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Charge Redistribution on Electronic Excitation. Dipole Moments of *cis*- and *trans*-3-Aminophenol in Their S_0 and S_1 Electronic States

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Abstract: Rotationally resolved electronic spectroscopy in the gas phase, in the absence and presence of an applied electric field, has been used to distinguish the two conformers of 3-aminophenol (3AP) on the basis of differences in their electric dipole moments. *cis*-3AP has $\mu = 2.3$ D, and *trans*-3AP has $\mu = 0.7$ D, in their ground electronic states. The two observed values are approximately equal to those expected on the basis of bond dipole additivity rules. However, these rules fail to predict the large change in both the magnitude and the orientation of μ when the two conformers of 3AP absorb light. *cis*-3AP has $\mu = 3.3$ D, and *trans*-3AP has $\mu = 1.7$ D, in their excited S_1 electronic states; the angles of orientation of μ with respect to the *a* inertial axis change by 13° and 38°, respectively. This effect is attributed to $^1L_b/^1L_a$ state mixing in the S_1 state.

Introduction

A light-induced change in the permanent electric dipole moment of a large molecule can have significant physical, chemical, and biological consequences. For example, a change in the magnitude of a dipole moment can strengthen or weaken the hydrogen bond between an acid and a base, leading to charge transfer in the extreme case.[1] A change in the orientation of a dipole moment of a solute can provoke a response from the solvent, leading to solvent reorganization and relaxation.[2] Changes in both the magnitude and the orientation of a dipole moment also can produce shifts, broadenings, and changes in the shapes of molecular electronic absorption and emission spectra, leading to solvatochromism.[3] These effects have been used to probe the electronic structures of many different systems, from chromophores in the condensed phase, to the band structure of semiconductors and crystalline materials, to complex biological systems.[4]

Our fundamental understanding of such phenomena will be greatly enhanced by measurements of the permanent electric dipole moments of the ground and electronically excited states of isolated molecules in the gas phase, unencumbered by the surrounding environment.[5] In this paper, we report Stark effect measurements of the fully resolved electronic spectra of 3-aminophenol (3AP) in a molecular beam that were designed to accomplish this objective. 3AP has been the subject of two recent studies. The first, by Shinozaki et al.,[6] described its S_1-S_0 excitation and fluorescence spectra under jet-cooled conditions. The second, by Robinson et al.,[7] described the vibrational overtone spectra of three different aminophenols, including 3AP. Both studies concluded that 3AP exhibits conformational isomerism in the gas phase and made assignments of the cis and trans isomers on the basis of differences in their vibrational frequencies.

cis-3AP and *trans*-3AP differ only in the positions of their hydroxy hydrogen atoms, as shown in Figure 1. As will be shown, this small difference in structure has only a small effect on the rotational constants of the isolated molecule, so that this property alone cannot be used to distinguish them. Yet changing the position of the hydroxy hydrogen atom also changes the orientations of the oxygen lone pairs of electrons, which should have a large effect on the dipole moments. In what follows, we show that this property can be used to distinguish the two isomers of 3AP. We also show that both the magnitudes and the orientations of the dipole moments of both conformers are significantly different in the two electronic states. To the best of our knowledge, this is the first experimental, structurally resolved observation of these effects in a large molecule.

Experimental Section

3AP was purchased from Aldrich Chemical Co. and was used without further purification. Its vibrationally resolved electronic spectrum was obtained using a pulsed jet apparatus. 3AP was heated to approximately 380 K and expanded into a vacuum through a 1 mm

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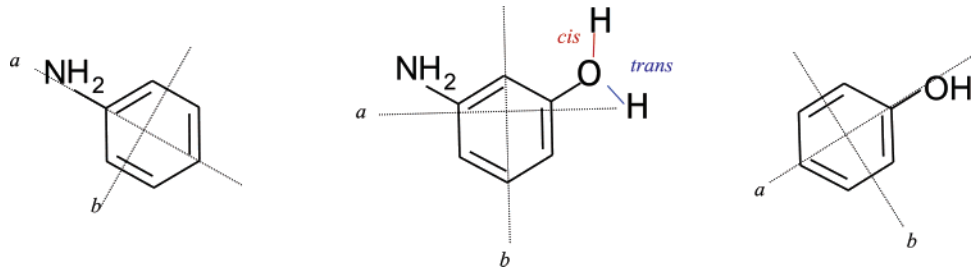

Figure 1. Structures of aniline, *cis*- and *trans*-3-aminophenol, and phenol in their respective principal axis frames.

diameter orifice pulsed valve using 2−4 atm He as the carrier gas. The UV light crossed the jet at a right angle and was generated by a frequency-doubled dye laser pumped by a Nd^{3+}:YAG laser, whose output was frequency doubled by a potassium dihydrogen phosphate (KDP) crystal. The resulting fluorescence was detected by a photomultiplier tube (PMT) located perpendicular to the interaction plane, processed by a boxcar integrator, and recorded on a chart recorder and/or a computer.

Rotationally resolved electronic spectra of the two origin bands of 3AP were recorded using a molecular beam apparatus. A detailed description of this apparatus has been given previously.[8] The molecular beam was generated by passing Ar carrier gas (500 Torr) through a heated (∼400 K) quartz source containing the sample. The gas was expanded through a 150 μm nozzle into a differentially pumped vacuum system. The beam was skimmed once at 2 cm downstream from the nozzle by a 1 mm skimmer and crossed with the laser beam in the low-resolution port 15 cm downstream from the nozzle. The ultraviolet radiation was produced by an Ar^+ pumped ring dye laser with an appropriate dye (R6G), which was intracavity doubled with a β-barium borate (BBO) crystal. The resulting fluorescence was collected by a set of spatially selective optics, detected by a PMT and photon counter, and processed by a data acquisition system. Relative and absolute frequency calibrations were performed using markers from a near-confocal interferometer and the I_2 absorption spectrum, respectively, which were simultaneously recorded with the PMT signal.

The Stark cell[5] consists of two spherical mirrors, identical to those used in the zero-field experiment, with two stainless steel (Type 304) wire grids (diameter = 5 cm, mesh #50, wire diameter = 0.001 in.) placed between the mirrors. One grid is above and the other grid is below the plane of the molecular and laser beams, separated by ∼1 cm with ceramic spacers. Two power supplies (Fluke 412B, 415B) were used to hold one grid at a positive voltage and the other at a negative voltage relative to a common ground. The electric field is perpendicular to the polarization of the laser radiation, yielding a $\Delta M = \pm 1$ selection rule. Electric field strengths were calibrated using the known value of μ_a in the ground state of aniline and the combination-difference method of spectral assignment, which yields a determined plate separation of 0.982 ± 0.004 cm.[5]

Results and Interpretation

The vibrationally resolved electronic spectrum of 3AP exhibits two origin bands located at 34 108.3 (A) and 34 467.4 cm^{-1} (B), as shown in Figure 2. To determine which of these bands correspond to the cis and trans isomers of 3AP, the rotationally resolved electronic spectrum of each band was obtained and analyzed. Figure 3 displays the experimental spectra of band A and band B. The top traces show the overall experimental spectra. The middle traces show a portion of each spectrum at full rotational resolution, and the bottom traces show the corresponding calculated spectrum. These spectra were fit using rigid rotor Hamiltonians[9] for both electronic states with the electronic transition moment (TM) parallel to the *a* inertial axis. Inspection of the observed rotational structure allows evaluation of the band type and subsequent determination of selection rules. An *a*-type spectrum was simulated due to the large central Q branch apparent in each of the experimental spectra. Once the spectra were fit reasonably well, it was noticed that some of the transitions in the experimental spectrum of band A were not found in the simulated spectrum. Ab initio calculations[10] predicted the S_1-S_0 TM's of both conformers to be slightly off the *a*-axis, in the *ab* plane. Upon addition of some *b*-type character, the transitions previously absent in the simulated spectrum of band A were then apparent. The final fit showed an *a*:*b* ratio of 95(3):5(2). A similar analysis of band B again revealed weak *b*-type transitions, yielding an *a*:*b* ratio of 93(3):7(2). In both cases, the hybrid band character was determined by choosing a set of single transitions from the spectrum (the set included at least one transition of each band type), and adjusting the intensity ratio to generate a spectrum that reproduced the intensity of the experimental spectrum.

Table 1 lists the parameters extracted from fits of both spectra. Note that the ground and excited state B and C rotational constants are known to 0.1 MHz and that the A constants have slightly larger deviations. Within this accuracy, the constants are different. The differences in the ground state constants show that the bands are due to different molecular configurations. Band B cannot, for example, be a vibronic band built upon band A. Comparison of the experimental rotational constants of both bands to the calculated constants of the cis and trans conformers

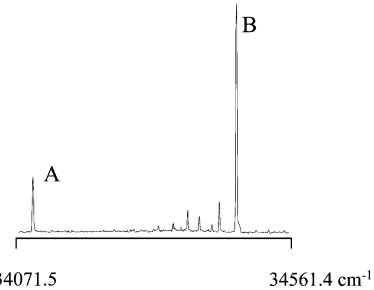

Figure 2. Vibrationally resolved $S_1 \leftarrow S_0$ electronic spectrum of 3-aminophenol.

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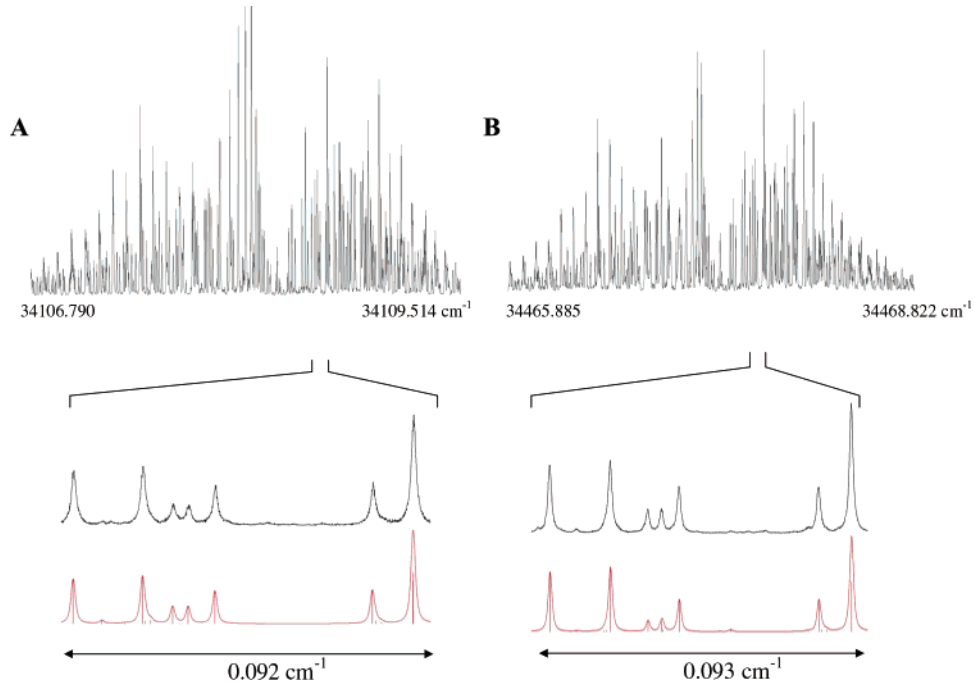

Figure 3. Rotationally resolved electronic spectra of band A (left) and band B (right) of 3-aminophenol.

Table 1. Inertial Parameters Derived from Fits of the Rotationally Resolved $S_1 \leftarrow S_0$ Fluorescence Excitation Spectra of Bands A and B of 3-Aminophenol

parameter	band A	band B
A'' (MHz)	3734.4(7)	3729.5(4)
B'' (MHz)	1823.1(1)	1828.2(1)
C'' (MHz)	1226.6(1)	1228.2(1)
κ''	−0.524	−0.520
$\Delta I''$ (amu Å^2)	−0.512	−0.479
A' (MHz)	3604.2(7)	3604.9(4)
B' (MHz)	1829.9(1)	1826.5(1)
C' (MHz)	1215.2(1)	1213.6(1)
κ'	−0.485	−0.487
$\Delta I'$ (amu Å^2)	−0.519	−0.446
origin (cm^{-1})	34 108.3(1)	34 467.4(1)
no. of lines assigned	114	155
OMC (MHz)	1.77	1.61
fwhm (MHz)	42	35
band type	*a*/*b* hybrid	*a*/*b* hybrid

Table 2. Comparison of Experimental and ab Initio Rotational Constants of *cis*- and *trans*-3-Aminophenol

rotational constants (MHz)	band A	band B	ab initio cis	ab initio trans
A''	3734.4	3729.5	3741.2[a]	3736.5[a]
B''	1823.1	1828.2	1824.6[a]	1829.0[a]
C''	1226.6	1228.2	1227.8[a]	1229.3[a]
ΔA	−130.2	−124.5	−132.7[b]	−123.9[b]
ΔB	6.9	−1.7	−10.2[b]	−0.7[b]
ΔC	−11.3	−14.7	−9.1[b]	−14.4[b]

[a] B3PW91/6-31G*. [b] HF/6-31G* and CIS/6-31G*.

shows similar trends (see Table 2). Both band A and the ab initio cis conformer have larger ground-state A constants and smaller B and C constants, when compared to the corresponding rotational constants of band B and the ab initio trans conformer. Similarly, the ΔA, ΔB, and ΔC values of band A ($\Delta A = A(S_1) - A(S_0)$, etc.) and the ab initio cis conformer, and of band B and the ab initio trans conformer are very nearly the same. Still, the differences are not large enough to warrant a definitive assignment. The numerical differences between the experimental constants and the calculated constants are larger than the differences between the two conformers.

An unambiguous assignment of the two conformers is made possible by measurements of their dipole moments using the Stark effect. Figure 4 shows an example of this effect, which is produced by applying an electric field to the sample. The top traces show a portion of the zero field spectra of bands A and B at full resolution, the same as those shown in Figure 3. The bottom traces show the same portions of the experimental spectra at an applied field of 1018 V/cm. The black trace is the experimental spectrum, and the red trace is a simulated spectrum. The influence of the applied electric field is evident by comparing the field-on and field-off spectra of the same transitions. Because the *M*-degeneracy is lifted by the field, there are many more allowed transitions and the spectrum is more congested. Nonetheless, the Stark spectra of the two conformers are clearly different, making it possible to distinguish them.

A special computer program has been written to fit these spectra.[5] The fitting process began with a simulation of the spectrum generated from the ground- and excited-state rotational constants and estimates of the ground- and excited-state dipole moment components. Estimates of the dipole moment components were obtained from the ab initio calculations.[10] Because the spectrum has a significantly greater number of transitions, more care must be taken when making assignments. The initial assignments were made for transitions in the least congested portions of the spectrum. Once a significant number of assignments had been made, a least-squares analysis was performed. The varied parameters include the band origin frequency and the ground- and excited-state dipole moment components. Additional assignments were then made and/or previous assignments were altered, and the least-squares fitting routine was repeated until the differences (OMC) between the experimental and simulated spectra were minimized. Once a reasonable spectrum was generated, the rotational constants were also allowed to vary; however, they generally varied only within

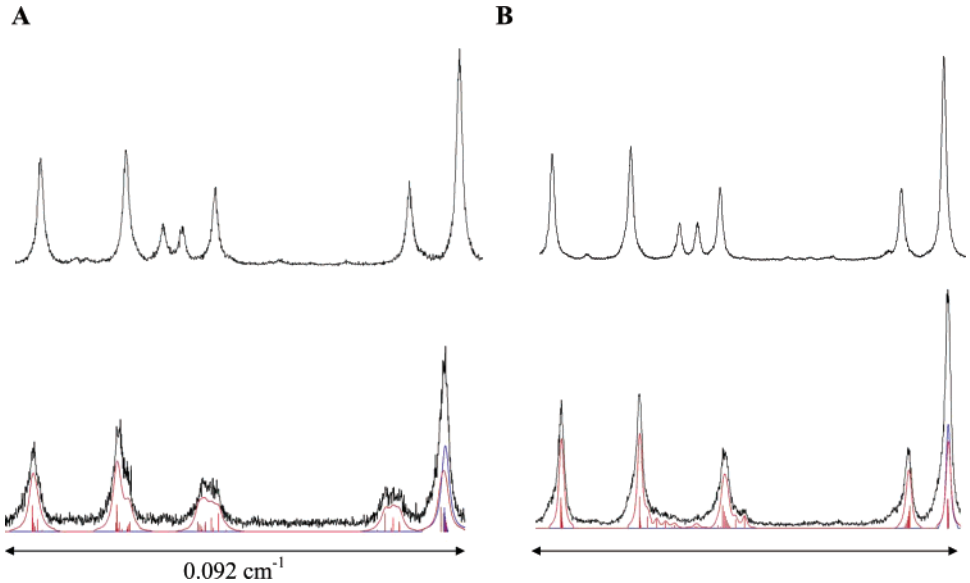

Figure 4. Portions of the rotationally resolved electronic spectra of bands A and B of 3-aminophenol in the absence (top) and presence (bottom) of an applied electric field of 1018 V/cm (cf. Figure 3).

Table 3. Experimental and Theoretical Values of the Dipole Moments (D) of *cis*- and *trans*-3-Aminophenol in Their Ground and Electronically Excited States

state	dipole moment	band A	cis (theory)	band B	trans (theory)
S_0	μ_a''	1.77(6)	1.92[a]	0.57(1)	0.47[a]
	μ_b''	1.5(2)	1.74[a]	0.5(1)	0.55[a]
	μ''	2.3(2)	2.59[a]	0.7(1)	0.72[a]
S_1	μ_a'	2.94(6)	2.26[b]	1.70(1)	0.74[b]
	μ_b'	1.5(2)	1.59[b]	0.1(1)	0.77[b]
	μ'	3.3(2)	2.76[b]	1.7(1)	1.07[b]

[a] B3PW91/6-31G*. [b] HF/6-31G* and CIS/6-31G*.

Table 4. Dipole Moment Components (D) of Aniline, *cis*-3-Aminophenol, *trans*-3-Aminophenol, and Phenol

dipole moment component	aniline	*cis*-3AP	*trans*-3AP	phenol
μ_a''	1.129[a]	1.77	0.57	0.133[c]
μ_b''	0[a]	1.5	0.5	1.271[c]
μ''	1.129[a]	2.3	0.7	1.278[c]
μ_a'	2.802[b]	2.94	1.70	0.29[d]
μ_b'	0[b]	1.5	0.1	1.27[d]
μ'	2.802[b]	3.3	1.7	1.30[d]

[a] Reference 12. [b] Reference 5. [c] Reference 13. [d] Korter, T. M., unpublished results.

the standard deviations determined in the zero-field spectrum. Table 3 lists the dipole moments (together with their components) that were determined from the fits of both bands A and B.

As expected, the dipole moments of the two conformers of 3AP are very different, 2.3 D in the ground state associated with band A, and 0.7 D in the ground state associated with band B. *cis*-3AP should have the larger value of μ because the C−N bond dipole (which points toward the ring) is enhanced by the lone pairs on oxygen in the cis conformer but attenuated by the lone pairs on oxygen in the trans conformer. The difference in the two measured values is well outside of the experimental error. Therefore, we assign band A to the cis conformer of 3AP and band B to the trans conformer of 3AP. The differences in the observed rotational constants (Table 2) are consistent with this assignment. Earlier assignments of the two conformers based on differences in their vibrational frequencies[6,7] are consistent with these conclusions.

An unexpected consequence of this assignment is the discovery that the magnitudes and the orientations of the dipole moments of *cis*- and *trans*-3AP are significantly different in the two electronic states. As shown in Table 3, the dipole moment is oriented roughly midway between the *a* and *b* axes in the ground states of both conformers. Yet this orientation changes dramatically when they absorb light. The S_1 states of both *cis*- and *trans*-3AP have their dipoles tilted significantly toward *a*, with $\mu_{a'}$ exceeding $\mu_{b'}$ by at least 1 D in both cases. Substantial charge reorganization occurs when 3AP absorbs light.

Discussion

Explanations for these behaviors are provided by comparisons of the properties of the ground and electronically excited states of *cis*- and *trans*-3AP with those of aniline and phenol, aromatic rings singly substituted with $-NH_2$ and −OH groups. Structures of these two molecules together with those of the conformers of 3AP in their respective principal axis systems are shown in Figure 1. Their dipole moments are listed in Table 4. In what follows, we ignore possible nonzero values of μ_c (the out-of-plane component of μ) in all four molecules.

First, we test the bond additivity rule for dipole moments.[11] Aniline has only a single in-plane component of μ in the ground state, with $\mu_a'' = 1.129$ D,[12] pointing into the ring. The corresponding dipole moment of phenol is oriented slightly off its *b*-axis, with $\mu_b'' = 1.271$ D.[13] This nearly bisects the C−O−H bond angle and points toward the lone pairs. Placing these two dipoles into the common coordinate system of 3AP, and adding them vectorially, leads to the predicted values of $\mu'' = 2.290$

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Table 5. Changes in Rotational Constants (in MHz) upon Electronic Excitation for Aniline, 3-Aminophenol, and Phenol

change in rotational constant	aniline[a]	*cis*-3AP	*trans*-3AP	phenol[b]
ΔA	−331.2	−130.2	−124.5	−336.9
ΔB	39.6	6.9	−1.7	1.3
ΔC	−17.8	−11.3	−14.7	−33.7

[a] Reference 14. [b] Reference 15.

and 1.143 D for *cis*- and *trans*-3AP, in approximate agreement with experiment (2.3 and 0.7 D). Theory also approximately agrees with experiment (cf. Table 3). It appears, then, that the usual bond dipole additivity rule holds in the ground state of 3AP; there is little or no interaction between the electrons that are responsible for the dipole moments of the two substituent groups in the isolated molecule.

Turning now to the electronically excited states of the four molecules, we note first that the S_1 states of aniline and phenol are both ^1L_b states.[14,15] Such states have interesting properties. As compared to the ground state, they are significantly quinoidal; their "parallel" ring C−C bond lengths are shorter than their "perpendicular" ones, and significant C−N or C−O bond length shortening occurs when the photon is absorbed. Rotationally resolved electronic spectroscopy in the gas phase has provided the principal evidence for such changes. As shown in Table 5, the *A* rotational constants of the S_1 states of both aniline[14] and phenol[15] are substantially less than those of the ground state, whereas only small changes in *B* and *C* are observed.

The two substituents in 3AP are meta to each other, incapable of communicating electronically without significant distortion of the benzene ring. Thus, it is intriguing to ask whether one substituent "dominates" in the excitation of 3AP to its S_1 state. Is S_1 3AP more similar to S_1 aniline, or more similar to S_1 phenol? How would such similarities be revealed in the properties of 3AP? Or are its properties different from those of its component parts?

The *a* and *b* axes of 3AP (both cis and trans) are oriented approximately midway between the corresponding axes in aniline and phenol (cf. Figure 1). Therefore, large decreases in both *A* and *B* are expected when 3AP absorbs light if its S_1 state resembles that of either of the two singly substituted molecules. This is not the case, as shown in Table 5. Only *A* decreases, by a substantially smaller amount; $\Delta A \approx -130$ MHz in *cis*- and *trans*-3AP, as compared to $\Delta A \approx -330$ MHz in both aniline and phenol. Similarly, ΔB of 3AP is significantly smaller than that of aniline, and much closer (in magnitude) to that of phenol.

A similar anomaly is observed in the dipole moment changes that are observed when 3AP absorbs light, as shown in Table 4. Whereas $\Delta\mu_a$ ($=\mu_a(S_1) - \mu_a(S_0)$) is large and positive in aniline, $\Delta\mu_b$ is zero. Such changes (or lack of them) are consistent with the quinoidal or hyperconjugated nature of its S_1 state. $\Delta\mu_a$ and $\Delta\mu_b$ are both relatively small in phenol, leading to the expectation that $\Delta\mu_a$ and $\Delta\mu_b$ should both be substantial in 3AP, because of the aforementioned rotation of its inertial axes. In fact, only μ_a changes substantially in both conformers of 3AP, again being large and positive. In contrast, $\Delta\mu_b \approx 0$ D in *cis*-3AP, and $\Delta\mu_b \approx -0.3$ D in *trans*-3AP. The angles of orientations of μ with respect to the *a* inertial axis change by 13° and 38°, respectively. Theory again qualitatively reproduces this behavior (cf., Table 3). We conclude, then, that the properties of both conformers of 3AP are different from those of its component parts.

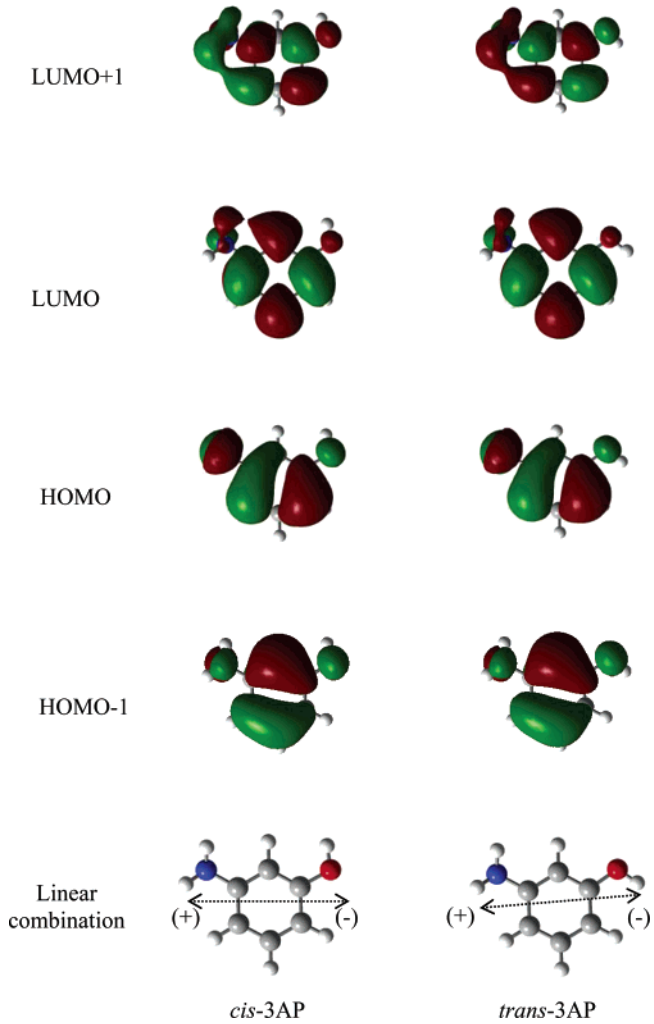

Figure 5. Molecular orbitals of *cis*- and *trans*-3-aminophenol as calculated by ab initio methods. Also shown is the linear combination wave function of the S_1 state. The dotted line illustrates the predicted $S_1 \leftarrow S_0$ transition moment orientation.

The S_1-S_0 electronic transition of aniline lies at 34 029 cm^{-1},[14] and that of phenol is at 36 349 cm^{-1};[15] thus, the energies of the 3AP excited states (at 34 108 and 34 467 cm^{-1}) are much more aniline-like than phenol-like. The S_1-S_0 TM's of aniline and phenol are each oriented along their respective *b* axes, perpendicular to the points of attachment of their substituent groups. Thus, if the S_1 states of *cis*- and *trans*-3AP were also ^1L_b states, and resembled either aniline or phenol, both transitions would be *ab* hybrid bands, with roughly equal admixtures of *a* and *b* character. This, again, is not the case. The S_1-S_0 origin bands of both conformers are essentially pure *a*-type; the spectra of *cis*- and *trans*-3AP exhibit only a small amount of *b* character.

Taken together, then, the observed rotational constants, permanent electric dipole moments, and S_1-S_0 electronic TM's of both conformers of 3AP all suggest that the bond dipole additivity rule, shown to be approximately valid in the case of

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the ground states, is not valid in the electronically excited states of *cis*- and *trans*-3AP.

It is likely that this breakdown in the bond dipole additivity rule has its origin in an electronic state mixing of the S_1 state. *cis*-3AP and *trans*-3AP are asymmetrically substituted benzenes. As we have discussed elsewhere,[16] and is well-known,[17] the nominal degeneracy of the two one-electron excitations that contribute to the ^1L_a and ^1L_b states of a symmetrically substituted benzene molecule is lifted by "off-axis" substituents, leading to electronic states that are neither pure ^1L_a or ^1L_b, but a mixture of the two zero-order states. An important diagnostic of such mixing is the orientation of the molecular electronic TM.[16] Beyond this, at least a CASSCF/MP2 calculation is required to account in detail for the degeneracy of the orbitals and their configuration interaction.[18]

Still, "low-level" calculations such as CIS/6-31G* are capable of reproducing most of the major effects. Figure 5 shows the HOMO-1($ø_2$), HOMO($ø_3$), LUMO($ø_4$), and LUMO+1($ø_5$) orbitals of *cis*- and *trans*-3AP, as calculated by this method. The corresponding orbitals of aniline and phenol are similar, except that they exhibit nodal planes that conform to the local C_2 symmetry of the substituted benzene ring. These give rise to canonically oriented TM's, parallel to the *b* axis in the case of ^1L_b states, and parallel to the *a* axis in the case of ^1L_a states. Apparently, in 3AP, once their orientations are established by a particular substituent, they are rotated away from the *a* or *b* axes by the second substituent. Thus, a nodal plane that is oriented along *a* in aniline (or phenol) is rotated away from this axis by the attachment of an −OH (or $-NH_2$) group. This is shown explicitly in Figure 5. The illustrated MO's are not "aligned" with respect to the nominal C_2 axes of either the $-NH_2$ or the −OH groups. Instead, they are now aligned with respect to a pseudo C_2 symmetry axis passing through the C_2 and C_5 carbons, and an axis approximately perpendicular to it. (The nodal planes are not perfectly aligned with respect to these axes, as there is a significantly higher electron density on the NH_2 side of the molecule.) Consequently, the S_1 state that results from excitation of 3AP by light is no longer a pure ^1L_b (or ^1L_a) state, but a linear combination of them. This explains why the excited-state rotational constants, dipole moments, and electronic TM's of both *cis*- and *trans*-3AP are not simply related to the corresponding properties of their "component parts".

The S_1 state of *cis*-3AP is described by the CIS calculation as being a linear combination of two one-electron excitations, $\Psi_c(S_1) = 0.34(ø_2ø_5) + 0.60(ø_3ø_4)$ with smaller contributions from other one-electron excitations. The S_1 state of *trans*-3AP is similarly described as $\Psi_t(S_1) = 0.35(ø_2ø_5) + 0.58(ø_3ø_4)$. The calculated TM orientations also qualitatively agree with the experiment, 0.3° with respect to *a* in *cis*-3AP, as compared to 13 ± 3°; and 12.3° with respect to *a* in *trans*-3AP, as compared to 15 ± 3°. The calculated permanent dipole moment reorientation angles agree less well with experiment; 6° versus 13° for *cis*-3AP, but 3° versus 38° for *trans*-3AP. The observed state mixing may also explain the large difference in the excitation energies of the two conformers (359 cm^{-1}, the cis ground state is calculated to lie at 115 cm^{-1} higher energy than the trans ground state), and the apparent lack of correspondence between the S_0 and S_1 vibrations in the isolated molecule.[6]

More generally, large changes in both the magnitudes and the orientations of the dipole moments of large molecules having asymmetric charge distributions in their electronic ground states are a likely result of their excitation by light. These dipoles are likely to be strongly dependent upon the size and shape of the subject chromophore, the degree of charge transfer that occurs on electronic excitation, and the distance over which charge separation and/or transfer occurs. Stark effect studies of rotationally resolved electronic spectra will provide a powerful tool for probing such changes and their dependence on the conformations of isolated molecules.

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