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Van der Waals Complexes of Tropolone with Carbon Dioxide

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van der Waals complexes of tropolone (TRN) with carbon dioxide have been synthesized by expanding mixtures of TRN and CO_2 in He in a supersonic free-jet expansion, and have been examined by laser-induced fluorescence excitation spectroscopy and by ab initio structural calculations. At higher partial pressures of CO_2 large clusters of $TRN(CO_2)_n$ are formed in which TRN excited to S_1 remains fluorescent. At sufficiently low partial pressures of CO_2, well-resolved blue-shifted features in the spectra due to $TRN(CO_2)$ and $TRN(CO_2)_2$ may be identified. Their microscopic solvent shifts and the effects of solvation on the proton tunneling doublets and vibrational frequencies of the chromophore have been measured. The experimental results and calculations all suggest that the CO_2 binds to TRN in the 1:1 complex in a fashion which is similar to common hydrogen-bonding addends. The CO_2 lies in the plane of the TRN ring and interacts with the keto oxygen and the hydroxyl hydrogen in such a way that the intramolecular hydrogen bond of TRN is partially disrupted, lengthening the $R_{O\cdots H}$ distance and opening the H−O−C angle. Consistent with this interaction, the proton tunneling rate is reduced so that the tunneling doublets can no longer be resolved, and the frequency of the out-of-plane wagging vibration of the two oxygen atoms in the chromophore increases. The microscopic solvatochromic shifts of these and other hydrogen-bonded complexes are well-correlated with the calculated binding energies of the addends to the chromophore and with their proton affinities. The latter correlation suggests that CO_2 acts as a weak proton acceptor in a hydrogen-bonding-like interaction with TRN.

Introduction

Since the advent of laser and supersonic expansion technologies, progress in answering fundamental questions about proton transfer reactions and the effects of solvation on them has been rapid and substantial. Recently, considerable attention has focused on tropolone (TRN) as a model for the study of intramolecular proton transfer reactions.[1−27] TRN is an attractive model because it has a simple chemical structure, readily forms van der Waals (vdW) complexes in supersonic expansions, is reasonably photochemically stable, has a relatively large quantum yield of fluorescence,[28] and is easy to observe by laser-induced fluorescence excitation (LIFE) methods.

Intramolecular proton transfer in TRN occurs by tunneling of the hydroxyl proton between the two oxygen atoms; the two tautomers are identical. Both the ground and first excited singlet states therefore have potential energy surfaces with symmetric double minima and a transition state of C_{2v} symmetry along the proton-transfer coordinates. The (+, −) parity degeneracy of the molecule's vibrational eigenstates is lifted by proton tunneling so that they are separated by energies Δ_v'' in S_0 and by Δ_v' in S_1. The magnitudes of these tunneling splittings are determined by the shape of the potential surface along the proton tunneling coordinate, and therefore depend on the energy and mode of vibrational excitation and the presence of substituent groups on the ring. The tunneling splittings of the zero-point levels in the S_0 and S_1 states are $\Delta_0'' = 0.974$ cm^{-1}, and $\Delta_0' = 19.9$ cm^{-1}, respectively.[6,29] Because parity is conserved in the electronic transition, vibronic bands in the $S_1 - S_0$ spectra appear as doublets; the origin band has a splitting $\Delta_{0,obs} = |\Delta_0' - \Delta_0''| = 18.93 \pm 0.05$ cm^{-1}, which is easily observed in the jet-cooled fluorescence excitation spectrum.[2,3,6] An analysis of the variations in $\Delta_{v,obs}$ is a valuable tool for elucidating the structural and dynamic effects on proton transfer caused by ring substitution[7,17] and deuteration.[13] Moreover, the relative intensities of the upper and lower components of a tunneling doublet can be used as a measure of the internal "temperature" of the chromophore, since a significant population difference will be produced in the ground $v = 0$ states of different parity under supersonic expansion conditions.[1]

The tunneling splittings also are strongly influenced by any intermolecular interactions, such as solvation, which can both perturb the molecule's vibrational couplings and change the barrier height and shape. To examine these effects at the molecular level, several groups have synthesized and studied the spectroscopy of a variety of $TRN(S)_n$ van der Waals (vdW) complexes.[1,11−27] The solvating species, S, which have been examined include rare gas atoms and a variety of nonpolar and polar molecules. Binding is dominated by dispersion in complexes with rare gases and nonpolar molecules (in which S is preferentially bound above the plane of the chromophore) and by hydrogen bonding at the keto and hydroxyl groups in complexes with water, methanol, and other such polar molecules.[1]

The rare gases Ar, Kr, and Xe are the simplest complexing agents studied, and the $TRN(RG)_n$ $n = 1$ and $n = 2$ species have been observed.[20] These complexes all have origin bands which are red-shifted with respect to the origin of the bare molecule, indicating greater stabilization of the excited state than the ground state upon complexation, consistent with an

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increase in the polarizability of the chromophore in the excited state. Empirical Lennard-Jones potential calculations[20] suggest that the most stable structures of these 1:1 complexes are those with the solvent atom located above the plane of the seven-membered ring. Additivity of the microscopic solvent shifts suggests that the 1:2 complex has a symmetric sandwich structure. Such structures are also supported by the observation of low-frequency bands in the LIFE spectra which have been assigned to intermolecular vdW stretching (ca. 40−44 cm^{-1}) and bending (ca. 18−19 cm^{-1}) modes.[30,31] In keeping with the weak coupling of the rare gas to the proton, the tunneling splittings in the S_1-S_0 spectra of the rare gas vdW complexes do not differ greatly from those of the bare chromophore.[20]

In contrast, the spectra of vdW complexes involving solvent molecules which are capable of forming intermolecular hydrogen bonds (water, methanol, and acetone) are very intense, are strongly blue-shifted with respect to the bare molecule, and show no evidence of tunneling splitting.[10,23,25] Previous work on hydrogen-bonded clusters of organic acids such as phenol has shown that the origin band of the cluster is generally red-shifted with respect to the bare molecule when the chromophore acts as a proton donor and is blue-shifted when it acts as a proton acceptor.[32] On the basis of these studies and the observation of strongly blue-shifted absorptions in the $\mathrm{TRN(H_2O)}_n$ and $\mathrm{TRN(CH_3OH)}_n$ spectra, one might conclude that TRN is acting as a proton acceptor in these clusters. However, other factors must also be at play in the tropolone system since complexes of TRN with species such as $\mathrm{CH_3COCH_3}$ which are incapable of proton donation are also known to exhibit similar strong blue shifts.[33]

Studying the solvation of TRN with carbon dioxide offers information about yet another "type" of solvent molecule. $\mathrm{CO_2}$ cannot donate a proton, but rather is a weak proton acceptor. It has no permanent electric dipole moment, but can exhibit strong intermolecular interactions via its large permanent electric quadrupole moment,[34] 7.5×10^{-40} C m^2. The interest in how TRN is solvated and the effects of that solvation on intramolecular proton transfer is complemented, in the case of $\mathrm{CO_2}$, by interest in the properties of the solvent itself, and its tendency to form clusters in extraction processes. We report here the first study of the effects of solvation by $\mathrm{CO_2}$ on intramolecular proton transfer, using TRN and its $\mathrm{TRN(CO_2)}_n$ vdW complexes as a model system.

Experimental Section

Laser-induced fluorescence excitation spectra of $\mathrm{TRN(CO_2)}_n$ van der Waals complexes were obtained with a pulsed supersonic free-jet spectrometer which has previously been described in detail.[35,36] Briefly, the excitation source for this spectrometer is a Lumonics Hyperdye 300 pulsed dye laser pumped by a Lumonics HyperEX 400 XeCl excimer laser. Exalite 376 (4×10^{-4} M in *p*-dioxane) and a mixture of BBQ and BPBD (1×10^{-4} M BBQ and 6.2×10^{-4} M BPBD in 2:3 v:v toluene:ethanol) were used to cover the excitation wavelength ranges required for this study. The excitation beam has a spectral bandwidth of less than 0.2 cm^{-1} and a typical energy of 0.2 mJ/pulse.

The dye laser beam crosses a pulsed supersonic free-jet expansion at right angles, and undispersed fluorescence is collected through an appropriate cutoff filter by an *f*/1 quartz biconvex lens located on the axis mutually perpendicular to both the excitation and the expansion axes. The gas mixture is expanded through a heated pulsed solenoid valve (General Valve Series 9) with a 760 mm orifice into a high vacuum chamber. The distance between the nozzle and the excitation beam can be varied by moving the valve on a precision screw thread while the system remains under vacuum. In a typical experiment, 20 psig backing gas pressures were used and the valve was pulsed at 20 Hz, resulting in an average operating pressure in the expansion chamber of $10^{-5}-10^{-6}$ mbar.

Helium is used as the backing gas in the expansion, and tropolone is introduced by passing the flowing He over a solid sample in a small stainless steel container heated to ca. 40 °C. van der Waals complexes of tropolone with $\mathrm{CO_2}$ were synthesized in the expansion by using a mixture of $\mathrm{CO_2}$ in He of known composition (0.1−4%) as the backing gas.

If a Boltzmann distribution of the population of the nondegenerate 0^+ and 0^- levels of the ground state is present in the expansion and the Franck−Condon factors for the two transitions in a given tunneling doublet are the same, then the relative intensities of the doublets may be used to obtain an estimate of the internal temperature of the bare tropolone chromophore. By varying the nozzle-to-excitation distance and the pressure of the backing gas, relative intensities as large as 3:1 were observed for the $0^+_+:0^-_-$ transitions which, together with the known spacing $\Delta_0'' = 0.974\ \mathrm{cm}^{-1}$, gives an internal vibrational temperature of TRN as low as 1.3 K. While the assumptions underlying this calculation cannot be assumed to apply under all expansion conditions, the relative intensities of the tunneling doublets may be used as a monitor of the conditions of the expansion so that approximately the same degree of cooling can be maintained throughout a series of experiments.

Tropolone (98%, Aldrich) was purified by recrystallization from *n*-hexane followed by vacuum sublimation at 35 °C three times before use. $\mathrm{CO_2}$ (99.5%) and UHP He (99.999%) were obtained from Matheson and were used as received.

Results and Discussion

(i) Spectroscopy and Microscopic Solvent Shifts. The spectra of TRN expanded together with various partial pressures of $\mathrm{CO_2}$ in He are shown in Figure 1. Because $\mathrm{CO_2}$ has a polarizability[37] of 2.63 Å^3, similar to that of Kr (2.52 Å^3), and has no permanent dipole moment, it was expected that complexation would occur primarily dispersively above the ring and that absorptions due to the vdW complexes would be at lower energies than those of the bare molecule. However, no new bands of significant intensity were observed in the region to the red of the origin of the bare TRN molecule. These experiments did reveal, however, that the fluorescence intensity of the bare molecule decreased dramatically as the partial pressure of $\mathrm{CO_2}$ increased and many new features, ascribed to vdW complexes, appeared to the blue.

The bands due to vdW complexes were assigned by (i) measuring their spectral displacements from the origin of the bare molecule and (ii) measuring their relative intensities as a function of $\mathrm{CO_2}$ partial pressure (Figure 2) and finding similarities. At lower $\mathrm{CO_2}$ concentrations, all bands of significant intensity can be assigned to two vdW species which predominate in the expansion under these conditions. One group of features appears at higher partial pressures of $\mathrm{CO_2}$ than those of the second group and is shifted further to the blue. These and other observations (vide infra) suggest that the two vdW species are $\mathrm{TRN(CO_2)}$ and $\mathrm{TRN(CO_2)_2}$.

At higher partial pressures of $\mathrm{CO_2}$ a number of other new bands appear which are reasonably assignable to additional individual $\mathrm{TRN(CO_2)}_n$ ($n > 2$) species. However, these bands are superimposed on a broad background that grows with increasing $\mathrm{CO_2}$ concentration, Figure 1c, making measurement of their relative intensities difficult. The broad background can

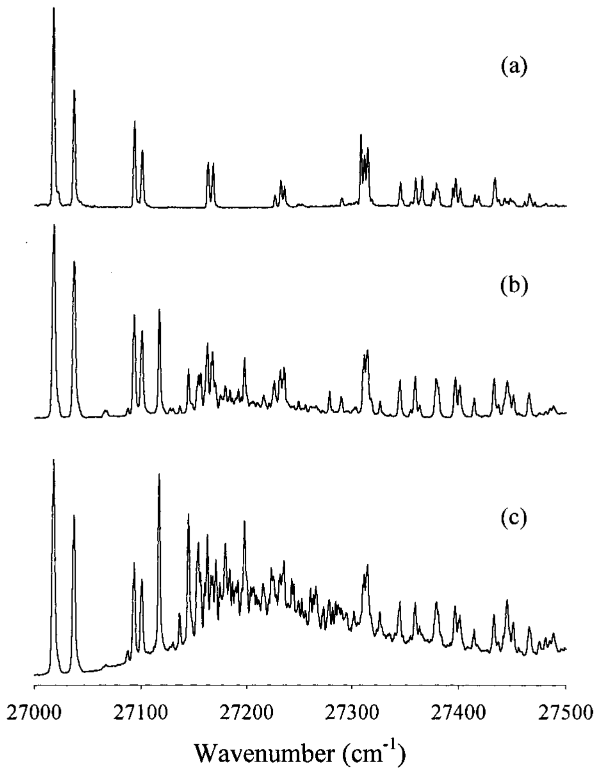

Figure 1. Laser-induced-fluorescence excitation spectra of (a) bare TRN, (b) TRN expanded with 0.5 Torr CO_2 in 20 psi He, and (c) TRN expanded with 4 Torr CO_2 in 20 psi He. Features in (b) and (c) not present in (a) are due to $TRN(CO_2)_n$ complexes.

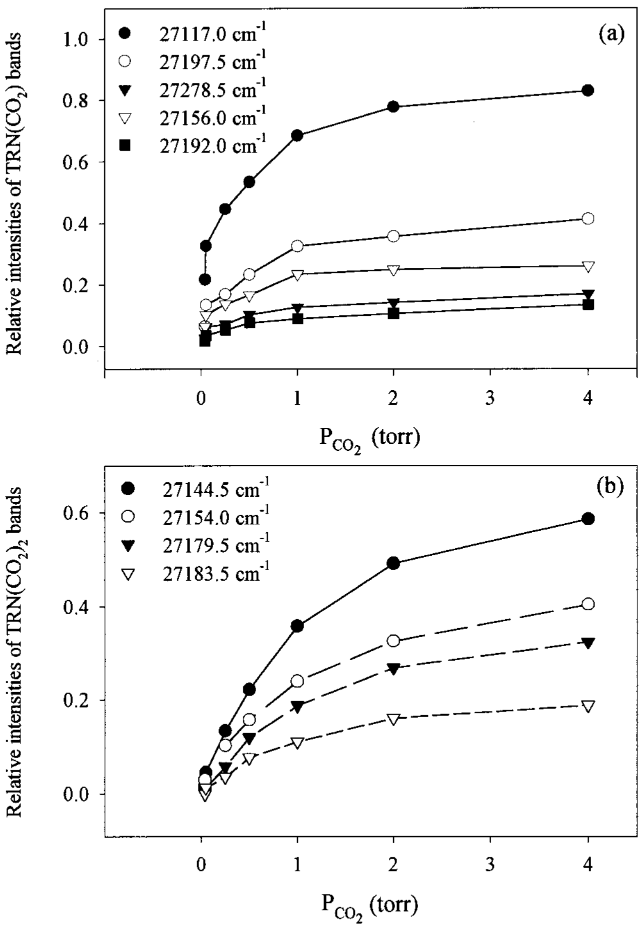

Figure 2. Relative intensities of bands in the $TRN(CO_2)_n$ spectrum assigned to (a) $TRN(CO_2)$ and (b) $TRN(CO_2)_2$, as a function of the partial pressure of CO_2.

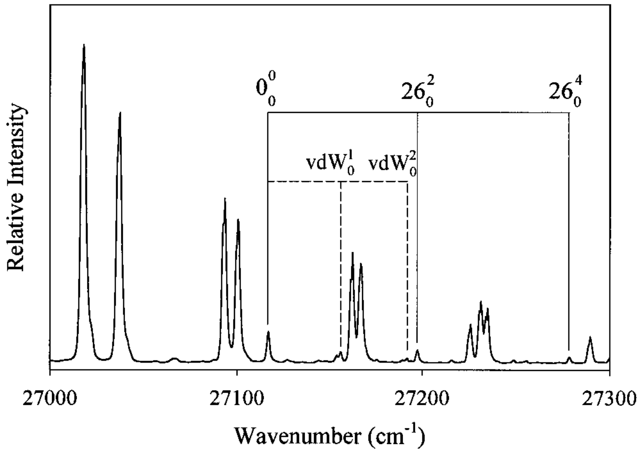

Figure 3. LIFE spectrum of $TRN(CO_2)$ complexes at low CO_2 concentration (0.02 Torr in 20 psi He). Bands due to $TRN(CO_2)$ are labeled.

reasonably be assigned to the overlapping features associated with an ensemble of TRN−CO_2 clusters of various sizes. It is notable that TRN remains fluorescent in these clusters. However, in the absence of mass-resolved measurements, neither the broad background nor the bands due to individual $TRN(CO_2)_n$ ($n > 2$) species superimposed upon it will be further examined here.

The only bands due to complexes which are still observable at the very lowest concentrations of CO_2 are shown in the spectrum in Figure 3. These five bands are assigned to the 1:1 complex of tropolone with CO_2, $TRN(CO_2)$. The band of lowest energy and highest intensity, at 27 117.0 cm^{-1}, is assigned as the electronic origin of this complex. This origin is shifted by $\delta = 99.0$ cm^{-1} to the blue of the origin of the bare TRN molecule. Ab initio calculations of δ (HF/6-31G** for S_0 and CIS/6-31G** for S_1) yield a value of 118 cm^{-1}, in good agreement with experiment.

Four other bands are built upon this origin. The relative intensities of all five bands are independent of the distance between the nozzle and the excitation laser beam and the pressure of He. These bands do not have relative intensities which depend on the temperature of the expansion, so none of them may be assigned to the upper ($- \leftrightarrow -$) component of a tunneling doublet. One therefore concludes that the tunneling doublets of the bare molecule have all collapsed in $TRN(CO_2)$, and the structure of the complex must be one in which the proton tunneling rate is significantly reduced.

The bands at 27 156.0 and 27 192.0 cm^{-1}, which are displaced 39.0 and 75.0 cm^{-1} respectively from the origin of the complex and exhibit a regular decreasing intensity profile, are assigned to a slightly anharmonic progression of one and two quanta in an S_1 intermolecular vdW vibrational mode.[30,31] There are two in-plane intermolecular vibrational modes in $TRN(CO_2)$, and one of them, involving a rocking motion of CO_2 relative to the TRN framework, has a calculated (scaled) frequency of 36 cm^{-1} in S_1.[38] Because this van der Waals vibration moves the CO_2 from one solvated tautomeric structure to the other, it is expected that this mode will be Franck−Condon active, consistent with the above assignment.

The other two bands at 27 197.5 and 27 278.5 cm^{-1} are shifted 80.5 and 161.5 cm^{-1} from the origin of the complex and have been assigned to the unsplit 26^2_0 and 26^4_0 transitions of $TRN(CO_2)$. (Note that the vibrational normal modes of a molecule are conventionally numbered consecutively based on

TABLE 1: Wavenumbers and Assignments of Vibrational Features in the $S_1 \leftrightarrow S_0$ LIFE Spectrum of TRN(CO_2)

wavenumber (cm^{-1})	shift from the origin of the complex[a] (cm^{-1})	rel int	assignment
27 117.0	0.0	100	0_0^0
27 156.0	39.0	31	vdW_0^1
27 192.0	75.0	15	vdW_0^2
27 197.5	80.5	50	26_0^2
27 278.5	161.5	21	26_0^4

[a] Values are ± 1.0 cm^{-1}.

TABLE 2: Wavenumbers and Assignments of Vibrational Features in the $S_1 \leftrightarrow S_0$ LIFE Spectrum of TRN(CO_2)$_2$

wavenumber (cm^{-1})	shift from the origin of the complex[a] (cm^{-1})	rel int	assignment
27 144.5	0.0	100	0
27 154.0	9.5	69	vdW
27 179.5	35.0	55	vdW
27 183.5	39.0	32	vdW

[a] Values are ± 1.0 cm^{-1}.

the frequency and symmetry of the mode; a_1 (from 1 to 14), a_2 (15 to 19), b_1 (20 to 26), b_2 (27 to 39) in TRN. The vibration labeled mode 26 is correctly assigned[39] to a mode of a_2 symmetry in TRN. The initial assignment[5] of this mode to a vibration with b_1 symmetry was incorrect, but the number 26, approriate for a mode of b_1 symmetry, has been retained in the subsequent literature.) These data are summarized in Table 1 and will be further discussed after the structures of the complexes have been introduced (vide infra).

On the basis of the pressure dependence studies, Figure 2b, four bands may be assigned to the complex of TRN with two CO_2 molecules. The electronic origin of TRN(CO_2)$_2$ is assigned to the band at 27 144.5 cm^{-1} which is shifted by $\delta = 126.5$ cm^{-1} from the TRN origin. The ab initio calculation gives $\delta =$ 136 cm^{-1}, in good agreement with experiment. Note that δ for the 1:2 complex (126.5 cm^{-1}) is not double that of the 1:1 complex (99.0 cm^{-1}). The three other bands attached to the vdW origin are reasonably assigned[30,31] to intermolecular vdW modes with frequencies of 9.5, 35.0, and 39.0 cm^{-1}, respectively. Ab initio calculations give scaled frequencies of 13, 25, and 36 cm^{-1} for these S_1 modes, in modest agreement with experiment. The experimental data are collected in Table 2.

(ii) Structures of the vdW Complexes. The structures of the TRN(CO_2)$_n$ species have been determined by analyzing their LIFE spectra, by calculating their structures using ab initio methods previously used successfully in examining mode-specific tunneling in TRN,[40] and by comparing the results of these measurements and calculations with those of related TRN vdW systems. First, blue shifts are observed when H_2O, CH_3OH, and CH_3COCH_3 are bound to TRN.[10,23,25,33] These species all have permanent dipole moments and the ability to hydrogen bond at the keto-hydroxyl structure of the TRN molecule. In general, microscopic blue shifts are observed when complexation stabilizes the ground state of a chromophore more than the excited state. In the cases of relevance here, a partial weakening of the intramolecular hydrogen bond occurs upon complexation because new intermolecular hydrogen bonds are formed with the solvent molecule. Because the excited state of TRN is more acidic than its ground state,[41] the weakening of the intramolecular hydrogen bond is more pronounced in S_1 than it is in the ground state, the complex is less stabilized in the excited state than in the ground state, and a microscopic solvent shift to the blue results. The blue shift observed upon complexation of CO_2 with TRN suggests that CO_2 also binds at the keto-hydroxyl groups and partially disrupts the intramolecular hydrogen bond. Second, the spectra of TRN(CO_2) and TRN(CO_2)$_2$ both display no measurable tunneling splittings. This suggests that the structure of these complexes is such that the rate of intramolecular proton transfer is significantly decreased, as is the case in other hydrogen-bonded TRN complexes.[10,23,25,33] Third, the observation of short progressions in mode 26 in both the bare molecule and the 1:1 complex allows the frequency of this mode in the two species to be compared, and provides some insight into the method of binding of CO_2 to the chromophore.

TABLE 3: Wavenumbers of Mode 26 in the Excited States of Bare TRN and TRN(CO_2)

vibrational state	wavenumber in TRN[a]	wavenumber in TRN(CO_2)[a]
26_0^2	70.0	80.5
26_0^4	138.0	161.5

[a] Displacement from the species origin.

To ensure a valid comparison with the collapsed doublets of mode 26 in the complex, the frequency of mode 26 in the bare molecule is taken to be the average of the differences between the wavenumbers of the lower and upper tunneling doublet components in the progression. Table 3 lists the frequencies of the bands in the 26_0^n progression of bare TRN and TRN(CO_2), and clearly shows that the frequency of mode 26 increases upon complexation with CO_2. Mode 26 involves largely out-of-plane motion of the oxygen atoms, together with some skeletal deformation.[39] The increase in the frequency of this mode upon complexation indicates that the restoring force is larger in the complex. If CO_2 is bound in the plane and interacts with the keto oxygen and hydroxyl hydrogen, then the force constant corresponding to out-of-plane motion of the oxygen atoms will increase because of the weak intermolecular interaction with CO_2. The frequency of this vibration will hence increase.

On the basis of the similarities to hydrogen-bonded complexes and the above spectroscopic evidence, it is likely that CO_2 binds in the plane of the TRN ring. To confirm this hypothesis, ab initio geometry optimization and force field calculations were performed on the ground state 1:1 complex at the HF/6-31G** level. Although an extensive search for local minima was not performed, the calculated global potential energy minimum for TRN(CO_2) has a structure in which the CO_2 lies in the TRN plane at the keto-hydroxyl region of the molecule. The structure of the ground state provided by these calculations is shown in Figure 4.

This structure is completely consistent with the available spectroscopic evidence. Although CO_2 does not possess a permanent dipole moment, it does have a large electric quadrupole moment[34] which can interact with TRN at its intramolecularly hydrogen bonded keto-hydroxy groups. A dipole–quadrupole interaction such as this will be weaker than the intermolecular hydrogen bonding interactions of TRN with H_2O or CH_3OH, will cause less disruption of the intramolecular hydrogen bond, and hence will result in a smaller solvatochromic blue shift than is observed in the more strongly bound vdW complexes.

Such a structure can also account for the collapse of tropolone's tunneling doublets in one of two possible ways. First, binding of the CO_2 molecule occurs at a position which, in the static structure, induces asymmetry in the potential surface along the proton tunneling coordinate. As is the case with H_2O, CH_3OH, and CH_3COCH_3, a static interaction such as this would be expected to increase the effective barrier height for proton transfer significantly[10,23,25,33] and to result in a partial preferential

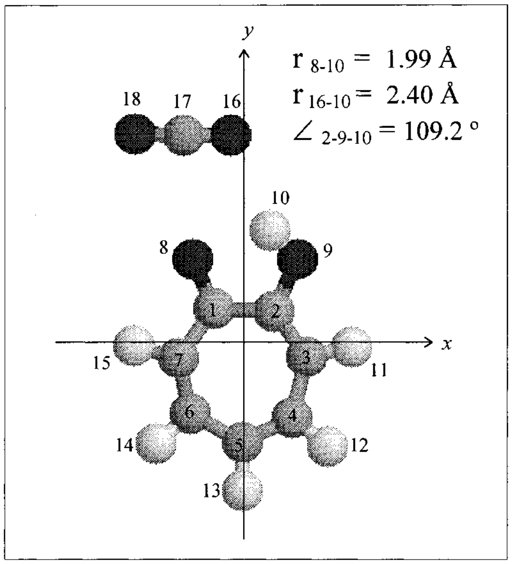

Figure 4. Structure of ground-state $TRN(CO_2)$ calculated at the HF/6-31G** level. The axis system is drawn with the origin at the center of mass of the bare molecule.

localization of the proton on one oxygen atom. Second, if the rate of proton tunneling is determined, in whole or in part, by the rate of CO_2 motion between the potential minima of the two tautomers, then solvation by CO_2 would be expected to reduce the tunneling rate substantially. The question is one of mechanism; does the solvent move as a consequence of proton transfer, or are proton transfer and solvent motion concerted? This question can in principle be answered by experiment if evidence can be found of "parity non-conserving" transitions, indicative of S_0 and S_1 surfaces which are of symmetry lower than C_{2v} along the proton tunneling coordinate in the complex. To our knowledge, no such transitions have ever been observed in TRN's van der Waals complexes, and this negative evidence might provide support for the concerted proton−solvent motion model. However, finding such bands would be difficult since Δ_0'' is only 0.974 cm^{-1} in the bare molecule and the "parity non-conserving bands", if present, would be difficult to resolve from the parity-conserving ones.

Finally, an in-plane structure such as that depicted in Figure 4 also accounts for the increase of the frequency of mode 26 upon complexing CO_2 with TRN, because the additional intermolecular "hydrogen bonds" formed in the plane will increase the restoring force associated with the out-of-plane motion of the oxygen atoms.

Similar ab initio calculations have also been performed on $TRN(CO_2)_2$; a minimum energy structure was found in which both CO_2 molecules are complexed in the TRN plane with the second CO_2 almost parallel to the C(2)−C(3) bond of TRN (cf. Figure 4). An extensive search for other potential minima was not performed, and there are likely other 1:2 structures which have local minima of similar energy. These calculations do indicate, however, that at least one of the preferred 1:2 structures is consistent with the spectroscopic evidence available. The modest incremental blue shift induced by complexation with a second CO_2 molecule must indicate a further disruption of the intramolecular hydrogen bond in the $TRN(CO_2)_2$ species.

The most important piece of experimental evidence about the structure of $TRN(CO_2)_2$ is that the microscopic solvent shift of the origin of the 1:2 complex is not double the shift of the 1:1 complex, indicating that the second CO_2 molecule is not bound to TRN at a location which is geometrically equivalent to that of the first. The structure of the 1:1 complex in Figure 4 shows that there is no geometrically equivalent position for the second CO_2 molecule to bind. In this respect the CO_2 complexes of TRN are similar to those of H_2O and CH_3OH. The microscopic solvent shifts for the n = 1, 2, and 3 complexes of TRN with H_2O, CH_3OH, and CO_2, summarized in Table 4, exhibit similar patterns.

TABLE 4: Microscopic Solvent Shifts in cm^{-1} for $TRN(H_2O)_n$, $TRN(CH_3OH)_n$, and $TRN(CO_2)_n$ (n = 1, 2, 3) Complexes

n	$TRN(H_2O)_n$[a]	$TRN(CH_3OH)_n$[a]	$TRN(CO_2)_n$
1	289.0	300.0	99.0
2	451.0	439.0	126.5
3	623.0		

[a] From refs 10, 23, and 25.

TABLE 5: Intramolecular Hydrogen Bond Lengths and C−O−H Angles in Ground-State TRN and "Hydrogen-Bonded" TRN Complexes, and Binding Energies of the Complexes, Calculated at the HF/6-31G Level**

complex	R- - -H (Å)	$\angle_{C-O-H}$ (deg)	solvent dipole moment (D)	binding energy (cm^{-1})
TRN	1.9394	107.48		
$TRN(CO_2)$	1.9934	109.16	0	1070
$TRN(CO_2)_2$	1.9900	109.22	0	1958
$TRN(CFH_3)$	2.0293	110.59	1.85	1349
$TRN(CF_3H)$	1.9888	109.08	1.65	1410
$TRN(H_2O)$[a]	2.1339	113.26	1.85	2385

[a] From ref 25.

As with the 1:1 complex, there is no evidence of tunneling splitting in the 1:2 complex, indicating that the tunneling rate is significantly slower in $TRN(CO_2)_2$ than in the bare molecule. This is not particularly surprising since the addition of a second CO_2 is not expected to increase the rate of proton transfer. Note also that there is no evidence of the 26_0^n progression in the spectrum of $TRN(CO_2)_2$, suggesting that the out-of-plane deformation of the TRN molecule is sufficiently disrupted in the 1:2 species to move the progression into the forest of lines at higher energy.

(iii) Effects of Solvation by Hydrogen-Bonded Solvents. The above analysis of solvent shifts suggests that a partial disruption of the intramolecular hydrogen bond is associated with the intermolecular binding in TRN's hydrogen-bonded complexes. This disruption can be quantified by calculating the intramolecular hydrogen bond distance, R_{O---H}, between the keto oxygen and the hydroxyl hydrogen, and the hydroxyl group's carbon−oxygen−hydrogen bond angle, $\angle_{C-O-H}$. The data for calculations at the HF/6-31G** level on TRN in the ground-state complexed with H_2O, CH_3F, CF_3H, and CO_2 are summarized in Table 5.

These data show that two important structural changes occur upon complexation: (i) the R_{O---H} distance increases significantly compared with that in the bare molecule (1.9394 Å) and (ii) the five-membered ring formed by the intramolecular hydrogen bond expands so that the C−O−H bond angle increases. Previous DFT calculations on the $TRN(H_2O)$ "ring" isomer at the 6-31+G′[2d,p] level show the same effect, but predict an even larger increase in the bond angle.[25] With the exception of $TRN(CF_3H)$,[42] these structural changes are more pronounced for those complexes with larger blue shifts such as CFH_3 and H_2O.

The COH···OCO distance (cf. Figure 4) is 2.40 Å for S_0, calculated at the HF/6-31G** level, and 2.34 Å for S_1, calculated at the CIS/6-31G** level. This result confirms that there is

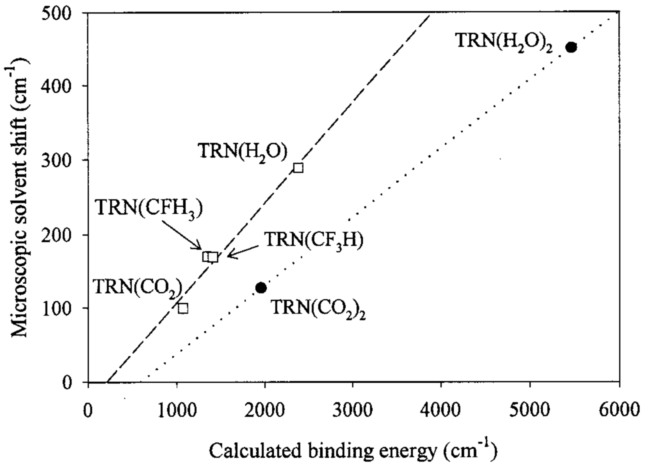

Figure 5. Microscopic solvent shifts of TRN(S)$_n$ vdW complexes vs binding energies calculated at the HF/6-31G** level. The $n = 1$ complexes are represented by open squares while $n = 2$ complexes are represented by closed circles. The regression line shown is calculated using the data for the $n = 1$ complexes only.

stronger intermolecular interaction between the CO_2 and the hydroxyl moiety of the chromophore in S_1 compared with S_0. The observed microscopic solvent shift to the blue must therefore be interpreted in terms of two competing trends: (i) an intermolecular hydrogen bonding-like interaction between CO_2 and TRN which is stronger in S_1 than S_0 and (ii) intramolecular hydrogen bonding which is disrupted by solvation to an even greater extent in S_0 than S_1.

A plot of the observed microscopic solvent shifts versus the calculated binding energies (Table 5) for some of the ground-state hydrogen-bonded TRN complexes studied to date is shown in Figure 5. The magnitude of the microscopic solvent shift increases with increasing binding energy, as anticipated, with the two quantities being in direct proportion for the 1:1 complexes. The data for the 1:2 complexes do not lie on the same line as those of the 1:1 complexes, but also exhibit the expected increase in spectral shift with binding energy. Note that the linear least-squares fits shown in Figure 5 have negative intercepts, likely due to basis set superposition error which results in calculated binding energies that are too large.

Given its acidity, particularly in S_1, and the structural changes produced by complexation noted above, TRN may act as a proton donor and the "hydrogen-bonding" solvents as proton acceptors in these vdW complexes. Thus, the gas-phase proton affinity of the solvent may be a useful measure of their interaction with TRN. The proton affinity, A_{H^+}, of a molecule, M, is defined as the negative of the enthalpy of formation of MH^+ from M and H^+, and is a quantitative measure of the ability of M to behave as a proton acceptor in a gas-phase complex. Figure 6 is a plot of the observed microscopic solvent shifts, δ, versus the proton affinities[43] of S for 1:1 TRN(S) complexes involving "hydrogen-bonding" solvents. The linear relationship between A_{H^+} and δ indicates that the ability of the solvent to "accept" the proton from TRN plays an important role in the binding of these solvents.

The interesting conclusion to be drawn from these comparisons is that CO_2 behaves in a fashion which is qualitatively similar to H_2O, CH_3F, CF_3H, and CH_3OH; i.e., it acts as a weak proton acceptor and binds to TRN by a van der Waals interaction which mimics weak hydrogen bonding. Neither of the correlations represented in Figures 5 and 6 should be taken as more than qualitative trends, however, because they do not account for the more subtle effects associated with differences in geometries among the various complexes.

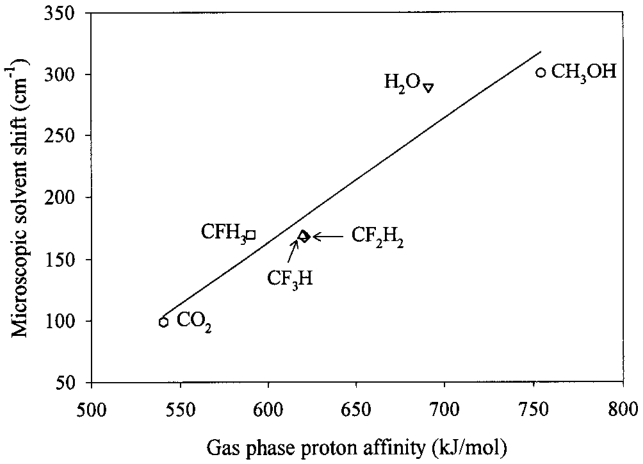

Figure 6. Microscopic solvent shifts, δ, vs solvent proton affinities, A_{H^+}, in 1:1 complexes of S with TRN. The proton affinities are taken from ref 43.

Conclusions

van der Waals complexes of tropolone with carbon dioxide may be synthesized by expanding mixtures of TRN and CO_2 in He in a supersonic free-jet, and may be examined by LIFE spectroscopy. At higher partial pressures of CO_2 large clusters of TRN(CO_2)$_n$ are formed in which TRN remains fluorescent but produces broad unresolvable bands. At sufficiently low partial pressures of CO_2 well-resolved blue-shifted features in the spectra due to TRN(CO_2) and TRN(CO_2)$_2$ may be identified. The microscopic solvent shifts, the effects of solvation on the proton tunneling doublets and chromophore vibrational frequencies, and ab initio calculations all suggest that in the 1:1 complex the CO_2 binds to TRN in a fashion which is similar to hydrogen-bonding addends. The CO_2 lies in the plane of the TRN ring and interacts with the keto oxygen and the hydroxyl hydrogen in such a way that the intramolecular hydrogen bond of TRN is partially disrupted, lengthening the R_{O---H} distance and opening the H−O−C angle. Consistent with this interaction, the proton tunneling rate is reduced to the extent that the tunneling doublets can no longer be observed in the spectra of the complex, and the out-of-plane wagging vibration of the two oxygen atoms in the chromophore increases in frequency.

The microscopic solvatochromic shifts of the complexes are well-correlated with the calculated binding energies of the addends to the chromophore, and with their proton affinities. The latter correlation suggests that CO_2 behaves in a fashion which is qualitatively similar to H_2O, CH_3F, CF_3H, and CH_3OH by acting as a weak proton acceptor in a hydrogen-bonding-like interaction with TRN.

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