J. Am. Chem. Soc. **1998,** *120,* 12573−12582

Conformationally Induced Changes in the Electronic Structures of Some Flexible Benzenes. A Molecular Orbital Model

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Received January 9, 1998

Abstract: High-resolution electronic spectroscopy experiments on several substituted benzenes in the gas phase have revealed a remarkable sensitivity of the orientation of the S_1-S_0 transition moment (TM) in the molecular frame to the conformation of the attached group. Here, we explore the origins of this effect by performing ab initio calculations on five conformationally flexible benzenes (toluene, ethylbenzene, *n*-propylbenzene, 2-phenethyl alcohol, and 3-phenylpropionic acid) using the configuration interaction singles method (6-31G* basis set). Comparisons of the theoretical predictions with the experimentally determined parameters show that there are two principal sources of the observed sensitivity: a "through-bond" effect caused by rotation of the substituent about the bond connecting it to the ring, which breaks the C_s symmetry of the parent molecule, and a "through-space" effect, apparently caused by interactions of the side chain orbitals with the π orbitals of the ring. "Purely electrostatic" interactions between the ring and the tail, while significant in some cases, result in TM orientations that do not agree with experiment. All three types of interactions produce mixings of the ring π^* orbitals, which in turn can lead to ${}^1L_a/{}^1L_b$ excited electronic state mixing in the isolated molecule. Possible photochemical and photophysical consequences of this effect are discussed.

Introduction

High-resolution electronic spectroscopy of flexible organic molecules has become a well-established technique for determining the preferred structures of the different accessible conformations of such molecules in a low-temperature, gas-phase sample.[1] This is because such spectra are sensitive to the shape of the molecule and possible changes in this shape produced by the absorption of light. Recently, we have applied this technique to a series of compounds containing benzene as a chromophore, including *n*-propylbenzene and other alkylbenzenes, 2-phenethyl alcohol, 2-phenethylamine, 3-phenylpropionic acid, several benzoic acid esters, and their water clusters.[2−8] Surprisingly, we found that the orientations of the S_1-S_0 electronic transition moment (TM) in the molecular frames of different conformers of the same molecule quite often are different, a phenomenon that had not been observed before.[9]

In electronic spectroscopy, the TM is the dipole moment of an oscillating charge density and, hence, is related to the wave functions of the electrons in the two states connected by the photon. For a molecular S_1-S_0 transition, the TM is

$$\langle \mu_{\mathrm{TM}} \rangle = \int \Psi^*_{S_1} \hat{\mu} \Psi_{S_0} \, d\tau_e \qquad (1)$$

where $\hat{\mu}$ is the electric dipole operator of the perturbing light field and the integral is over the coordinates of the electrons. $\langle \mu_{\mathrm{TM}} \rangle$ therefore represents the electronic charge migration or displacement that occurs in the chromophore during the transition. Thus, if the orientations of the TM vectors of two conformers of the same molecule are different, then their electronic wave functions must also be different, in either the ground electronic state (S_0) or the excited electronic state (S_1), or both. In other words, *there is a conformationally induced change in the electronic structure of the isolated molecule.*

The existence of such changes could be extremely significant. Electrons are the "glue" that holds molecules together. Additionally, the distribution of electrons in a molecule is intimately linked to its reactivity. Thus, if two conformers of the same molecule have different electronic structures, then their reactivities also could be quite different. In the same way, the attachment of a weakly bound solvent molecule to a solute (as in a van der Waals or hydrogen-bonded complex) might also

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[9] That such a phenomenon might occur has been suggested in previous work on indole and its derivatives (ref 10). Additionally, Johnson et al. (ref 11) have observed differences in the S_1-S_0 TM orientations of the two OH rotamers of the 1- and 2-naphthols.

10.1021/ja980104y CCC: \$15.00

change its electronic structure. If so, the properties of an isolated molecule in the gas phase and in the condensed phase could be quite different. These phenomena are intrinsically interesting. Beyond this, the compounds examined to date are structurally related to aromatic amino acids and, as such, have physiological roles (e.g., the amine is a neurotransmitter). Detailed studies of the nature of such interactions could lead to a much improved understanding of the local environment and its influence on the dynamical behavior of proteins.[12]

Here, we focus on the factors that might be responsible for the observed conformationally induced changes in the electronic structures of five flexible benzenes. The molecules considered are toluene, ethylbenzene, *n*-propylbenzene, 2-phenethyl alcohol, and 3-phenylpropionic acid. Each consists of an aromatic ring to which a "tail" is attached. We address the following questions: What kinds of ring−tail interactions are responsible for the observed changes? Are they electrostatic, covalent, and/or nonbonded? Do these interactions produce changes in the electronic structure of the S_0 state, the S_1 state, or both? Why are these changes so sensitive to the conformation of the attached group? Why do they vary significantly from one group to another? And would they be expected to be important in other types of molecules?

Our approach to answering these questions is theoretical. We begin with ab initio calculations on toluene. Typically, the attachment of a substituent like the methyl group to a benzene molecule produces an excited-state ordering ^1L_b, ^1L_a in Platt's notation,[13] leading to a $S_1(^1L_b)-S_0$ transition that is polarized parallel to the short axis (the *b* axis) and a $S_2(^1L_a)-S_0$ transition that is polarized parallel to the long axis (the *a* axis) of the molecule. The ab initio calculations correctly reproduce this state ordering scheme and the corresponding TM orientations. Then, we examine the effects of static charge on the predicted TM orientations, exposing the toluene molecule to point charges placed at various positions around the ring. Next, we examine the effect of geometrical distortions on the TM orientations, in the absence of added charge, both in toluene (rotation of the CH_3 group about the C_1-C_α bond) and in ethylbenzene (rotation of the C_2H_5 group about the C_1-C_α bond and rotation of the terminal CH_3 group about the $C_\alpha-C_\beta$ bond). Finally, we perform a series of calculations on *n*-propylbenzene (an example of an alkylbenzene with several torsional degrees of freedom), 3-phenylpropionic acid (with the strongly polar −COOH group in the γ-position of the side chain), and 2-phenethyl alcohol (whose polar −OH end group can interact with the π system of the ring). Several conformations of each of the latter molecules were examined. And, in each case, we compare the S_1-S_0 TM orientations predicted by theory with those observed experimentally, to determine which of the postulated interactions make the largest contributions to the observed TM orientation angles. Particular emphasis is placed on the gauche conformers, in which significant TM rotations often are observed. The results are interpreted in terms of an orbital mixing picture which, in turn, can produce $^1L_a/^1L_b$ electronic state mixing in the isolated molecule.

Table 1. Comparison of Observed and Calculated S_1-S_0 TM Orientations in Five Substituted Benzenes and Their Conformers, as Determined from Experiment and Theory (CIS, 6-31G* Basis Set)

molecule	conformer	$\theta_{obsd}{}^a$ (deg)	$\theta_{calcd}{}^a$ (deg)	ref
TOL	t	0 ± 4	0	
EBZ	t	0 ± 4	0	
PBZ	t	0 ± 18	0	6
PBZ	g	−26 ± 4 or 30 ± 4	−28	6
PPA	t	0 ± 18	0	4.5
PPA	g	−40 ± 4 or 69 ± 4	−58	4,5
PEA	t1	0 ± 18	0	8
PEA	t2	0 ± 18	−3	8
PEA	g1	−33 ± 3 or 52 ± 3	−30	8
PEA	g2		−10	8
PEA	g3	0 ± 18	−8	8

[a] θ is the angle between the S_1-S_0 TM vector and the line bisecting the C_2-C_3 and C_5-C_6 bonds, perpendicular to the point of attachment of the substituent (the *b* axis in toluene). Positive values of θ correspond to clockwise rotations.

Methods and Structures Generated/Investigated

The ab initio calculations were performed using Gaussian 94.[14] The methods employed were the Hartree−Fock (self-consistent field (SCF)) method for the ground S_0 state and the configuration interaction taking only single substitutions into account (CIS)[15] method for the excited S_1 and S_2 states, using the 6-31G* basis set. Benchmark calculations have been reported elsewhere.[8,16] Here, it is sufficient to note that the S_1-S_0 TM orientations calculated using the CIS/6-31G* method are in excellent agreement with those determined experimentally, as shown in Table 1. However, in most cases, the signs of the TM orientation angles cannot be determined experimentally. In contrast, theory yields both their magnitudes and their signs. Thus, in what follows, we compare the theoretical results on different model compounds with those obtained for the molecules themselves, also from theory.

Procedurally, we first calculated the optimized geometry of the ground state using the HF/6-31G* method. Then, we evaluated the HF/6-31G* wave function of the ground state and the CIS/6-31G* wave function of the excited state, both at the same HF-optimized geometry. (Recall that all electronic transitions induced by light are vertical). Finally, we used the CIS method to determine the orientation of the electronic TM, for transitions between S_0 and the S_1 or S_2 states. Five molecules were investigated: toluene (TOL), ethylbenzene (EBZ), *n*-propylbenzene (PBZ), 3-phenylpropionic acid (PPA), and 2-phenethyl alcohol (PEA). First, the effect of point charges on the predicted TM orientation in TOL was examined. In some cases, the charges chosen were equivalent in magnitude and spatial arrangement to the partial charges in the substituent atoms in PBZ, PPA, and PEA and were taken from the Mulliken population analysis[17] for the specific conformer being considered. In other cases, an arbitrary point charge was placed at various positions around the TOL ring. But in all cases, no further geometry optimizations in the presence of charge were performed; we simply used the CIS method to examine the influence of charge on the predicted TM orientation of the bare TOL molecule.

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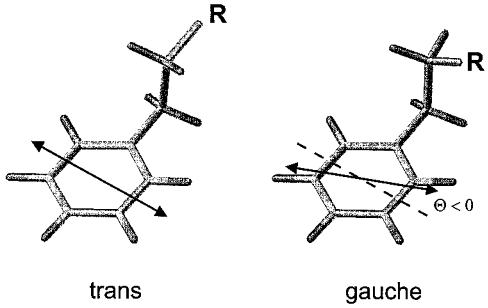

Figure 1. Schematic representation of a monosubstituted benzene in the all-trans conformation and in the gauche conformation. "R" indicates any polar or nonpolar side group. The trans conformer has C_s symmetry; the gauche conformer has C_1 symmetry. θ is the angle of rotation of the S_1-S_0 transition moment (TM) vector, measured in a clockwise fashion from the *b* axis of the trans conformer.

In the second series of calculations, the point charges were removed and the effect of changing the conformation about the C_1-C_α bond was investigated, again at the HF/CIS/6-31G* level of theory. Ground- and excited-state TOL and EBZ geometries were optimized to transition-state structures representing the barriers along the TOL-methyl, EBZ-ethyl, and terminal methyl torsional coordinates. The TOL-methyl torsion was further investigated by performing a linear synchronous transit ("LST" keyword) scan of the path connecting the two geometries.

The third and final series of calculations was performed on the gauche conformers of PBZ, PPA, and PEA. Starting from a HF/6-31G*-optimized geometry, a set of new geometrical arrangements was generated. First, the β-CH_2 group was removed from each molecule in its gauche conformation. Then, the two remaining fragments were saturated by hydrogen atoms, yielding a TOL molecule with a second molecule (CH_4 in the case of PBZ, HCOOH in the case of PPA, and H_2O in the case of PEA) in its vicinity. The idea behind this transformation (and the subsequent ones) was to generate a TOL molecule in which the gauche part of the side chain is in the same relative orientation with respect to the ring as in the complete molecule but is disconnected from the benzene moiety. The TOL portion of the molecule freezes the TM in an orientation that is parallel to the short axis of the ring so that the influence of the substituent on this orientation could be investigated independently.

Obviously, saturation of the two fragments leads to severe steric crowding; the two replacement hydrogens are very close to each other (0.5 Å). To avoid this, the TOL molecule was then rotated by 180° about an axis perpendicular to the benzene plane, going through the geometric center of the six carbon atoms. This transformation gives rise to a new set of structures. Again, the TM is frozen by the methyl group in these structures but the replacement hydrogen atoms are no longer in close proximity. The geometries generated in this way were subsequently used for single-point calculations at the CIS/6-31G* level of theory, and the orientation of the TM vector in each new structure was determined using the CIS method.

Results

1. Electrostatic Interactions between the Substituent Atoms and the Ring. The first set of calculations was designed to explore the effect of external charge on the predicted S_1-S_0 TM orientation in toluene. First, we chose the charges to be the same as the partial charges on the atoms belonging to the terminal groups of the side chains in PBZ, PPA, or PEA, "R" in Figure 1. Thus, beginning with the optimized geometry of a TOL molecule and its *b*-axis-oriented S_1-S_0 TM, we placed these equivalent charges at positions corresponding to the positions of the substituent atoms and then recalculated the orientation of the TM, thereby examining the effect of external charge on the TM orientation.

Table 2. Calculated S_1-S_0 TM Orientation Angles of Toluene in a Field of Point Charges Corresponding to the Indicated Molecule, Compared with the Corresponding Value for the Complete Molecule Itself, Also from Theory

		θ (deg)[a]	
molecule	conformer	TOL + charges	complete molecule
PBZ	g	5	−28
PPA	g	49	−58
PEA	g1	0	−30
PEA	g2	0	−10
PEA	g3	10	−8

[a] θ is measured clockwise from the *b* axis of toluene.

The results of these calculations are listed in Table 2. In this table (and in the ensuing discussion), θ is defined as the angle between the calculated TM vector of the gauche conformer and the calculated TM vector of the corresponding trans conformer. The latter is always parallel to the short axis of the conformer in the plane of the benzene ring. (A negative value of θ indicates a counterclockwise rotation, as shown in Figure 1.) By examining the data in Table 2, we see that the placement of point charges in the manner described above produces significant rotations of the S_1-S_0 TMs in some cases, for example, $\theta = 49°$ for a TOL molecule that is in the field of point charges corresponding to the gauche conformer of PPA. However, the calculated TM angle in *g*PPA itself, while similar in magnitude, is opposite in sign; $\theta = -58°$. In the *g*1 and *g*2 conformers of PEA, the two calculations do not agree at all. The point charges do not produce any rotation of the TM, whereas a significant rotation is predicted (and observed) for both conformers of the complete molecule itself. Different schemes or procedures for population analysis have been a matter of discussion for many years.[18] But the discrepancies between the predictions of the calculations and the experimental observations are so large in the present case that it is unlikely that partial charges derived from more sophisticated schemes will change the following conclusion. Although electrostatic interactions between the ring and the tail can produce changes in the orientation of the S_1-S_0 TM of the bare molecule, interactions of this type are not responsible for the observed behavior of these substituted benzenes.

Still, it is instructive to ask why charges have any effect at all. To address this question, we placed a simple point charge (±0.2 esu) at various positions around the ring in the TOL molecule and examined its effect on the predicted orientation of the S_1-S_0 TM, using the CIS method. The results of these calculations are shown in Figure 2. Significant changes in the TM orientation are again predicted to occur when the charge is present. More importantly, as shown in Figure 2, there is a kind of nodal plane structure in the resulting TM orientation "surface". Positive values of θ are observed when the charge is on one side of the nodes, whereas negative values of θ of the same magnitude are observed when the charge is placed in the corresponding position on the other side of the nodes. Further, positive and negative charges have symmetrically equivalent effects. Significantly, the nodal plane structure in both cases mimics the symmetry of the molecule itself; it has the same shape as the electronic wave functions themselves. Thus, we conclude that the principal effect of charge is to lower the symmetry of the interactions between the ring and its surroundings.

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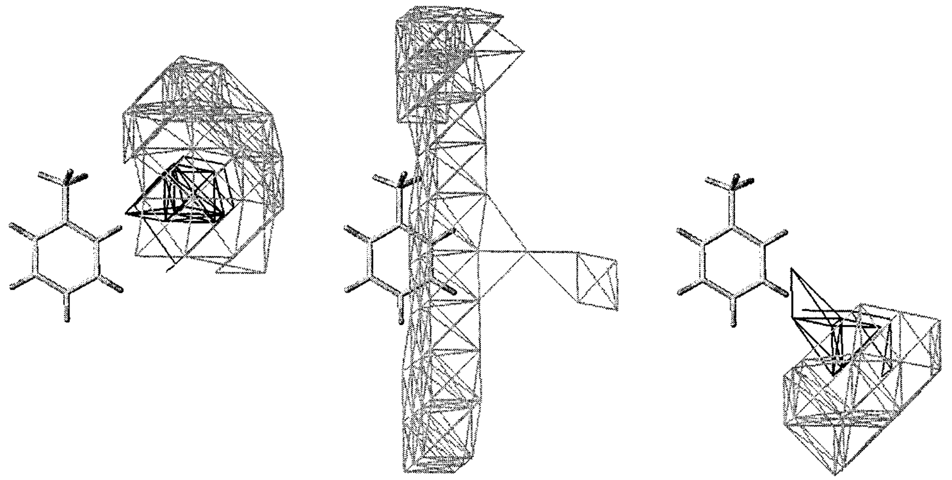

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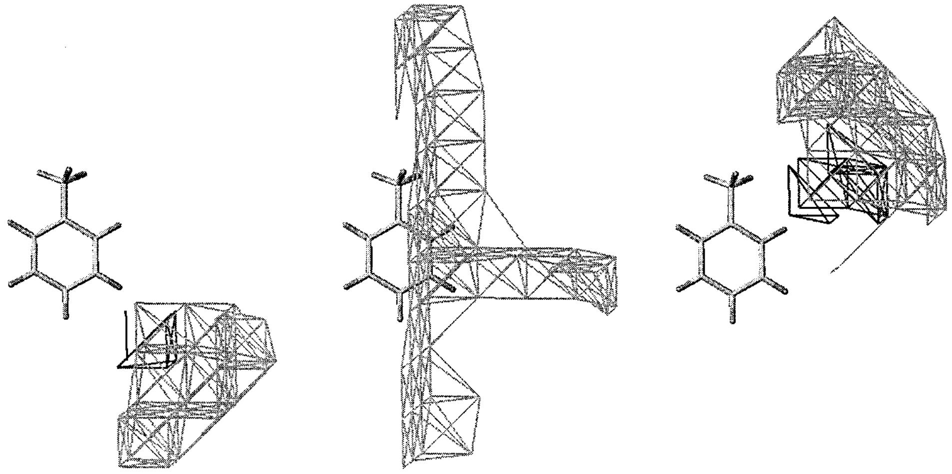

Charge: +0.2 au, Θ < -5° Charge: +0.2 au, -5° < Θ < +5° Charge: +0.2 au, Θ > +5°

Figure 2. TM "surfaces" of toluene, showing the effect of a point charge (±0.2 au) on the orientation of the S_1-S_0 electronic transition moment in the isolated molecule. Darker regions indicate larger $|\theta|$ values. The charge was placed on a rectangular grid lying between 2 and 8 Å from the molecule, only "above" and on "one side". The spacing between grid points is 2 Å; a total of 151 grid points is shown.

2. Effect of Conformational Change. Next, we examined the influence on the S_1-S_0 TM orientation of geometrical distortions of TOL and EBZ along different torsional coordinates, in the absence of added charge. Figure 3 shows the results for TOL. Here, beginning with the optimized HF/6-31G* geometry, we rotated the methyl group to selected positions along the torsional coordinate and calculated the S_1-S_0 TM orientation for each selected geometry using the CIS method. Large changes were observed. Thus, as shown in Figure 3, rotation of the methyl group about the C_1-C_α bond in TOL produces large changes in the predicted S_1-S_0 TM orientation angle, by as much as ±32° with respect to *b*. The predicted changes are periodic in the torsional angle ϕ, showing maxima (and minima) every 120°, thus following the CH_3 motion exactly. Now, in orientations of the CH_3 group other than a "perpendicular" one, with one C−H bond of the methyl group perpendicular to the ring (ϕ = 30, 90, 150°, etc.), the plane of symmetry perpendicular to the ring plane (and containing the C_1-C_α bond) is broken by the CH_3 group. Thus, we conclude that the effect of conformational change on the orientation of the S_1-S_0 TM in TOL is similar to that of added charge; symmetry plays the dominant role. Breaking the plane of symmetry perpendicular to the ring, either with added charge or with a distorted substituent, produces significant changes in the electronic structure of the aromatic ring.

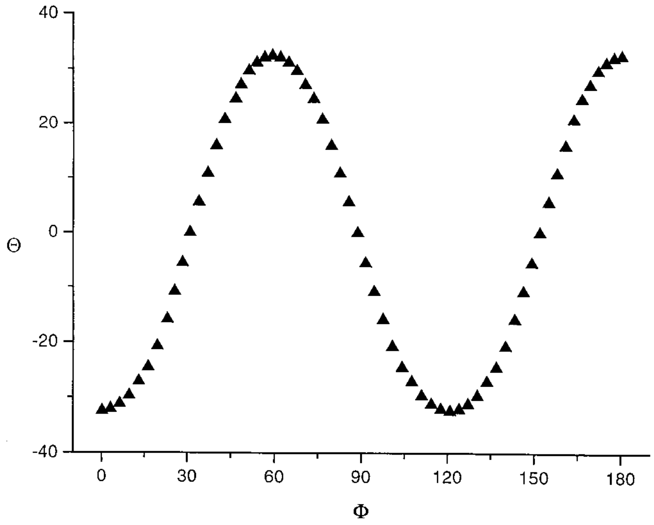

Figure 3. Angular dependence of the S_1-S_0 TM orientation of toluene on the torsional motion of the methyl group, according to theory. θ is measured relative to the *b* axis; ϕ = 30, 90, 150° correspond to perpendicular orientations of the methyl group.

The CIS calculations also provide information about the influence of conformational change on the orientation of the

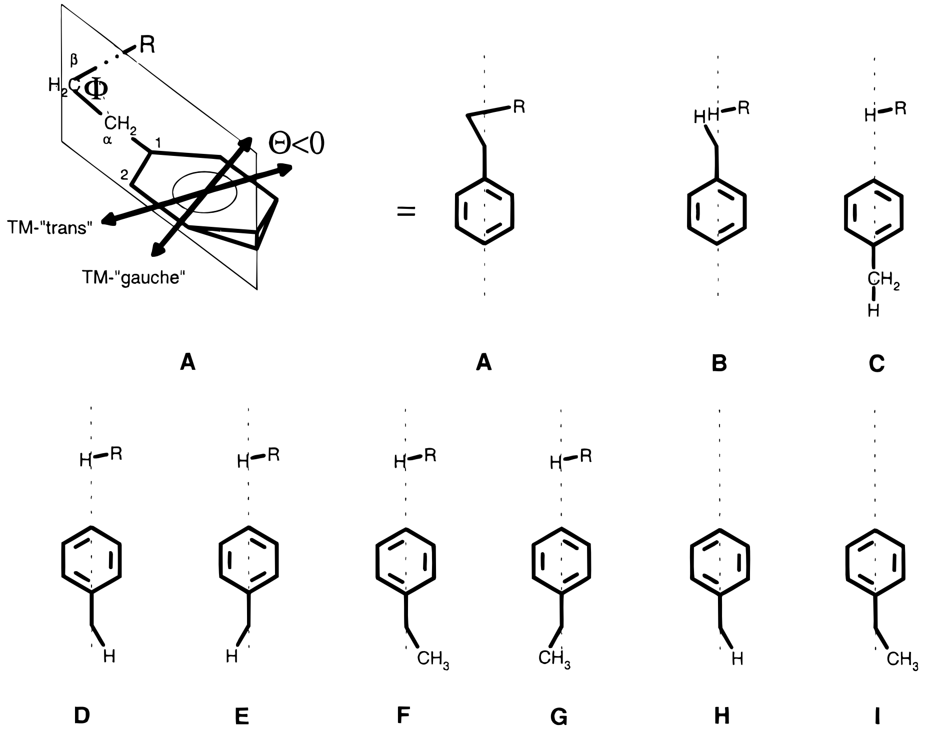

Figure 4. Graphical representation of the geometries used in the calculations on *n*-propylbenzene (PBZ), 3-phenylpropionic acid (PPA), 2-phenethyl alcohol (PEA), and their analogues. θ is the angle of rotation of the S_1-S_0 TM vector (see Figure 1). ϕ is the out-of-plane torsional angle of the β-CH_2 group, measured from the $C_2-C_1-C_\alpha$ plane. The perpendicular symmetry plane ($\phi = 90°$) is indicated by a dotted line. "R" stands for CH_3 (PBZ), COOH (PPA), and OH (PEA), respectively.

S_2-S_0 TM of TOL. In agreement with expectation, this transition is predicted to be *a*-axis polarized in a symmetrical TOL, with the CH_3 group in a perpendicular orientation with respect to the ring. However, rotation of this group about the C_1-C_α bond also produces a significant rotation of the S_2-S_0 TM, toward the *b* axis, which again follows the motion of the methyl group, as in the case of S_1-S_0 TM. The behavior of the two TMs is thus complementary.

Similar effects were observed in the calculations on EBZ. Here, rotation of a fixed C_2H_5 group about the C_1-C_α bond produced significant rotations of the S_1 and S_2 TM vectors, which again were complementary. The largest change observed, a 30° rotation of the S_1 TM, is with the β-carbon in the plane of the ring. However, rotation of the terminal methyl group in EBZ about the $C_\alpha-C_\beta$ bond, with the bridging CH_2 group in a perpendicular orientation, has little or no effect on the predicted TM vector orientations. We conclude that the S_1 (S_2) TM will be parallel to the short (long) axis of the isolated molecule as long as the plane containing the long axis bisects the attached CH_3 or C_2H_5 group. We further observe that the magnitude of TM rotation apparently depends on the distance between the symmetry-breaking group and the center of the ring.

3. "Through-Bond" and "Through-Space" Interactions. Given the observations that rotations of attached groups about the C_1-C_α bond produce significant rotations of the TM vectors and that the TM rotations produced by different substituents are different (Table 1), the two effects need to be examined independently. Figure 4 shows the structures that were designed to accomplish this goal. Structure A represents the optimized gauche geometry of one of the three molecules; R stands for CH_3 (PBZ), COOH (PPA), or OH (PEA). Structure B represents a hypothetical geometry, in which the β-CH_2 group is removed and replaced by two "saturating" hydrogen atoms, yielding a TOL molecule with an HR molecule in its vicinity. Structures C−I represent equivalent geometries produced by a 180° rotation of TOL about the axis perpendicular to the ring, a rotation that eliminates the steric crowding between the two replacement H atoms. Structure C represents a geometry in which a symmetric TOL (one CH_3 hydrogen lies exactly in the symmetry plane perpendicular to the ring plane) is exposed to the substituent HR, on the side of ring opposite to the methyl group.

As will be seen, the optimized gauche conformers of the molecules investigated have C_1-C_α torsional angles ϕ that differ from 90°, breaking the vertical plane of symmetry. Structure D represents the rotated equivalent of these conformations, with the CH_3 group of TOL rotated in an identical manner. In structure E, the rotated CH_3 group of TOL is reflected through the broken symmetry plane, corresponding to a rotation in the opposite direction. Structure F is the equivalent of D, but with a methyl group in the β-position, which in turn is equivalent to EBZ and the β-CH_2 group in A. Structure G represents again the mirror image of F with respect to the CH_2-CH_3 moiety. Structures H and I correspond to D and F, respectively, but HR is omitted, to examine explicitly the effect of removing the substituent.

The results of the TM calculations on each of these structures are summarized in Table 3. The data on PBZ are especially revealing. By comparing the calculated TM orientation angles for structures C−I, we see that the θ values of structures D and H are identical to that of the gauche conformer of PBZ itself. The common property of this conformer of PBZ and structures D and H is that they all have the same value of the torsional angle ϕ (=75°). Changing the angle ϕ from 75 to 90 to 105°, as in going from structures D to C to E, changes the TM orientation from $\theta = -27$ to -4 to 21°. In contrast, removing the substituent has little effect on the value of θ; compare D (−27°) with H (−28°) or F (−25°) with I (−28°). Thus, we conclude that the TM orientation in PBZ depends solely on ϕ, the torsional angle about the C_1-C_α bond. As in TOL itself, rotation of the TM is caused by a symmetry-breaking rotation

Table 3. Calculated S_1-S_0 TM Orientation Angles of *n*-Propylbenzene, 3-Phenylpropionic Acid, and 2-Phenethyl Alcohol (A), Compared to the Corresponding Values for Fragments C−I (See Figure 4), Also from Theory

		θ (deg)[a]							
molecule	conformer	A	C	D	E	F	G	H	I
PBZ	g	−28	−4	−27	21	−25	17	−28	−25
PPA	g	−58	−32	−43	−22	−47	−20	−9	−11
PEA	g1	−30	−40	−12	−59	−24	−56	23	17
PEA	g2	−10	−27	3	−50	−10	−45	22	15
PEA	g3	−8	−7	−13	−2	−13	−2	−5	−5

[a] θ is measured clockwise from the *b* axis of toluene.

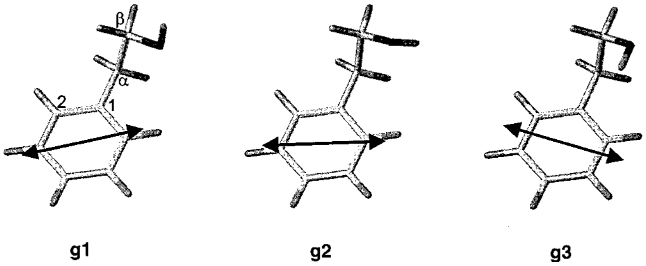

Figure 5. Gauche conformers of 2-phenethyl alcohol. Adapted from ref 8. Copyright 1998 American Chemical Society.

of the C_1-C_α bond attaching the substituent to the ring, a kind of "through-bond" effect.

Substituent effects are more important in the more polar molecules, PPA and PEA. Consider PPA, in which HR is a formic acid molecule. Comparing the results for structures D and H (or F and I), also shown in Table 3, we see that in this case removing the substituent produces a significant change in the calculated value of θ, 34° (or 36°). Clearly, "through-space" interactions with the substituent in PPA are important. In addition, there also are substantial through-bond effects in PPA; changing the angle ϕ from 83.9 to 90 to 96.1°, as in going from structures D to C to E, changes the calculated value of θ from −43 to −32 to −22°.

Also of interest is the possible additivity of the two effects, through-bond interactions with the rotated C_1-C_α group and through-space interactions with the substituent, HR. In the case of PPA, addition of the θ values for structure H, representing a nonsymmetric TOL, and structure E, the mirror image of structure H in the vicinity of a formic acid molecule, gives nearly the same value of θ as for structure C, in which only the through-space effect is present. The two values differ by 1°. Other values are the same to within 5°, suggesting that the two effects are approximately additive.

We now examine the validity of the above "rules" by performing similar calculations on 2-phenethyl alcohol (PEA). Three gauche conformers of PEA have been identified in a low-temperature, gas-phase sample, *g*1−*g*3.[8] Their structures are shown in Figure 5. Also shown are the TM alignments predicted by the CIS/6-31G* calculations, and observed experimentally. Conformer *g*3, which has the terminal OH group directed toward the benzene ring, is predicted to be the most stable. Its TM is aligned close to the short axis of the benzene ring, at $\theta = -8°$. Conformers *g*1 and *g*2, in which the OH group is directed away from the ring, are predicted to lie at higher energies (6.17 and 8.89 kJ/mol, respectively) and to have more significantly rotated TM's, $\theta(g1) = -30°$ and $\theta(g2) = -10°$. Clearly, the S_1-S_0 TM orientations in PEA are extremely sensitive to both the position and the orientation of the terminal OH group.

The first rule derived above is that TM reorientation is produced by rotation about the C_1-C_α bond, breaking the C_s symmetry of the substituted molecule. All three gauche conformers of PEA exhibit this behavior. As shown in Table 3, this torsion-induced rotation of the TM is observed in all three conformers, increasing in the order $g3 < g1 < g2$ (compare the results for structures D, C, and E of the three conformers). The corresponding torsional angles predicted by theory increase in approximately the same order, $\phi(g3) = 86.8°$, $\phi(g2) = 98.6°$, and $\phi(g1) = 99.4°$, confirming the above rule. (Note that the values of ϕ for the g1 and *g*2 conformers of PEA are greater than 90°, showing that the β-carbon and the substituent R are located on the same side of the (perpendicular) plane, unlike PBZ and PPA, which have values of ϕ that are less than 90°.)

The second rule derived above is that the TM reorientation is produced by "through-space" interactions with the substituent, HR. In PEA, HR is a water molecule, with two lone pairs of electrons. Comparison of the results for structures D and H (or F and I) of the three gauche conformers of PEA shows that the contribution of the substituent differs significantly from one conformer to the next, increasing (in magnitude) in the order $g3 < g2 < g1$. Conformer *g*3 is the conformer in which neither lone pair is directed toward the plane containing the phenyl ring (Figure 5), conformer *g*2 is the conformer in which one lone pair is directed toward the plane, and conformer *g*1 is the conformer in which both lone pairs are directed toward the plane. Thus, we conclude that the oxygen atom lone pair electrons play a dominant role in through-space interactions with the ring.

Finally, we note that the rule of approximate additivity holds true also for PEA. As for PBZ and PPA, addition of the θ values for structures E and H (or G and I) gives approximately the values for structure C. The values for structures C parallel those for the complete conformers A. Thus, while the agreement is not quantitative, the rules delineated above appear to account reasonably well for the observed behavior.

Discussion

Having identified empirically some of the factors that are responsible for the observed changes in the S_1-S_0 TM orientations of five conformationally flexible benzenes, we now discuss the results from a more fundamental point of view. In particular, we examine the connection between the observed changes and the electronic structures of the molecules themselves. In what ways do the identified ring−tail interactions modify these electronic structures? Are there changes in the wave functions of the ground state, the excited state, or both? Further, is benzene special, or could these effects be important in other molecules as well? If so, why (or why not)? These are not new questions.[19] But it turns out that the ab initio calculations provide valuable new information that can help us answer them.

Figure 6 shows contour plots of the principal one-electron MOs that contribute to the S_1-S_0 electronic transition of PPA, as calculated for the optimized trans and gauche conformers by the HF/6-31G* method. (Qualitatively similar plots were obtained for the remaining molecules.) We see from these plots that, whereas *the nodal planes of all four orbitals (HOMO-1, HOMO, LUMO, and LUMO+1 in order of increasing energy) are parallel to either the long or the short axis of the benzene ring in the energy-optimized* ***trans*** *(or symmetrical) conformer, the same is not true in the energy optimized* ***gauche*** *conformer*. Folding the side chain to one side or the other produces a rotation of the nodal planes of the LUMO and LUMO+1 orbitals of the gauche conformer with respect to the correspond-

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[19] See, for example: Hill, W. G.; Mason, S. F.; Peacock, R. D. *J. Chem. Soc., Perkin Trans.* **1977**, 1262.

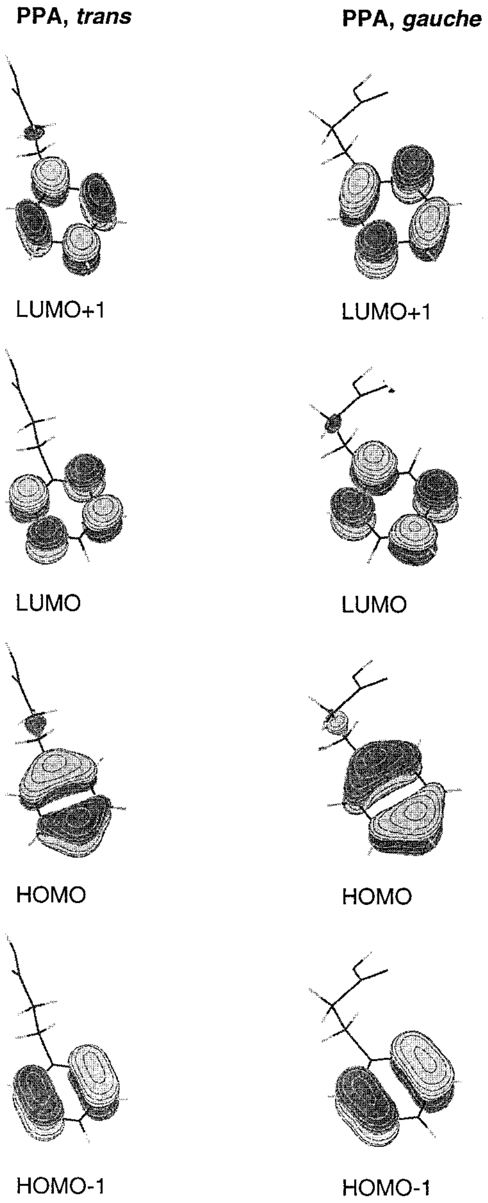

Figure 6. Comparison of selected MO's of the trans and gauche conformers of PPA resulting from the HF wave functions. Pictures drawn with MOLDEN. The contour levels are 0.05.

ing orbitals of the trans conformer. A kind of orbital mixing occurs, of the unoccupied orbitals of the ground state. That is, each of the gauche LUMO and LUMO+1 orbitals may be written as linear combinations of the corresponding trans LUMO and LUMO+1 orbitals with complementary mixing coefficients. In contrast, the nodal structures of the occupied HOMO-1 and HOMO orbitals are relatively unaffected by conformational change.

It is important to note that the occupied orbitals are energy optimized in an SCF treatment of the ground state. Thus, their shape and form should be nearly basis-set independent. However, the same may not be true for the unoccupied orbitals. For this reason, we have also compared the natural orbitals extracted from the CIS calculations on the two conformers of PPA. This comparison is shown in Figure 7. We see again that there are larger differences between the nodal patterns of the LUMO and LUMO+1 orbitals of trans and gauche PPA than there are between the corresponding patterns of the HOMO-1 and HOMO orbitals of the two conformers. We conclude, then, that the shape and form of the unoccupied orbitals also are meaningful.

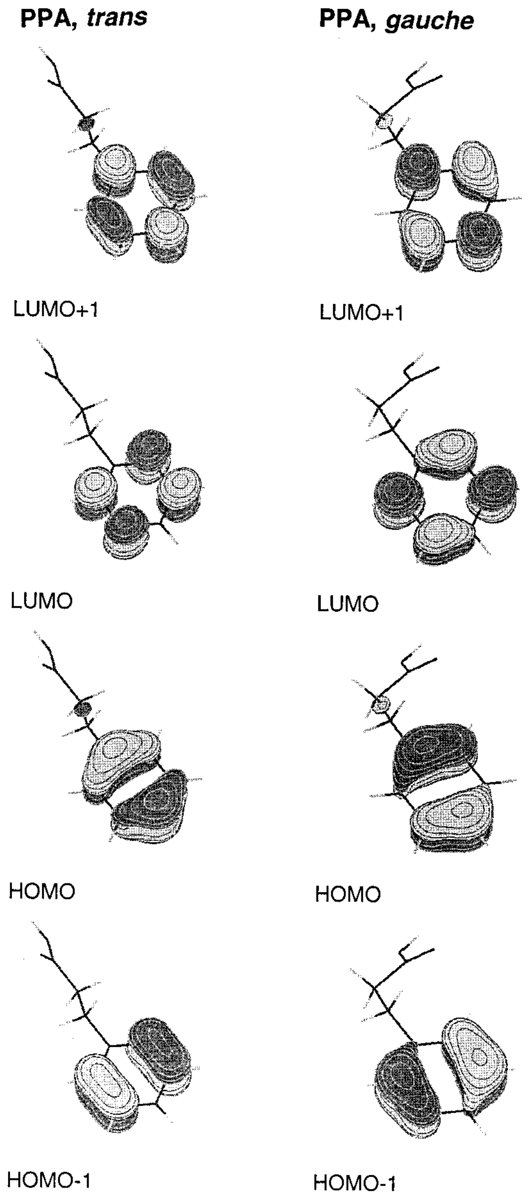

Figure 7. Comparison of selected natural orbitals of the trans and gauche conformers of PPA extracted from the CIS calculations. Pictures drawn with MOLDEN. The contour levels are 0.05.

The observation that the unoccupied orbitals are principally mixed by conformational change appears to have a simple explanation. This explanation comes from a comparison of the photoelectron and electron transmission spectra of toluene.[20] These data show that the major interactions between the methyl group orbitals and the π orbitals of the ring are with the filled orbitals, not the unfilled ones. That is, there are large shifts (~0.5 eV) in the energies of the ring π orbitals, but only small shifts (~0.1 eV) in the energies of the π^* orbitals when the methyl group is attached to the ring. This difference in the degree of interaction is important because it locks the HOMO-1 and HOMO orbitals in place and makes them much less susceptible to other, smaller perturbations, such as those discussed here. In contrast, the more diffuse LUMO and LUMO+1 orbitals are more easily perturbed by additional substituents, since their interactions with the attached CH_3 group orbitals are much smaller. For this reason, then, we believe that the observed conformationally induced changes in the $S_1 \leftarrow S_0$ TM orienta-

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[20] Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295.

Table 4. S_1-S_0 TM Orientation Angles Calculated from the Molecular Orbital Model (See Text)[a]

molecule	conformer	CIS expansion coefficients				contribution		TM orientation angle (deg)			
		c_1	c_2	c_3	c_4	L_b	L_a	θ_{estd}[b]	θ_{estd}[c]	θ_{estd}[d]	θ_{calcd}
PBZ	g	0.37	0.43	−0.31	0.28	0.64	0.36	−11	−11	−33	−28
PPA	g	0.31	−0.34	0.38	0.36	0.44	0.56	−37	−40	−62	−58
PEA	g1	0	0	0.51	−0.48	0.00[e]	1.00[e]	−35	−32	−30	−30
PEA	g2	0	0	0.51	0.47	0.00[e]	1.00[e]	−21	−18	−7	−10
PEA	g3	0.42	0.46	0.24	−0.22	0.79	0.21	−12	−9	−10	−8

[a] θ is measured from the *b* axis of toluene. [b] Based on eq 5. [c] Based on a Mulliken population analysis of the transition densities on ring carbon atoms only. [d] Based on a Mulliken population analysis of the transition densities on all heavy atoms. [e] See text.

tions of substituted benzenes are primarily caused by changes in the shapes of the unoccupied orbitals, not the occupied ones. In other words, it is the electronic structure of the excited (S_1) state that is primarily affected, not that of the ground (S_0) state.

The orbital mixing identified above can lead to electronic state mixing in the isolated molecule. Within the framework of MO theory, the wave function of an electronically excited state can be written as a linear combination of single excitations from occupied orbitals to unoccupied ones:

$$\Psi = \sum_n c_n \Psi_{occ} \Psi_{unocc} \tag{2}$$

(Higher order excitations; doubles, triples, etc., can be included when necessary.) In many cases, the majority of the coefficients c_n are zero. Thus, in benzene itself, only the HOMO-1, HOMO, LUMO, and LUMO+1 orbitals play a significant role, for the lower excited states. The S_1 (^1L_b) state has the wave function

$$\Psi_{L_b} = c_1 \Psi_H \Psi_L + c_2 \Psi_{H-1} \Psi_{L+1} \tag{3}$$

and a *b*-axis-oriented TM, whereas the S_2 (^1L_a) state has the wave function

$$\Psi_{L_a} = c_3 \Psi_H \Psi_{L+1} + c_4 \Psi_{H-1} \Psi_L \tag{4}$$

and an *a*-axis-oriented TM.[21] The S_1 and S_2 states of substituted benzenes can similarly be described by eqs 3 and 4, providing that the symmetry of the orbitals is preserved. This is the case for the trans conformers of the molecules considered here. However, this is not the case for the gauche conformers of PBZ, PPA, and PEA. As we have seen, their one-electron MOs ψ_L and ψ_{L+1} are linear combinations of the corresponding trans MOs. Thus, to describe their S_1 states, eq 3 should be modified to read

$$\Psi_{S_1} = c_1 \Psi_H \Psi_L + c_2 \Psi_{H-1} \Psi_{L+1} + c_3 \Psi_H \Psi_{L+1} + c_4 \Psi_{H-1} \Psi_L \tag{5}$$

By comparing eq 5 with eqs 3 and 4, we see that the S_1 state wave functions of the gauche conformers are linear combinations of the two benzene-like state wave functions ^1L_b and ^1L_a, i.e., the two states are mixed by the folding of the tail. This accounts for the *ab* hybrid characters of their $S_1 \leftarrow S_0$ transitions.

Shown in Table 4 are the expansion coefficients c_1-c_4 determined from the CIS calculations on the gauche conformers of PBZ, PPA, and PEA. Each of these coefficients provides a numerical estimate of the contribution of each one-electron excitation to the electronic wave function of the S_1 state (cf. eq 5). According to this picture, the S_1 state of the gauche conformer of PBZ is a mixture of the zero-order ^1L_b and ^1L_a states of benzene, since all coefficients are nonzero. By normalizing these to unity and summing the individual contributions of each of the states, we find that the S_1 state of *g*PBZ is 64% ^1L_b and 36% ^1L_a in character. The S_1 state of *g*PPA is 44% ^1L_b and 56% ^1L_a. Thus, the normal ordering of the states is inverted in this case. And the S_1 states of the *g*1, *g*2, and *g*3 conformers of PEA are, according to the calculation, 0%, 0%, and 79% ^1L_b in character. However, examination of the MO's of the *g*1 and *g*2 conformers shows that the energy ordering of the LUMO and LUMO+1 orbitals is switched (compared to toluene) and, therefore, that the S_1 states of these two conformers are actually pure ^1L_b states. This demonstrates a remarkable sensitivity of the electronic structure of the isolated molecule to conformational change.

We can use this model to estimate the S_1-S_0 TM orientations of each of the above conformers, for comparison with the calculated values (and experiment). The essential idea is the following. Each of the excitations in eq 5 has a uniquely defined orientation and zero-order oscillator strength. Therefore, we can estimate θ by adding the four components together, taking both the signs and the magnitudes of the coefficients into account. The resulting values of θ_{estd} are also shown in Table 4, in three columns. The first set of values (−11, −37, etc.) was computed by using the calculated coefficients of the ring carbon atom p_z orbitals to estimate the relative contributions of each component to the excited-state wave function. These estimates agree reasonably well with the calculated values of θ for the gauche conformers of PEA. However, there are significant differences for *g*PBZ and *g*PPA. We attribute these differences to changes in the partial charges of atoms other than the ring carbon atoms. This was confirmed by performing a Mulliken population analysis on the calculated transition densities, to estimate the changes in the partial charges of all atoms on S_1-S_0 excitation, and then calculating the TM vector directly from these changes. To test this approach, we first used only the partial charges on the ring atoms to calculate the TM orientation, leading to the second set of θ_{est} values (−11, −40, etc.). These values are in excellent agreement with the first set of values, showing that our partitioning of the partial charges obtained from the Mulliken analysis is reliable. Then, finally, we estimated θ using the partial charges on all atoms, leading to the third set of values in Table 4 (−33, −62, etc.). These values are in very good agreement with the values of θ calculated directly from the wave functions, θ_{calcd}, for all five conformers. Thus, we conclude that the observed sensitivity of the electronic structure of these substituted benzenes to conformational change is a consequence of ring−tail interactions, evidenced by a mixing of the ring π^* orbitals and a nonzero transition density on atoms of the tail, which can lead to state mixing (and in some cases, state reordering) in the isolated molecule.

There are a number of possible problems with the above model. For example, although the theoretical results are reasonably stable with respect to basis set expansions beyond 6-31G*,[8,16] the aforementioned agreement with experiment could

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[21] Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: Reading, MA, 1996; p 394.

be the result of a fortuitous cancellation of errors in small basis sets that neglect electron correlation. That such correlation effects are important in benzene is clear from the CASSCF calculations of Roos and co-workers.[22] Here, it was found that the S_1 (^1L_b) state is well represented by CIS but that doubly and triply excited configurations together make a ∼16% contribution to the S_2 (^1L_a) state. Optimization of the excitation energy of the S_2 state required a CASPT2 treatment with 12 active π orbitals, suggesting that a similar increase in the active space might be required for the calculations described here. However, our model is based on transition moment orientations, not excitation energies. If the ground state is adequately described by the HF configuration, then contributions from doubly and triply excited configurations to the $S_1 \leftarrow S_0$ transition moment should be small, since they enter through a product of two small coefficients. Thus, we believe such effects are relatively unimportant for the specific property considered here.

There is an interesting connection between our model and other recently proposed models of the electronic states of benzene, most notably that which describes such states as linear combinations of the two Kekulé structures.[23] This model provides a convincing basis for understanding the anomalous shifts in the frequencies of certain vibrational modes on electronic excitation, since motions along these coordinates lead to an avoided crossing between two diabatic surfaces and to changes in the mixing coefficients. From this perspective, breaking the symmetry of the benzene with an off-axis substituent also will change the relative contributions of the two Kekulé structures, rotating the TM. However, as shown here, the chemical nature of the substituent and its orientation with respect to the ring also are significant.

An important question, so far not yet addressed, is whether benzene is unique or whether such conformationally induced changes in electronic structure might be observed in other molecules as well. Benzene is unusual in the sense that two degenerate, zero-order, one-electron excitations with very different properties contribute equally to its S_1 state. Thus, relatively small perturbations can have a significant effect on its electronic structure. But there are many other molecules with similar properties that might also exhibit conformationally dependent electronic structures. Substituted naphthalenes and other even alternant hydrocarbons provide one example.[11] Additionally, Philips and Levy[10] have examined the possibility that different conformers of several indole derivatives and tryptophan analogues might exhibit differently oriented S_1-S_0 TMs. Although expected, these differences have yet to be observed. More recently, Walden and Wheeler[24] have found theoretical evidence for a conformationally dependent, through-space spin delocalization from the π system of the indole fragment onto the alanyl side chain of the tryptophan radical cation. And Leuck et al.[25] also have observed conformational symmetry-breaking effects in the resonance Raman spectra of some methoxy-substituted benzenes, which are presumably related to the effects described here. All of these systems are similar in the sense that more than one electronic excitation contributes to the properties of the excited state. Presumably, conformationally induced changes in electronic structure will not be as important in systems in which only a single configuration dominates a given excited-state wave function.

Still, one should be alert to the possible chemical consequences of such an effect. One example is the behavior of twisted intramolecular charge-transfer (TICT) states. First put forth by Grabowski et al.[24] and widely employed, the TICT hypothesis was proposed to account for the unusual fluorescence behavior of (*N*,*N*′-dimethylamino)benzonitrile (DMABN) in polar solvents. Two emissions are observed in such environments: a normal emission, observed in nonpolar solvents and assigned to the ^1L_b state, and a red-shifted emission, also observed in polar solvents and assigned to the ^1L_a state. Grabowski et al.[26] proposed that this state was formed via a “dynamic relaxation” of DMABN with internal twisting of the dimethylamino group, coupled with an electron transfer from the amino nitrogen to a π^* orbital of the attached benzonitrile, which in turn is stabilized by the polar solvent. Debate continues concerning the validity of this model.[27] However, it is apparent from the present work that the substituent itself, distorted along some nontotally symmetric vibrational coordinate, could produce significant state mixing and/or reordering. So could an off-axis solvent molecule. The possible photophysical consequences of conformationally induced changes in electronic structure also need to be explored. Here, the example of intramolecular vibrational relaxation in the alkylbenzenes comes immediately to mind.[28] Yet to be examined is the possible role of electronic state mixing in the dynamic behavior of the photoexcited state. Thus, the discovery of the sensitivity of the electronic structure of a chromophore to the conformation of an attached group could have broad chemical, physical, and biological consequences.

Conclusions

A series of HF/CIS/6-31G* quantum chemical calculations has been performed on several flexible benzenes to investigate the factors that are responsible for the observed sensitivity of the optical transition moment (TM) orientation to the conformation of the attached group. The factors examined include purely electrostatic, covalent, and nonbonded interactions between the ring and the tail. Electrostatic interactions can be ruled out as a source of the observed behavior because the TM orientations derived from calculations on a toluene molecule exposed to point charges do not agree with those that are experimentally observed, both in toluene and in structurally related molecules. However, in some cases, a significant TM rotation is predicted in the presence of added charge, a phenomenon that deserves further elucidation.

The two remaining factors are found to be important. The first is a covalent, or “through-bond”, effect. Even a slight rotation of the substituent about the bond connecting the side chain to the benzene ring, breaking the plane of symmetry perpendicular to the ring, has a significant influence on the predicted TM orientation. This effect is found to be most important in benzene derivatives having nonpolar side chains, such as *n*-propylbenzene. The second factor is a nonbonded, “through-space” effect. Polar groups such as −COOH and −OH attached to the tail also produce significant rotations of the TM vector, as in 3-phenylpropionic acid (PPA) and 2-phenethyl alcohol (PEA). This effect is believed to be mediated by interactions between either bonding π orbitals (as in PPA) or occupied lone pair orbitals (as in PEA) and the π orbitals of

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[22] Roos, B. O.; Andersson, K.; Fülscher, M. P. *Chem. Phys. Lett.* **1992**, *192*, 5.

[23] See: Shaik, S.; Zilberg, S.; Haas, Y. *Acc. Chem. Res.* **1996**, *29*, 211 for a review.

[24] Walden, S. E.; Wheeler, R. A. *J. Am. Chem. Soc*. **1997**, *119*, 3175.

[25] Lueck, H. B.; Hudson, B. S.; Friedrich, D. M.; Zgierski, M. Z. *J. Raman Spectrosc*. **1997**, *28*, 455.

[26] Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

[27] See, for example: Howell, R.; Phillips, D.; Petek, H.; Yoshihara, K. *Chem. Phys.* **1994**, *188*, 303. Mordzinski, A.; Sobolewski, A. L.; Levy, D. H. *J. Phys. Chem. A* **1997**, *101*, 8221.

[28] Smalley, R. E. *J. Phys. Chem.* **1982**, *86*, 3504.

the ring. In such cases, both “through-bond” and “through-space” effects are important, in an approximately additive way, further demonstrating that purely electrostatic effects play a relatively minor role.

Examination of the one-electron MOs obtained from theory also shows that it is the unoccupied benzene π^* orbitals that are mainly influenced by interactions with the tail; the occupied benzene π orbitals are relatively unaffected. Thus, the observed conformationally induced change in electronic structure is principally an excited-state phenomenon, not a ground-state one. The observed perturbations produce a mixing of the low-lying π^* orbitals, principally LUMO and LUMO+1. Since both of these orbitals participate in optical transitions to the S_1 and S_2 states, this can lead to excited electronic state mixing and/or state reordering in the isolated molecule. In these systems, at least, the orientation of the electronic TM in the isolated molecule is like that of a compass needle, whose direction in space is extremely responsive to the surrounding environment.

Acknowledgment. This work has been supported by NATO (CRG No. 960687), NSF (CHE-9617208, INT-9722029), and the Pittsburgh Supercomputing Center (CHE-960010P). We also acknowledge support from EPSRC and BBSRC, the award of a CASE studentship to J.A.D. in collaboration with the Central Laser Facility at the Rutherford Appleton Laboratory, the EPSRC Laser Support Facility for the loan of a laser system, and the donors of the Petroleum Research Fund, administered by the ACS. Finally, we thank Y. Haas, J. M. Hollas, P. Joireman, K. Jordan, T. Korter, J. Murrell, and J. Ribblett for their helpful discussions and suggestions and W. G. Richards for his continuing encouragement. Conversations with Professor Jordan about electronic structure calculations were especially helpful.

JA980104Y