm^{-1}) of Prominent ν(C=O/C=C) Modes of Tropones 2 and 3 and ν(C=O) Modes of Precursors 4 and 5

compd	N_2 matrix at 13 K	calcd[a]	previous[b]
4	1718	1723.9 (292)	1688
2	1607	1607.5 (139)	1506
	1615	1615.6 (204)	
5	1721	1724.8 (314)	
	1731		
3	1605	1605.1 (305)	
		1609.7 (125)	
1		1596.1 (123)	1553
		1636.0 (178)	

[a] Calculated at the B3LYP/6-31G* level and scaled by a factor of 0.9510. The calculated IR intensities are in parentheses (km·mol^{-1}). [b] Reference 12.

be due to Fermi resonance, one of them might arise from the strong mixing of the C=O and C=C stretching modes.[9,10] Indeed, the calculated vibrational modes of **3** (at the B3LYP/6-31G* level) between 1500 and 1800 cm^{-1} show complex mixing between the C=O and C=C stretching modes. (See Supporting Information, Figure S3.) It should be noted that the C=O/C=C band observed at 1547 cm^{-1}, located on the lower-wavenumber side of the intense C=O/C=C band at 1605 cm^{-1}, was shown to be more intense than the corresponding band in the predicted spectrum of **3**.

On the basis of the preceding result for phenoxybenzotropone reported by Chapman et al.,[22] we tentatively ascribed the IR band observed at 2128 cm^{-1} upon the photoirradiation of **5** to carbon monoxide.[23] The decarbonylation of tropone and its benzo-annelated derivatives is induced by thermal excitation or electron-impact excitation, and the mechanisms of these processes have been studied in detail.[24] Chapman et al. indicated that phenoxybenzotropone showed similar decarbonilation in an argon matrix, and generated carbon monoxide showed an IR band at a smaller wavenumber. They suggest that the reaction proceeds via the cyclopropanone intermediate. Given these earlier results, we believe that CO was formed during the photoirradiation of **5** by means of the further reaction of **3** (Scheme 3). The decomposition of the cyclopropanone intermediate would proceed efficiently under photoirradiation conditions (as it does in the case of naphthocyclopropenone[21]) to produce anthracene and CO. Indeed, the weak UV−vis bands with vibronic structures that we observed at 371 nm could be ascribed to anthracene.[25]

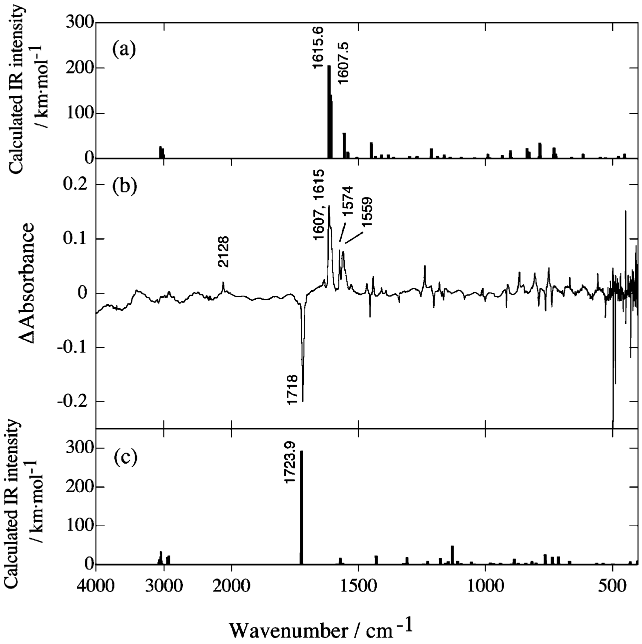
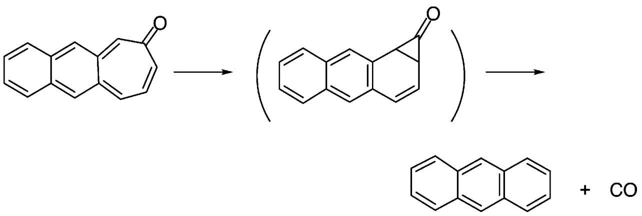


Figure 3. (a) IR spectrum of **2** calculated at the B3LYP/6-31G* level. (b) Difference IR spectrum before and after irradiation of a nitrogen matrix containing **4** with a high-pressure mercury lamp for 2.5 h. (Peaks pointing up correspond to the product, and peaks pointing down correspond to the decomposed precursor.) (c) IR spectrum of **4** calculated at the B3LYP/6-31G* level.

SCHEME 3



Matrix Spectra of Benzotropone. Prompted by unexpected results for **3**, we reexamined the IR spectra of **2** by using a nitrogen matrix. We photolyzed **4** in a similar manner to observe the IR spectrum of **2** in a nitrogen matrix. Matrix-isolated precursor **4** was photolyzed upon irradiation by a high-pressure mercury lamp with a UV-cut filter (λ > 290 nm). Upon irradiation, the observed UV−vis absorption spectra were similar to those reported in EPA glass at 77 K,[12] which indicates the generation of **2** (Supporting Information). In the difference IR spectrum for the photolysis (Figure 3), new IR bands ascribed to products and carbon monoxide appeared with the concomitant diminution of the bands of **4**.

The generation of **2** was confirmed by the good correspondence between the observed and calculated IR bands, as shown in the Figure. The intense C=O/C=C bands of **2** were observed at 1607 and 1615 cm^{-1}, and the C=O band of **4** was observed at 1718 cm^{-1}. The C=O/C=C bands of **2** were observed at much higher wavenumbers than the IR band observed previously (1506 cm^{-1}). Although the IR bands observed at 1574 and 1559 cm^{-1} (on the lower-wavenumber side of the intense C=O/C=C bands) were more intense than predicted, the observed C=O/C=C bands differed significantly from the multiple bands previously observed in the $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ matrix.[12]

The mixing of the C=O and C=C stretching in **2** was also observed in the calculated vibrational patterns, as in the case of **3** (Supporting Information). As theoretically predicted, the intense C=O/C=C band of **3** (1605 cm^{-1}) was located at a slightly lower wavenumber than the bands of **2** (1607 and 1615 cm^{-1}). We ascribe this shift to the increase in the contribution of **3b** induced by the benzo-annelation of **2**. Thus, although the peak shift from **2** to **3** was small, the enhancement of aromaticity in the benzo-annelated tropones that is predicted by the theoretical calculations[14] was confirmed.

As discussed above, the IR spectra of the tropones in nitrogen matrices showed fair agreement with the calculated IR spectra. However, the IR spectra of **2** observed in the nitrogen matrix differed significantly from the spectra observed in a $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ matrix at 118 K.[12] The observed difference may arise from structural changes induced in the tropones by the surrounding media.

Polarized resonance form **2b** has a larger dipole moment than nonpolarized form **2a**, and in media with higher dielectric constants, the electrostatic stabilization of **2b** must be higher than that of **2a**. Accordingly, the contribution of the polarized resonance form may increase in polar media, and this increase may change the molecular structure. Thus, the molecular structures of the tropones might be sensitive to interactions with the surrounding media.

To examine the effect of the surrounding media on the tropones, we performed SCRF calculations using the Onsager dipole-sphere model for **2**. In this model, the solute occupies a spherical cavity within the solvent field. The optimum cavity radius for **2** was estimated to be 4.30 Å. Geometrical optimizations and subsequent frequency analyses were executed for four representative media: carbon tetrachloride ($\epsilon = 2.23$), tetrahydrofuran (THF, $\epsilon = 7.58$), methanol ($\epsilon = 32.63$), and water ($\epsilon = 78.39$). The changes in the dipole moment, in the atomic charge on the O atom, and in the length of the C=O bond of **2** clearly showed the increased contribution of polarized resonance form **2b** with the increasing dielectric constant of the surrounding medium (Figure 4). A reduction of the bond alternation in the benzotropone frame was revealed concomitantly with the elongation of the C=O bond (Supporting Information). In the region where the dielectric constant is small, the molecular structure of **2** varies drastically.

The IR spectra obtained for the various media showed intriguing differences (Figure 5). The normal calculation (B3LYP/6-31+G* level), which corresponds to the calculation on a molecule isolated in vacuum, predicted one intense C=O/C=C band (mode 45, Figure 5e). The spectrum obtained at this computational level was almost identical to the spectrum obtained at the B3LYP/6-31G* level (Figure 3). Strong mixing of the C=O and C=C stretching modes was observed in the normal and SCRF results (Figure 6). The IR band for mode 45 obtained from the normal calculation showed atomic motions similar to those of the corresponding mode in H_2O (a polar medium): this IR band was shifted to a lower wavenumber (from 1601.6 to 1582.5 cm^{-1}) with increasing dielectric constant. However, there were other remarkable changes in the spectra: the intensities of two IR bands (modes 42 and 43) drastically increased with increasing dielectric constant (Table 2).

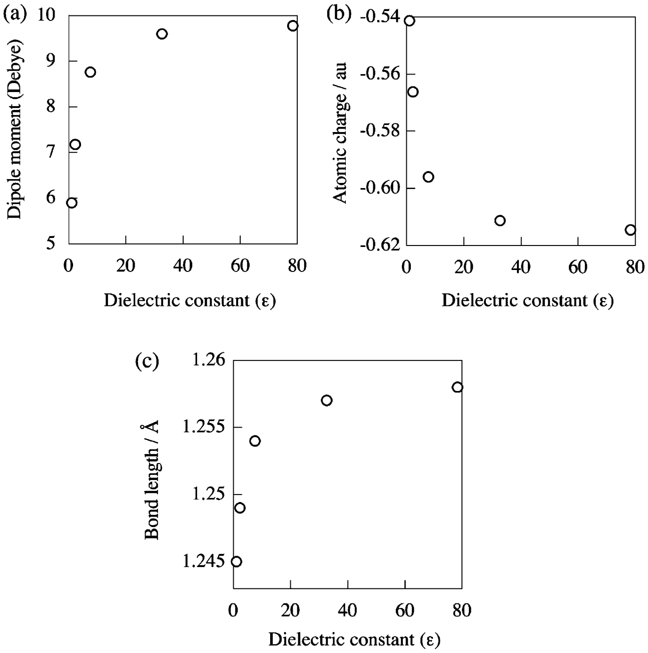


Figure 4. (a) Dipole moment, (b) atomic charge on the O atom, and (c) and C=O bond length for **2** obtained using SCRF calculations for various media.

The changes in these bands were observed even in the medium with a low dielectric constant (CCl_4, $\epsilon = 2.23$). The $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ (25:25:4) matrix should have a dielectric constant that is intermediate between the values for CCl_4 (2.23) and THF (7.58). (The dielectric constants of $CFCl_3$, CF_2BrCF_2Br, and $CHCl_3$ are 3.00, 2.34, and 4.81, respectively.[26]) The four C=O/C=C bands at 1594, 1538, 1506, and 1438 cm^{-1} observed in the $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ matrix should correspond to vibrational modes 45, 44, 43, and 42, respectively, which are predicted to be at 1593.5, 1552.8, 1539.6, and 1509.2 cm^{-1}, respectively, in CCl_4. These bands showed isotropic shifts to lower wavenumbers (2, 2, 14, and 4 cm^{-1}, respectively) upon ^{18}O labeling.[12] These shifts were predicted to be 4, 1, 12, and 7 cm^{-1}, respectively, for ^{18}O-labeled **2** surrounded by CCl_4: the predicted shifts corresponded well to the observed isotropic shifts. Thus, the multiple C=O/C=C bands observed in the $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ matrix reflected the geometrical change in **2** induced by the relative polarity of the surrounding medium. From these results, we concluded the following: the most intense C=O band observed in a nitrogen matrix was ascribed to vibrational mode 45, and the most intense C=O band observed in the $CFCl_3$−CF_2BrCF_2Br−$CHCl_3$ matrix was ascribed to vibrational mode 43. Owing to the increased contribution of **2b**, the mixing between C=O and C=C stretching vibrations was altered. That is, in the polar media, the stretching vibration of the elongated C=O bond mixed strongly with the C=C stretching skeletal vibrational modes appearing at lower wavenumbers. In the spectra of **2** and **3** in nitrogen matrices, some IR bands observed on the lower-wavenumber side were shown to be more intense than the calculated bands. This difference may be due to a medium effect of the nitrogen matrix. Thus, we confirmed that the molecular structures of tropones are sensitive to the contributions of their polarized resonance forms, and that contribution can be changed by interaction with the surrounding medium.

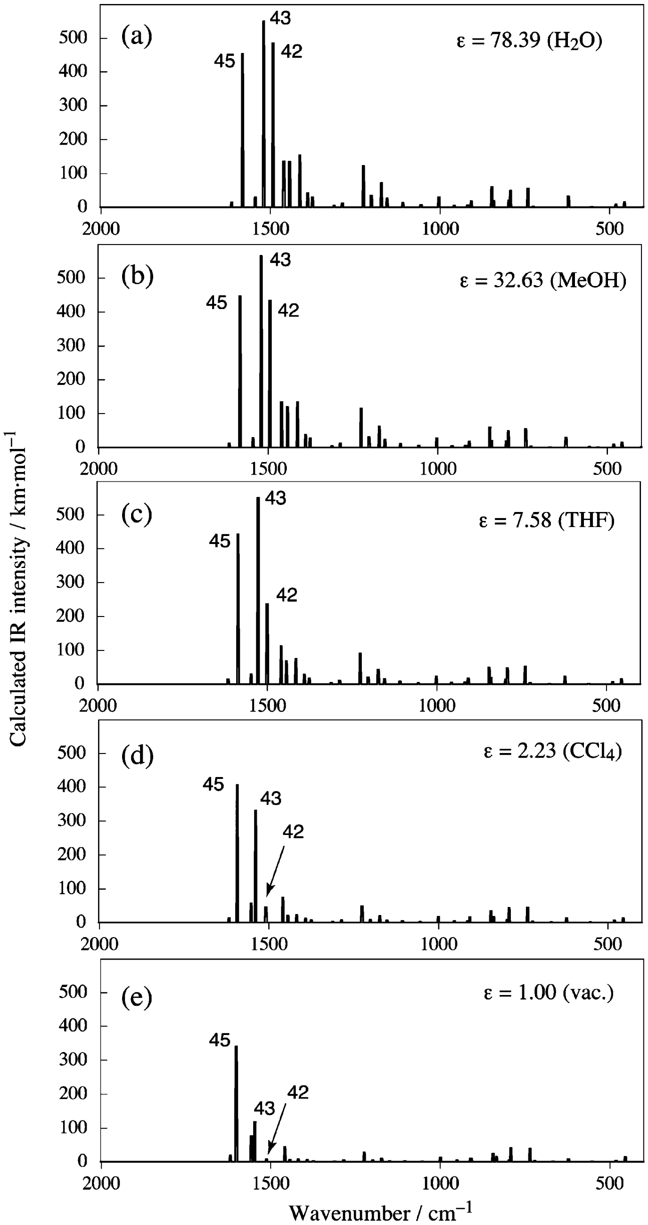


Figure 5. (a−d) IR spectra of **2** in various media calculated using the SCRF Onsager dipole-sphere model (B3LYP/6-31+G* level). (e) IR spectra of **2** calculated at the B3LYP/6-31+G* level. Vibrational frequencies were scaled by a factor of 0.9614.

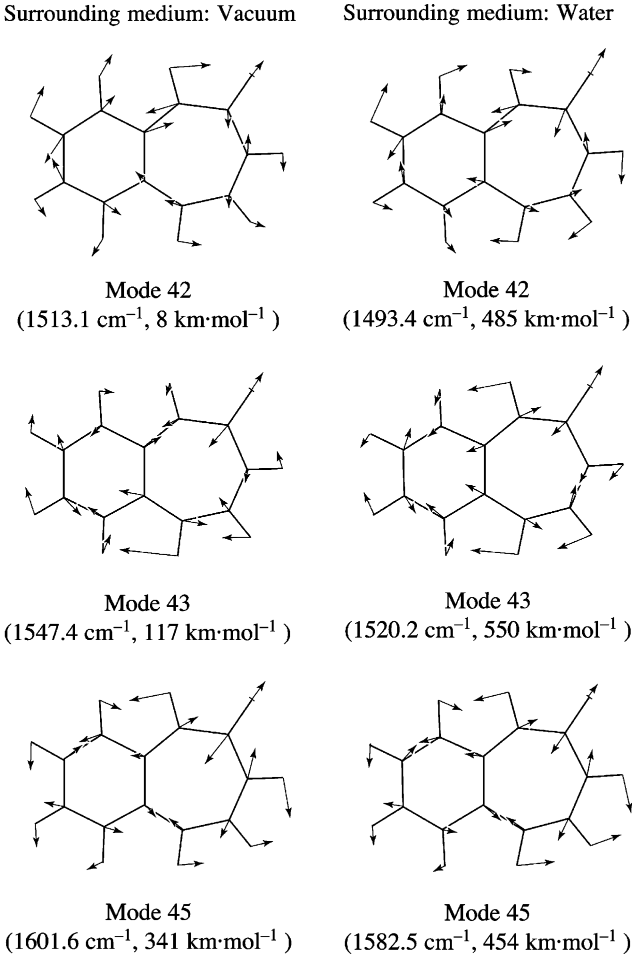


Figure 6. (Left) Selected C=O/C=C stretching modes of **2** calculated at the B3LYP/6-31+G* level. (Right) Corresponding C=O/C=C stretching modes of **2** obtained by means of the SCRF Onsager dipole-sphere model (B3LYP/6-31+G*), assuming an ϵ value of 78.39 (water).

TABLE 2: Vibrational Frequencies, ν (cm^{-1}), and IR Intensities, I (km·mol^{-1}), of ν(C=O/C=C) Modes of 2 and 3 Obtained by Means of SCRF Calculations

	mode 42		mode 43		mode 44		mode 45		mode 46	
ϵ value	ν^a	I	ν^a	I	ν^a	I	ν^a	I	ν^a	I
1.00	1513.1	8	1547.4	117	1557.7	76	1601.6	341.0	1618.8	19
2.23	1509.2	45	1539.6	331	1552.8	56	1593.5	405.7	1618.0	14
7.58	1501.2	237	1527.3	550	1548.0	30	1586.4	443.3	1616.3	14
32.63	1494.9	434	1521.4	566	1545.3	29	1583.2	446.7	1615.0	12
78.39	1493.4	485	1520.2	550	1544.8	30	1582.5	453.7	1614.7	14

[a] Frequencies were scaled by a factor of 0.9614.

Conclusions

The IR spectra of 3,4-benzotropone (**2**) and naphtho[2,3-*c*]tropone (**3**) isolated in nitrogen matrices at 13 K were directly observed. These tropones were generated in the matrices by the photoisomerization of 6,7-benzobicyclo[3.2.0]hepta-3,6-diene-2-one (**4**) and naphtho[2,3-*f*]bicyclo[3.2.0]hepta-3,6-diene-2-one (**5**), respectively. The observed IR bands of the photoproducts were in good agreement with the theoretically predicted IR bands. The prominent C=O/C=C bands of **2** were observed at 1607 and 1615 cm^{-1}, and the corresponding band of **3** was observed at 1605 cm^{-1} with shoulder peaks. The C=O band of **3** was observed at a slightly lower wavenumber than the bands of **2**, which indicates the enhanced contribution of the polarized resonance form induced by benzo-annelation.

The IR spectra of **2** in the nitrogen matrix differed from those observed in the $CFCl_3-CF_2BrCF_2Br-CHCl_3$ matrix. Self-consistent reaction field calculations on **2** using the Onsager dipolar-sphere model revealed that the structures of the tropones were sensitive to the surrounding media. Owing to the increased contribution of the polarized resonance form, the mixing between the C=O and C=C stretching vibrations was altered. In the polar media, the stretching vibrations of the elongated C=O bond mixed strongly with the C=C stretching skeletal vibrational modes appearing at lower wavenumbers. This mixing is the origin of the multiple C=O/C=C bands observed in the spectra of the $CFCl_3-CF_2BrCF_2Br-CHCl_3$ matrix.

Supporting Information Available: UV−vis absorption spectra observed during the photolysis of **4**; calculated and observed IR data; calculated energies; Cartesian coordinates of the optimized geometries of the tropones and their precursors; and details of the SCRF Onsager dipole-sphere model calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Barrow, M. J.; Mills, O. S.; Filippini, G. *J. Chem. Soc., Chem. Commun.* **1973**, 66.

(2) Ogasawara, M.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3277.

(3) Creswell, R. A. *J. Mol. Spectrosc.* **1974**, *51*, 111.

(4) Bertelli, D. J.; Andrews, T. G., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 5280.

(5) Bertelli, D. J.; Andrews, T. G., Jr.; Crews, P. O. *J. Am. Chem. Soc.* **1969**, *91*, 5280.

(6) Redington, R. L.; Latimer, S. A.; Bock, C. W. *J. Phys. Chem.* **1990**, *94*, 163.

(7) Sanna, N.; Ramondo, F.; Bencivenni, L. *J. Mol. Struct.* **1994**, *318*, 217.

(8) Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 967.

(9) Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 972.

(10) Krebs, v. A.; Schrader, B. *Liebigs Ann. Chem.* **1967**, *709*, 46.

(11) Junge, H. *Spectrochim. Acta, Part A* **1968**, *24*, 1951.

(12) Ohkita, M.; Nishida, S.; Tsuji, T. *J. Am. Chem. Soc.* **1999**, *121*, 4589.

(13) Zambelli, N.; Trinajstic, N. *Z. Naturforsch., B* **1971**, *26*, 1007.

(14) Ohkita, M.; Sano, K.; Suzuji, T.; Tsuji, T. *Tetrahedron Lett.* **2001**, *42*, 7295.

(15) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(16) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(17) Wong, M. W.; Wiberg, K. B. *J. Chem. Phys.* **1991**, *95*, 8991.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.

(21) Sato, T.; Niino, H.; Yabe, A. *J. Phys. Chem. A* **2001**, *105*, 7790.

(22) Chapman, O. L.; Busman, S. C.; Trueblood, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 7067.

(23) The wavenumber, 2128 cm^{-1}, was too small for carbon monoxide isolated in a nitrogen matrix. The IR band of carbon monoxide isolated in a nitrogen matrix was reported to be observed at 2140 cm^{-1} (Dubost, H.; Charneau, R.; Harig, M. *Chem. Phys.* **1982**, *69*, 389). However, in the present case, the carbon monoxide band can be observed at a different wavenumber from that of ideally isolated carbon monoxide. This is because the generated carbon monoxide must stay in the same matrix cage with naphthalene. They may keep some interaction with each other. In a similar reaction observed by Chapman et al. in an argon matrix (ref 22), an IR band ascribed to carbon monoxide was observed at 2110 cm^{-1}. This band was observed at a wavenumber that is 28 cm^{-1} smaller than that of ideally isolated carbon monoxide (2138 cm^{-1}; Jiang, G.. J.; Person, W. B.; Brown, K. G. *J. Chem. Phys.* **1975**, *62*, 1201), indicating the interaction between carbon monoxide and the naphthalene derivative. In our case, the observed shift was 12 cm^{-1}, indicating a smaller interaction. This difference might come from the phenoxy substituent in Chapman's experiment. IR studies using the ^{18}O isotopomer would be required to make a definitive assignment of this feature.

(24) Holzmann, G.; Frenking, G.; Steiner, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1943.

(25) Perkampus, H.-H. *UV−Vis Atlas of Organic Compounds*, 2nd ed.; VCH: Weinheim, Germany, 1992.

(26) *CRC Handbook of Chemistry and Physics*, 81st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2000.